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ENVIRONMENTAL MANAGEMENT IN THE PULP AND PAPER INDUSTRY

Volume 1

UNITED NATIONS ENVIRONMENT PROGRAMME

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Number 1 (in 2 volumes)	Environmental Management in the Pulp and Paper Industry

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FOREWORD

The pulp and paper industry occupies an important position in the chain which links a vast primary resource, the forest ecosystem, to an essential commodity, paper. Whilst it is critically important that paper be available to meet cultural, information and other human requirements, it is equally essential to protect and enhance the human environment.

This 2-volume publication on Environmental Management in the Pulp and Paper Industry provides a useful base of environmental information and data relating to the industry. It covers a number of areas of priority concern:

- Emission of air and water pollutants;
- Raw materials preparation;
- In-plant measures for sulphite pulping and recovery;
- In-plant measures for sulphate pulping and recovery;
- Mechanical and chemimechanical pulping and bleaching;
- De-inking and other secondary fibre systems;
- Paper making;
- Primary and secondary effluent treatment methods;
- Treatment of bleach plant effluents;
- Alternative utilization of spent liquors;
- Effluent disposal by irrigation.

It is expected that this publication will enable the integration of environmental considerations into the planning, designing, construction and operation of pulp and paper mills.

It is with a feeling of satisfaction and gratitude that I wish to acknowledge the Swedish International Development Authority's financial support to IVL-Consulting Ltd., an affiliate of the Swedish Water and Air Research Institute, which enabled it to undertake the present work for the United Nations Environment Programme.

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M.K Tolba

Dr. Mostafa K. Tolba
Executive Director
United Nations Environment Programme

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Paper Fibre and Allied Products Division, Water Pollution Control Directorate, Fisheries and Environment Canada, Ottawa, Canada.

Arun G. Bijur,
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Industrial Impact Section, Division of Environmental Impact Evaluation, National Environment Board, Bangkok, Thailand.

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Portugal.

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Environmental Sanitation Agency - CETESB, São Paulo, Brazil.

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Geneva, Switzerland.

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Environmental Sciences Division, The Institute of Paper
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(former President of the Finnish Pulp and Paper Research
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Nils Jirvall, Head.
Sub-division for Pulp, Paper and Food Industries, National
Swedish Environment Protection Board, Solna, Sweden.

M. Judt, Senior Industrial Division Officer.
Chemical Industries Section, Industrial Operations Division, United Nations Industrial Development Organization, Vienna, Austria.

K. Kadavanich,
Kimberly-Clark Thailand Ltd., Thailand.

Dr. Milos Krofta, President.
Krofta Engineering Corporation, Lenox, Massachusetts, U.S.A.

Y. Kuninaka, Manager.
N° 1 Pulping Department, Kasugai Mill, Oji Paper Company, Kasugai City, Aichi Prefecture, Japan.

B. Kyrklund, Chief.
Pulp and Paper Branch, Forest Industries Division, Food and Agriculture Organization of the United Nations, Rome, Italy.

W.J. Lacy, Director.
Technical Support Division, U.S. Environmental Protection Agency, Washington, U.S.A.

D. Larré, Director.
Industry and Environment Office, United Nations Environment Programme, Paris, France.

Nabiel Makarim, Deputy Assistant to the Minister.
Ministry of Development Supervision and Environment, Jakarta, Indonesia.

Dr. Irene Meister, Vice President, International.
American Paper Institute, New York, U.S.A.

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de Aguas Residualas y Recept., Secretaria de Salubriad y Asistencia, Ministry of Health, Mexico.

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Maria Luisa Otero d'Almeida, Chief.
Chemical Laboratory, I.P.T., São Paulo, Brazil.

H.D. Paavila, Director.
Environmental, Energy and Supply Service, Canadian Pulp
and Paper Association, Montreal, Canada.

Pedro M. Picornell, Executive Vice President.
Paper Industries Corporation of the Philippines (PICOP),
Makati, Metro Manila, Philippines.

Dr. N.L. Ramanathan, Director.
Environment Division, Department of Science and Technology,
Technology Bhavan, New Delhi, India.

A. Rose, Délégué Général Adjoint.
CEPAC, Brussels, Belgium.

Saica,
Zaragosa, Spain.

V.A. Shagaev, Chief, Technologist.
Giprobum, Leningrad, U.S.S.R.

Pentti Sierila, Director.
Central Association of Finnish Forest Industries, Helsinki,
Finland.

Star Paper Mills Ltd.,
India.

P.V.R. Subrahmanyam,
National Environmental Engineering Research Institute,
India.

T. Suzuki, Vice Chairman.
Environmental Conservation Committee, Japan Paper Association,
Tokyo, Japan.

Thessalian Pulp and Paper Industries Ltd.,
Larissa, Greece.

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Bulacan, Philippines.

Hugo E. Velez, Chief.
Division of Pollution Control, CICELPA-INTI, Buenos Aires,
Argentina.

K.C. Virmani,
Ballarpur Industries Ltd., India.

A. Wirjoasmoro,
Ministry of Industry, Bureau Data and Industrial Analysis,
Jakarta, Indonesia.

The drafting of this document was undertaken by IVL-Consulting Ltd., Stockholm, Sweden, under the direction of Dr. Hans Norrström, Technical Director, with contributions by:
Bo Alberth; Rolf Anderson; Inger Andersson; Hans Hargbäck;
Kristina Idner; Nils Kjellberg; Lars Landner; Stig Larsson;

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Environmental Management in the Pulp and Paper Industry

Volume 1

Volume 2

PART I - EMISSION OF AIR AND WATER POLLUTANTS

CONTENTS

1. INTRODUCTION

1.1 Pulp and paper production

Pulp and paper have a very important position in society. They are used for many purposes in the home, commerce, industry and education. The raw material is normally virgin plant fibres but an increasing amount is recycled fibres.

In 1974 the world production of pulp was close to 123 million tonnes and of paper 157 million tonnes (Table 1.1 and Appendix 1). A major share of this was produced in Europe and North America - 85 % of the pulp and 78 % of the paper. The growth rate of the industry of Asia (including Oceania), Latin America and Africa is high, however, and the relative share of Europe and North America is decreasing.

Table 1.1 Production of paper and paperboard by continents 1974 and 1978 and prediction for 1982 (in million tonnes)(1,2)

	Production 1974	Production 1978	Predicted capacity 1982
North America	68.5	71.4	80.1
Europe (incl. USSR)	54.5	56.1	74.6
Asia & Oceania	27.4	32.1	43.7
Latin America	5.1	6.4	10.3
Africa	1.3	1.5	2.3
Total	156.7	167.5	211.0

Most of the pulp is today produced from temperate zone softwoods (Table 1.2) but the utilization of hardwoods (including those from tropical forests with broadleaved trees) has increased rapidly over the last decade and a future growth is foreseen. Today approximately 30 % of the total amount of wood used for industrial purposes is hardwood.

Table 1.2 Total fibre consumption for paper in 1974 and a capacity prediction for 1982. The estimated fibre sources are indicated (2)

Type of fibre	1974 Consumption million tonnes		1982 Capacity million tonnes	
Wood fibres	114		152	
hardwoods[a)]		28		38
softwoods[a)]		86		114
Non-wood fibres	7		12	
Recycled fibres	39		47	
Total	160		211	

a) the relative share of softwood and hardwood pulp is estimated

Another source for raw material is recycled paper which in 1974 made up 39 million tonnes of the total fibre consumption. An increased use of recycled paper can be foreseen in view of the rising cost of virgin fibres but the growth rate will probably be modest and declining.

Non-wood fibres (bagasse, bamboo, straw etc) in 1977 supplied less than 5 % of the total fibre consumption for conversion to paper. It is estimated that until 1982 the capacity for producing these pulps will increase by around 1.5 million tonnes (Table 1.3 and Appendix 2) primarily in China, Latin America and Southern Asia. Many of the mills producing pulp from non-wood fibres are small (capacity less than 10 000 tonnes/year) and relatively old. It should be noted, however, that in certain regions non-wood fibres constitute an important raw material for the pulp and paper industry.

Table 1.3 Non-wood fibre pulping capacity estimated for 1978 and 1982 (million tonnes) (2)

	1978	1982
North America	0.7	0.7
Europe (East and West)	1.2	1.2
Asia	6.5	7.5
Latin America	1.1	1.5
Africa	0.3	0.3
Other	0.6	0.7
Total	10.4	11.9

1.2 Environmental impact of the pulp and paper industry

Production of pulp and paper affects the environment in a number of ways. Pollutants are discharged into the air and water, noise is generated and the mill buildings and stacks constitute a feature of the landscape.

Noise from the process equipment and from internal and external means of transport is a feature of all mills or factories. Moreover, the landscape picture is affected, especially by pulp and paper mills; the process equipment can be 50-100 m in height, with chimney stacks rising to between 100 and 150 m.

The air and water pollutants originating from the wood components and from the normal process chemicals may be termed process discharges. In addition, the mills emit a certain amount of auxiliary chemicals, e.g. chelating agents and slimicides.

Most of the solid water pollutants from pulp and paper mills consist of fibres escaping from the process. The rest consists of solid inorganic salts, bark and wood fragments, mineral fillers etc. These form deposits mainly close to the point of discharge. However, the finest particles are carried long distances by water, making it turbid.

The dissolved water pollutants from the process can be classified into coloured material, easily and slowly biodegradable material, toxic material and salts. The coloured material originates mainly from the wood lignins. Highly-coloured effluents are those from the bleaching and screening departments in a pulp mill.

The coloured compounds are relatively stable to biodegradation. Under certain conditions they reduce the penetration of solar rays into water and thereby reduce the biological activity in the water and on the bottom.

Part of the material emitted from pulp and paper mills is rapidly degraded by the micro-organisms in the water. In the biological degradation of organic material, dissolved oxygen is consumed. In extreme cases this can lead to oxygen depletion, which severely affects aquatic life.

Examples of toxic components in the effluents are free chlorine from the bleach plant and resin and fatty acid soaps from mechanical as well as chemical pulping and bleaching.

Gases and dust are emitted from pulp and paper mills. Sulphur dioxide, some hydrogen sulphide and other malodorous compounds are emitted from sulphate mills and sulphur dioxide from sulphite mills. Small amounts of chlorine and chlorine dioxide are also emitted from the bleach plants, but will normally not cause any effects outside the mill area. The solid material, the particulates, consists mainly of inorganic salts. It should be pointed out, however, that by far the greater part of the chemicals (including the sulphur compounds) are recycled and reused within the process in modern mills.

In conclusion the main environmental impact comes from the pulping and bleaching of chemical pulps. The pollution load from mechanical pulping and paper making is usually lower.

Literature reference list Chapter 1

1. Pulp and Paper International 21(1979) 8, 22-23

2. Pulp and paper capacities 1977-1982. FAO 1977

2. FIBROUS RAW MATERIAL

2.1 Classifications of fibres

Plant fibres are the dominating raw material for pulp and paper. In addition minor amounts of synthetic fibres are used for special papers. The plant fibres can be classified into a number of subgroups (Table 2.1) according to origin.

Table 2.1 Classification of plant fibres

Subgroup	Species
Grain hairs	Cotton, kapoc
Bast fibres	Flax, jute, hemp, ramie, kenaf
Fibres from grasses and other monocotyledons	Straw, esparto, bagasse, bamboo, papyrus, reed
Leaf fibres	Abaca, sisal, aloe
Wood fibres	Softwoods, hardwoods

.2 Types of cells and their dimensions

Coniferous woods, or softwoods, are anatomically simpler than hardwoods. The fibrelike cell element called tracheid both gives support to the conifer and simultaneously serves as part of the transport system.

Fortunately, the tracheids, which are of the greatest importance in papermaking, present 90 % of the tree volume. The other cell types in conifers, longitudinal wood parenchyma, ray tracheids and ray parenchyma which in the living tree have the function of transporting and storing, water and nutriment, are shorter compared with the tracheids.

In leafy trees or hardwoods, there is a complex collection of cell elements. The most important ones are libriform fibres (fibres).They give support to the tree and comprise about 50 % of the tree volume. The other fibrelike elements are wide and thin-walled vessel cells, which form the liquid conductive vessels in the wood. The vessel cells have very characteristic features so they are quite helpful in identification of hardwood species in pulp. Several hardwoods may also contain varying amounts of intermediate cell elements, as for instance fibre tracheids. A relatively high proportion of the wood material in hardwoods is formed by short parenchyma cells, whose papermaking potential is poor.

Table 2.2 summarizes the average length and width of a number of fibres. Some of the fruit and bast fibres are long and also rather wide. The grass fibres tend to be rather slender and short.

The softwood fibres have an average length of 3 mm as compared to 1-2 mm for hardwoods. Bamboo and bagasse fibres have dimensions comparable to those of hardwood fibres.

Table 2.2 Dimensions of tracheids and libriform fibres for some species (2,3,4,5,6,7,8,9,11,12,13)

Group	Species	Length, mm		Diameter, µm	
		min-max	average	min-max	average
Grain hairs	Cotton	10-45	25	20-40	25
Bast fibres	Flax	20-60	32	14-20	20
	Jute	1-5	2.5	15-25	18-20
	Hemp	5-55	25	13-41	25
	Ramie	20-250	120	20-80	50
	Kenaf	0.6-6.0	1.5	14-40	25
Fibres from grasses and other monocotyledons	Cereal straw	0.6-3.1	1.5	7-27	13
	Rice straw	0.7-3.5	1.5	5-15	9
	Esparto	0.5-1.8	1.4	7-14	10
	Bagasse	0.8-2.8	1.6	10-34	20
	Bamboo	1.5-4.4	2.3	7-27	18
	Reed	0.3-4.0	1.2	3-32	12
Leaf fibres	Abaca	2-13	6.0	10-30	24
	Sisal	0.8-8.0	3.0	8-40	20
Softwoods	Jack pine	1.5-5.7	3.5	28-52	40
	Scandinavian spruce	1.5-5.5	3.5	24-59	35
Hardwoods	European beech	0.4-2.3	1.3	25-39	29
	European aspen	0.5-1.5	1.0	13-37	21
	Red gum	0.5-1.4	1.0	12-20	17
	Eucalyptus globulus	0.6-1.4	1.0	14-20	18
	Gmelina arborea	1.0-1.2	1.1	28-38	32
	Mangrove	1.2-2.6	1.7	16-29	25
	Willow	0.4-1.1	0.7	10-29	20
	Oak	0.4-1.9	1.2	10-35	21
	Teak	0.6-2.0	1.3	16-29	25

2.3 Chemical composition

Wood substance is essentially composed of carbon, hydrogen and oxygen. There are also various amounts of inorganic constituents (ash content). The elementary composition of the organic part of dry wood, with surprisingly small variations, is about:

Carbon (C): 50 %
Hydrogen (H): 6 %
Oxygen (O): 44 %.

The corresponding chemical composition can be written approximately as $C_{1.5}H_{2.1}O_{1.0}$ (9). The composition of annual plants (grass etc) is very similar, the carbon content being a little lower and the oxygen content a little higher than the values shown above.

The strong similarity in composition of all fibre material used for pulp fabrication is the basic reason why pulp mills using the same pulping method, but very different raw materials, generate similar quantities of polluting substances.

The wood and plant fibres consist of the following main components: cellulose, hemicelluloses, lignin, extractives and inorganics. The distribution of these components varies between wood and plant species, within various parts of the tree and within various parts of the fibre. There are also differences between different plants within the same species because of variations in the composition of the soil.

If, however, the species are classified into three groups: softwoods, hardwoods and annual plants, it is found that the quantitative distribution of the five component groups falls within approximate limits indicated in Table 2.3.

Table 2.3 Chemical character and content in woods and plants of fibre components (9,10)

Fibre component	Approximate composition of base molecules	Approximate degree of polymerization DP	Degree of crystallization	Approximate content of:		
				softwoods %	hardwoods %	annual plants (straw, bagasse) %
cellulose	$C_6H_{12}O_6$	1000 - 10 000	crystalline	35-45	40-50	30-40
hemicelluloses	$C_6H_{12}O_6$ $C_5H_{10}O_5$	50 - 500	amorphous	25-30	20-40	20-35
holocellulose	-		-	65-70	60-80	70-80
lignin	$C_9H_9O_2(OCH_3)$	5 - 100	amorphous	26-33	19-40	12-20
extractives	terpenes $(C_5H_8)_n$, etc resin acids (C_{20},$H_{30}O_2$ etc) fatty acids (C_{18},H_{32},O_2 etc) phytosterols ($C_{29}H_{50}O$ etc)	1 - 3	-	2-4	1-5	0-3
inorganics (ash content)	alkali carbonates silica	-	-	0.2-0.6	0.2-4	2-18

The content of lignin, the "glue" between the fibres, is relatively constant in softwood and highly variable between hardwood species. the lowest values are found in annual plants. The amount of holocellulose (cellulose and hemicelluloses) accordingly varies between 60 and 80 % in hardwoods, compared to 65-70 % in softwoods and 75-85 % in annual plants. The last figure, however, would amount to 75-85 % if the inorganic content did not constitute such a large share of the plants (12-18 %, average approximately 8 %). The inorganic content of wood is low although there are exceptions in certain tropical hardwoods.

The cellulose varies relatively little between woods and annual plants in spite of the very different physical appearance of the two groups. Some hardwoods are, however, more rich in cellulose than softwoods and annual plants. Table 2.4 gives more data of some species.

The content of cellulose in the raw material considerably influences the chemical pulp yield since only about 10 % is dissolved in a kraft pulp cook. This contributes to the high kraft pulp yield of certain hardwoods compared to softwoods, although the main reason is the fact that hardwood hemicelluloses are dominated by xylans and softwood hemicelluloses by glucomannans, the former being more stable during alkaline pulping conditions. 50-80 % of the hemicelluloses are broken down to saccharinic acids in alkaline processes, and to monosaccharides in acidic processes, respectively. Both types of compounds are easily dissolved in the cooking liquors. Almost all lignin is dissolved from the wood when chemical pulp is manufactured. The organic constitutents dissolved from the wood into the spent liquor are responsible for a main part of the pollution of the recipient unless they are efficiently recovered at the mill.

Table 2.4 Chemical composition of fibrous raw materials (1,3,4,5,7,9,11,12,13,14)

Group	Raw material	Cellulose[a]	Lignin	Hot water soluble	Alcohol-benzen soluble	Ash
				%		
Grain hairs	Cotton linters	80-85	3	1.0	3-11	1-4
Bast fibres	Cotton stalk	38-44	22-29	8-17	4-7	3-4
	Jute	64	11-21	1.1	1.2	0.5
	Kenaf	33-45	9-17	3-15	2-8	1-4
	Ramie	66-69	0.6	5.5		
	Crotalaria	36-52	14-18	5-17	1-7	
Fibres from grasses and other monocotyledons	Cereal straw[b]	34-40	16-20	9-15	2-5	4-11
	Rice straw	28-41	10-17	13-17	1-7	14-22
	Esparto	33-38	17-19	9-15	1-5	6-8
	Bagasse	26-39	19-22	3-11	3-11	1-5
	Bamboo	35-47	22-30	16-21	3-6	1-5
	Reed	33-43	18-23	8-12	5-8	3-6
Leaf fibres	Abaca	56-70	5-12	0.5-4	1-2	0.5-2
	Sisal	65-78	7-10	0.5-3	1-2	0.5-2
Softwoods	Jack pine	41	28	3.7	3.3	0.2
	Scandinavian spruce	43	29	2.3	1.8	0.4
	Scots pine	43	29	3.9	4.8	0.4
	Southern pines[c]	41-44	25-28	2.5-2.4	2.5-3.6	0.2
Hardwoods	European beech	41	22	1.5	1.8	0.4
	American aspen	52	19	2.1	2.9	0.4
	Red gum	43	26	4.3	1.4	0.4
	Eucalyptus globulus	47	20	2.4	1.5	0.4
	Gmelina arborea	46		6	4	0.8
	Salai	50	27	8.9	4.3	1.8
	Birch	41	20	1.5	2.8	0.4
	Tropical hardwoods mixed	35-49	22-32	1.5-10	1-10	0.5-3

a) measured as alphacellulose
b) wheat, barley, oats, rye
c) including loblolly pine, shortleaf pine, longleaf pine, slash pine, red pine, white pine

Literature reference list Chapter 2

1. Escolanto, E.U., Francia, P.C., Semana, J.A.
Proximate chemical composition of some commercial grades of abaca (Musa textilis Nec) fibres
Philippine Journal of Science, vol. 100, No 2, 1971

2. Fibrous raw materials
Paper vol 183, No 4, 1975, p 197

3. Harrar, E.S.
Houghs encyclopedia of American woods, 1957

4. Isenberg, I.H.
Pulpwoods of United States and Canada. The Institute of Paper Chemistry, Appleton, 1951

5. Mandon, R.N.
Summary of investigations carried out at the cellulose and paper branch on suitability of agricultural residues for pulp, paper and board, Indian Pulp and Paper, Dec 1975-Jan 1976

6. McGovern, J.N.
Physical properties of fibres and pulps from wood and non-wood plant fibres
PTJ 1971, August 1960

7. Misra, D.K.
Installation and operation of chemical recovery systems in soda pulp mills utilizing wheat, straw and bagasse as raw material
Tappi CAR 58, p 7-22

8. Misra, D.K.
Industrial experiences and problems involved in stock preparations and paper making using non-wood fibrous materials
Tappi CAR 43, p 119-167

9. Rydholm, S.
Pulping processes
Interscience Publishers, N.Y. 1965

10. UN/FAO
Evaluation of mixed tropical hardwoods for pulp and paper manufacture, J. Navarro, Rome 1976

11. UN/FAO
Guide for planning pulp and paper enterprises, 1973

12. UN/FAO
Proceedings of the conference on pulp and paper development in Asia and the Far East held in Tokyo, 1960

13. UN/FAO
Pulping and papermaking properties of fast growing plantation on wood species, Rome 1975

14. Varadhan, R., Swamy, V.S.R., Murthy, N.U.S.R.
Rice straw as a raw material for papermaking
Ippta Vol XI, No 4, 1974

3. PROCESS DESCRIPTIONS

3.1 The yield and process define the pulp type

The fibrous raw material is composed principally of cellulose, hemicelluloses and lignin (table 2.3). Cellulose is composed of long chains of identical chemical units. Lignin is the "glue" keeping the fibres together in the living plant. Lignin contains chromophoric groups giving the fibre a more or less coloured appearance.

High yield pulp does not generally form a strong paper. It is necessary to remove the major part of the lignin from the fibres in order to improve the strength characteristics of the pulps. In the process a large part of the hemicelluloses are also removed. Depending on the amount of lignin removed the characteristics of the pulp change and the pulp yield drops.

There are no well defined yield limits between various groups of pulps. The following table gives a rough indication of the yields for the main pulp groups.

Pulp group	Pulp yield %	Process examples
Mechanical	90-97	Stone gwd, RMP, TMP
Chemimechanical	85-95	Cold soda
Semichemical	60-85	NSSC
Chemical	40-60	Sulphite, sulphate
Dissolving	30-45	Sulphite, sulphate

Chemical and dissolving pulps are both of the chemical pulp type which means that the fibres are liberated by chemical dissolution of the lignin middle lamella. Thus no mechanical action in refiners or beaters is required for fibre separation (except possibly for the treatment of knots and rejects).

Semichemical pulps are treated by a chemical pulping process followed by a treatment in mechanical fiberizing equipment (2). When the cooking yield of the semichemical pulp is as high as 85-95 % the term chemimechanical pulps is often used. The properties of chemimechanical pulps are more similar to those of mechanical than to chemical pulps even though some characteristics may be drastically changed. In mechanical and chemimechanical pulping the recovery of dissolved wood components and chemicals is very rarely undertaken.

In this publication mechanical and chemimechanical pulps are treated as one group and semichemical, chemical and dissolving pulps are treated as another separate group of pulps. The reason for this is that chemical recovery is common practice in the manufacture of the latter pulps, but not in the manufacture of the former.

3.2 Preparation of fibrous raw material

In the manufacture of pulps the preparation of the fibrous raw material is a vital operation for the quality of the pulp. The aim is to handle and store the raw material in an economic and efficient way and to prepare it in a suitable form for pulping. The unit operations involved in the preparation are the following:

- storage and handling of the fibrous raw material

- separation of inorganic impurities such as stones, sand etc.

- separation of organic impurities such as bark, pith, nodes etc.

- cutting and screening of the fibrous raw material.

The processes differ widely, however, depending on the type of fibrous raw material and the quality required for the material going to the pulping operation.

When handling wood the first step is usually debarking (Figure 3.1). The bark is removed from the log by friction either by other logs (barking drums), by mechanical tools or by water jets (hydraulic debarking). The barking drums can be operated with or without water addition. The debarking result is usually better and the wood losses lower in wet debarking.

After the wet debarking the bark and bark particles are separated from the water by mechanical screens or sedimentation and then pressed to remove water. Also in dry debarking the bark is sometimes pressed to remove water.

The clean logs are then chipped to produce wood fragments of suitable size for the pulping operations (about 30 x 30 x 4 mm). The chips are screened to remove any that are too large or too small and are then transported to storage bins or chip piles. In the case of stone groundwood production, the logs are cut to suitable length (usually 0.9 to 1.5 meters) but are not chipped.

The preparation of straw and bamboo is similar to that of wood except that no debarking is necessary. Instead there may be additional screening stages after the chipper (or cutter) to remove dust, nodes etc.

The most important aim of the pretreatment of bagasse is to remove as much as possible of the pith cells (Figure 3.2). Presence of pith leads to high chemical consumption and problems in the pulping operation and also to impaired paper and pulp characteristics.

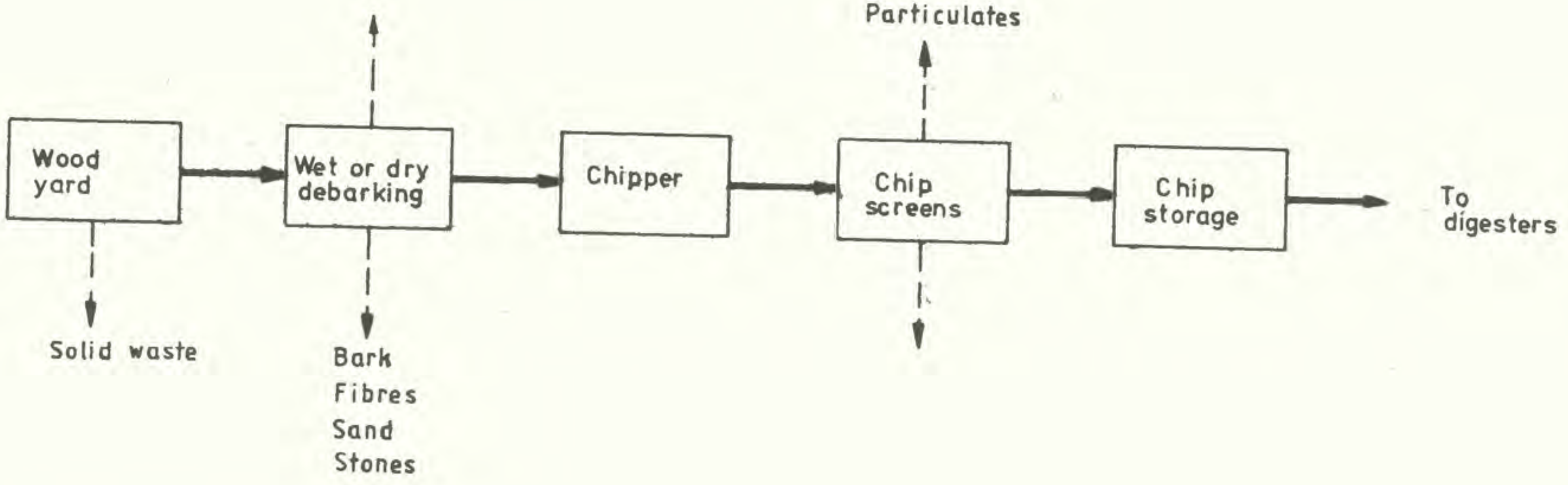


Figure 3.1 Preparation of wood

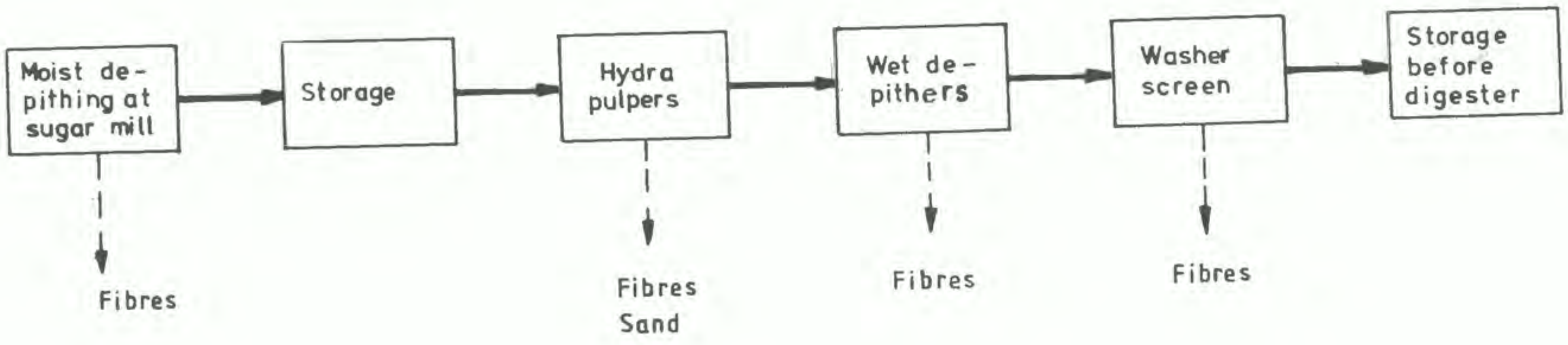


Figure 3.2 Preparation of bagasse

Bagasse is delivered from the sugar mill (with or without partial depithing) to storage in bale or bulk form. For the depithing, dry, moist and wet methods can be employed. Dry depithing can be done only after the bagasse has dried in storage. Moist depithing is applied directly on the bagasse as it comes from the sugar mill and it is then conveyed to storage from where it goes through the wet depithing and is fed to the pulping unit.

The trend today is toward bulk storage of bagasse. In the Ritter storage system, a lactic acid culture is added to control the biological reaction during storage. In other bulk storage systems acid or alkaline water could be used (3). In conventional bulk storage the pile is sprinkled with water to prevent the temperature from increasing due to fermentation of residual sugar and to prevent drying out with consequent fire hazard (3).

Several annual plants can be harvested only during a short period of the year. Such is the situation for straw, reed and bagasse. Almost a year's supply of raw material must therefore be stored at the mill, which requires a large storage area.

The annual plants are cut to pieces either in cutters and dry screened or in hydrapulpers and wet screened. The screening separates nodes, stones etc.

3.3 Mechanical and chemimechanical pulping

The aim of the pulping process is to liberate the fibres and prepare them in a form suitable for paper making. In mechanical pulping the fibres are liberated by mechanical actior only, while in chemimechanical pulping the bonding between the fibres is softened by a chemical treatment. The fibre liberation is then achieved by mechanical action.

The type of wood economically available is an important factor in selection of the groundwood process applied. Softwood does not necessarily require pretreatment and has thus been the traditional raw material of the stone groundwood process, and more recently of the refiner mechanical pulping (RMP) and thermomechanical pulping (TMP) methods. The low strength of hardwood mechanical pulps can be substantially improved by a chemical pretreatment which also may decrease the power demand. This development made possible the use of large stands of hardwood for mechanical pulping. Sawmill wastes are another source of raw material for the mechanical processes which use wood chips.

For pulping of non-wood fibrous raw materials chemical pretreatment is normally necessary to obtain the desired strength properties of the finished paper.

In the stone groundwood process logs are fed to the grinders and are forced hydraulically against the rotating grindstone, specifically designed for the purpose. The pocket-type grinder is most common although the magazine, ring and continuous or chain types are being installed in new mills. The grinding occurs in the presence of a large quantity of water which acts both as a coolant and a carrier to sluice the pulp from the grinder.

The pulp slurry is passed through screens to remove dirt and shives. Oversize rejects may be passed through a disc refiner and returned to the system ahead of the fine screens. The pulp slurry is then thickened on a decker to between 10 and 15 percent consistency and discharged to a stock chest for mill use, bleached, or thickened further for transport to other mills.

In the refiner groundwood process the chips are first washed and then refined. Disc type refiners are used which contain discs between which the wood passes together with a stream of water.

The pulp is discharged from the refiners diluted to a consistency of about eight percent and moved by a high-density pump to the secondary units following which it is diluted to low consistency and subsequently screened and freed of dirt in centri-cleaners. Screen rejects are refined and returned to the process ahead of the screens.

A recent development in refiner groundwood is equipment in which the lignin between the fibres are softened with steam and the chips refined in the range of 110-130°C. This process is called thermomechanical pulping. A flow diagram is shown in Figure 3.3. The strength characteristics of this pulp are superior to those of other mechanical pulps and thus its use reduces the percentage required of the more expensive chemical pulp in the newsprint furnish to provide adequate strength.

In the production of cold soda pulp, chips are treated at atmospheric or elevated pressure with sodium hydroxide. The chemical demand varies from 2 to 10 percent of the weight of the wood depending on the wood species used and the pulp quality desired. The liquor is recycled after fortification. Subsequent separation of chips and liquor is normally accomplished by screw or roll presses. The treated chips are then handled in a manner similar to that used in manufacturing refiner groundwood.

The liquor most commonly used in chemimechanical pulping contains buffered sodium sulphite. Chips are first impregnated with the liquor and heated to a maximum temperature of 135 to 150°C. The chips are then refined and treated in roughly the same way as indicated for cold soda pulps.

The brightness of the mechanical, thermomechanical and chemimechanical (pH 4-8) pulps is normally in the range 55 to 65 % ISO. The cold soda pulps are usually darker than the mechanical pulps. To increase the brightness and widen the

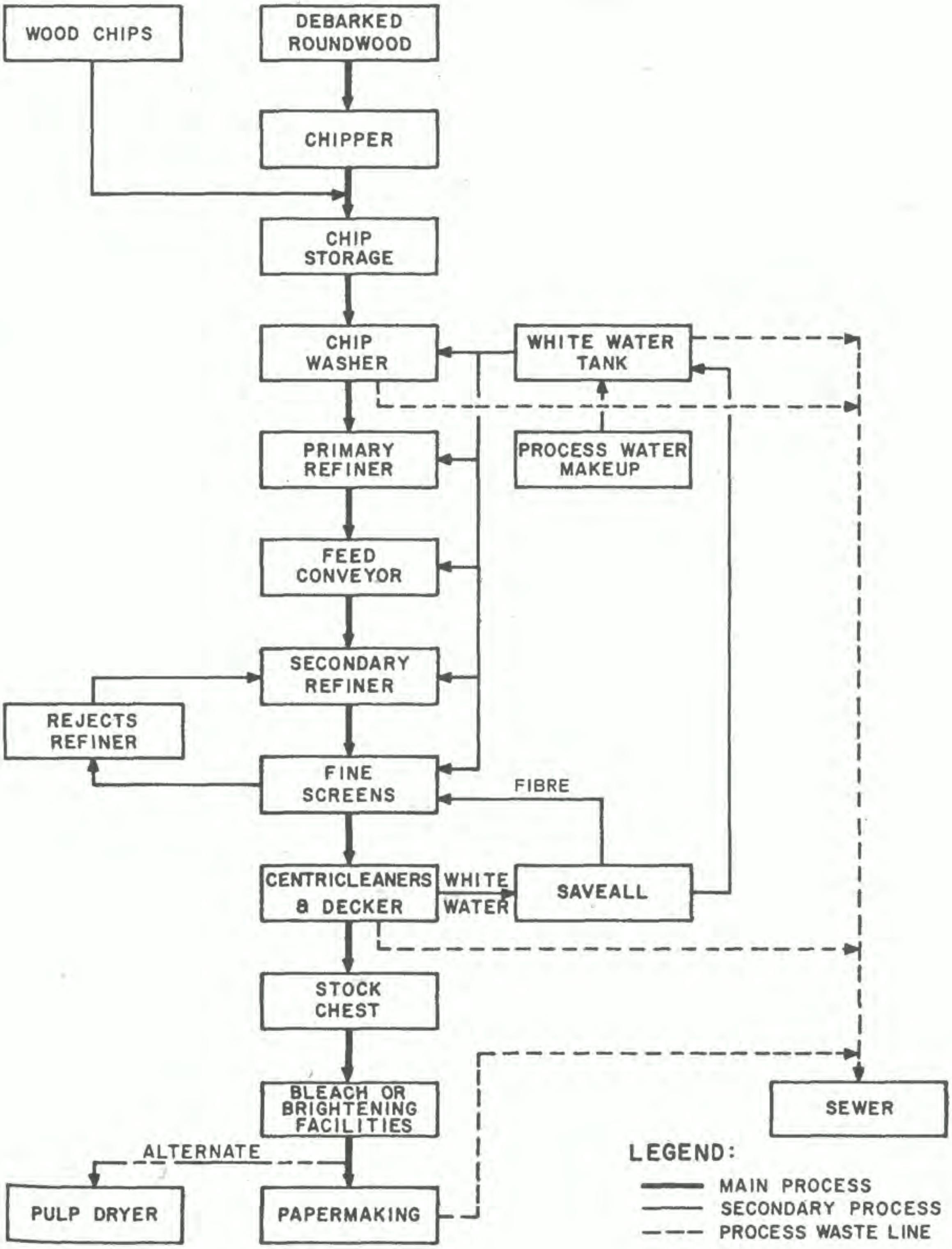


Figure 3.3. Principal flow diagram of the thermomechanical pulping process (TMP).

use of these pulps in writing and printing grade papers a bleaching is undertaken. The most common bleaching agents for these pulps are peroxides and dithionites (hydrosulphites). By a single stage peroxide bleaching the brightness may be increased by about 10-20 % ISO while dithionite normally give 5-10 % ISO increase. By two stage bleaching even higher brightness values can be achieved.

The bleaching is normally carried out in a separate bleaching stage i.e. a retention tower or directly in the refiner followed by a retention tank (refiner bleaching).

Sometimes cold soda pulps are bleached in multistage sequences with chlorine compounds (chlorine, hypochlorite). The quality of the resulting pulp is then approaching that of bleached chemical pulp.

3.4 Sulphate and soda pulping

In the sulphate process an alkaline cooking liquor, containing sodium hydroxide and sodium sulphide, is used. In the soda process only sodium hydroxide is used. The chemicals in the cooking liquor are, normally recovered and reused. A simplified process flow sheet is given in Figure 7.3. There are several variants of the process, here only the most essential ones are dealt with.

The cooking can be carried out in batch or in continuous digesters. In batch cooking the digester is filled with the raw material. During and after the filling direct steam is added until most air is removed. After this operation the cooking liquor (white liquor) is introduced and the cook is started by raising the temperature. The cooking temperature is maintained for a given period, then the pressure is decreased by release of steam and gases and the contents of the digester is emptied to a blow tank.

In a continuous digester the above operations take place continuously. Usually a continuous digester is equipped with a washing zone so that part of the washing of the pulp occurs in the digester.

The pulp blown from the digester is washed in a system often consisting of several stages through which pulp and washing liquid are passing in counter-current fashion. Before or after washing the pulp is screened to remove solid impurities e.g. knots and fibre bundles.

In many cases a white pulp is the desired end-product. The unbleached pulp is then treated with chlorine compounds (chlorine, chlorine dioxide and hypochlorite) in several stages. Between the bleaching stages the pulp is treated with sodium hydroxide to remove the degraded lignin fragments.

After bleaching the pulp is screened again to remove any remaining impurities and then dried or brought to an integrated paper mill.

The liquor from the pulp washing (black liquor) which contains the dissolved wood solids and residual cooking chemicals, has a relatively low concentration of dry solids (10-20 %). It therefore has to be concentrated before burning. Evaporation is carried out up to a dry solids content of 55-68 %. Two different methods are used, one is based totally on indirect evaporation of the liquor with steam in a multiple effect evaporator. In the other, the final part of the evaporation is carried out by direct evaporation with flue gases from the recovery furnace.

The black liquor is burned in specially designed furnaces; the most common is a conventional recovery boiler operating with reducing conditions in the bottom zone. In the upper part of the furnace more air is introduced and the reduced components (e.g. H_2S and hydrocarbons) emitted from the bottom part are oxidized. On the bottom of the furnace a smelt is formed consisting mainly of Na_2CO_3 and Na_2S.

The smelt from the furnace is continuously removed and dissolved in a dissolving tank. The liquor (green liquor) is then treated with lime to convert carbonate to hydroxide in the causticizing process. The resulting liquor, "white liquor" is then ready for use in the digester.

Most sulphate mills recover the sludge resulting from causticizing (lime mud) and reburn it to lime in a rotary kiln. Fluidized bed calciners are used at some mills instead of the rotary kilns.

Beside the conventional recovery boiler there are other processes for the liquor burning such as:

a) Broby
b) Denayer-EPI-Markumber
c) Tampella smelter
d) SCA-Billerud
e) Copeland
f) Sonoco
g) Zimpro.

Processes a-c are simplified and cheaper types of recovery boilers. The amount of steam generated is smaller than in conventional boilers.

Processes d-g are mostly used for semichemical recovery processes but can also be used for soda pulping. d-f are normal combustion processes and g is wet combustion under high pressure.

3.5 Sulphite and neutral sulphite pulping

The sulphite pulping process to produce chemical pulp is carried out in basically the same type of equipment as the sulphate or soda process. Batch digesters are commonly used for sulphite pulping, but simple continuous digesters are frequent for semichemical processes. In this instance, however, the fibrous raw material is treated with a solution containing dissolved SO_2, hydrogensulphite or sulphite ions with a pH value between 1.5 and 12 (Table 3.1).

Table 3.1 Composition of the cooking liquor in sulphite pulping

Type of cook	pH	Reacting component
Acid sulphite	1.5	dissolved SO_2, H^+
Bisulphite	3–5	HSO_3^-
Neutral sulphite (NSSC)	8	SO_3^{2-}

By acid sulphite or bisulphite pulping chemical pulps can be produced. Neutral sulphite pulping is usually limited to the production of chemimechanical or semichemical pulps. The base in the cooking liquor is calcium, magnesium, sodium or ammonium. Calcium can, however, only be used for acid sulphite pulping and magnesium only for acid and bisulphite pulping, due to limited solubility at higher pH values.

After the cook the pulp is washed and the reclaimed cooking liquor is treated to recover the pulping chemicals. The washed pulp can be bleached and dried in the manner described for sulphate and soda pulps.

Recovery of pulping chemicals is in practice limited to sodium and magnesium base liquors since calcium is impossible to recover. When sodium is used the inorganic compounds form a sulphide and carbonate smelt on the bottom of the furnace as in a sulphate pulp recovery furnace. The SO_2 formed is absorbed in the chemical recovery system.

At the combustion of ammonium base liquors, the ammonia is oxidized mainly to nitrogen, and cannot be recovered. Sulphur is oxidized to sulphur dioxide which can be recovered in an ammonia scrubber.

When magnesium is recovered the evaporated liquor is burnt in a furnace and the magnesium compounds are converted to magnesium oxide. The magnesium oxide is collected in a dust separator and then dissolved in water. The magnesium containing solution is then used to absorb sulphur dioxide from the flue gases and then used again as cooking acid after suitable adjustments.

For the recovery of magnesium base liquors a number of system exists e.g. Babcock Wilcox, Ahlström and the Fläkt system. Chemical recovery in sodium base pulping is performed mainly by three methods: the Broby, the SCA-Billerud, the New Ebara, the Tampella and the cross-recovery method. A sodium-based sulphite or NSSC mill is often combined with a kraft mill by a common recovery system (cross-recovery).

Neutral sulphite semichemical pulping, usually called NSSC, is used for production of pulps with a yield of 60-85 % usually with sodium as the chemical base.

After evaporation to about 60 % D.S. the spent liquor can be burned in a furnace.

3.6 Waste paper treatment

Waste paper has become a major economic factor in the paper and paperboard industry. The 1976 level of waste paper recovery and utilization in some countries is shown in Table 3.2.

Table 3.2 Waste paper recovery and utilization in paper and paperboard manufacture

	Total amount of fibres used (1000 tonnes)	Waste paper used (1000 tonnes)	Waste paper recovery rate (%)	Waste paper total fibre furnish rate (%)
Canada	12 100	816	-	6.7
USA	53 700	12 200	25.0	22.7
Brazil	2 008	610	28.2	30.4
Colombia	275	103	-	37.5
Germany, Fed. Rep.	5 995	2 839	33.1	47.4
Italy	4 208	2 081	35.8	49.5
Sweden	5 100	428	29.6	8.4
United Kingdom	3 809	2 014	28.6	52.9
Japan	16 322	6 264	42.2	38.4
India	1 023	81	-	7.9
Philippines	301	94	21.5	31.2
Australia	984	493	33.7	50.1
New Zealand	763	36	-	4.7

A variety of waste papers are used to make several grades of pulp. Most waste papers must be sorted and carefully classified since

a) not all papers are suitable

b) certain types are desirable for some reclaimed pulps and not suitable for others

c) paper which can be successfully processed by one process could be troublesome if mixed with paper requiring different treatment.

Waste paper treatment may be classified into two general categories:

- processing mechanically without use of chemicals
- processing by means of chemical treatment such as is employed by deinking mills.

If the aim is to obtain a reasonably even product with no special demands for brightness or colour for use in e.g. certain packaging papers it may be sufficient to use mechanical treatment of the waste followed by screening operations. If, however, a relatively high and stable brightness is required and if the product must be free from residual ink, then a more elaborate flotation deinking or washing deinking operation, involving chemical addition and cleaning must be considered.

Much of the equipment required for waste paper processing is very similar for both processes. Some of the following operations are therefore included in all waste paper systems.

- Defibering in pulpers
- coarse screening
- final defibering
- deinking
- bleaching
- cleaning/screening
- dewatering/thickening.

The overall design for each mill must, however, depend on the quality and the cleanliness of the waste paper utilized as well as the specific end uses for the products manufactured.

An example of a simple treatment system is given in Figure 3.4

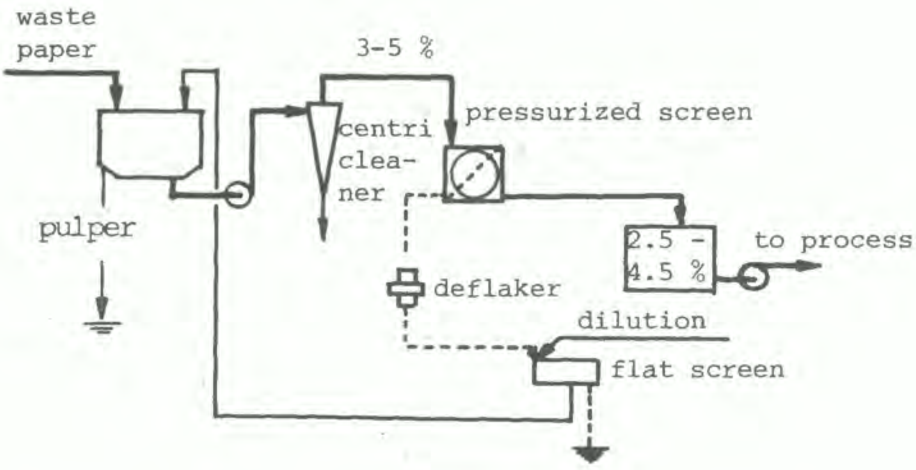


Figure 3.4 Waste paper treatment system

The paper is processed in a pulper (equipped with screens to remove heavy impurities) and then screened in a cyclone and a pressure screen. The reject from the pressure screen may be treated and returned to the process. The pulp may also be thickened and then homogenized in a refiner before being pumped to the paper mill. The trend today is towards less defibering in the pulpers and towards achieving the final breakdown of fibre bundles by use of deflakers at a consistency of about 4 % or frotapulpers at about 20 %.

Deinking operations serve the need to eliminate carbon black, ink particles, fillers, starches and fine dirt which are present in the waste papers. For deinking of waste papers two methods exist:

- washing on drum filters
- flotation.

One important distinction between the washing and the flotation system is that in the flotation almost all filler and dissolved contaminents remain with the fibres. In filter washing dissolved solids and other suspended solids are removed with consequent lower yields.

A flotation deinking system is shown in Figure 3.5.

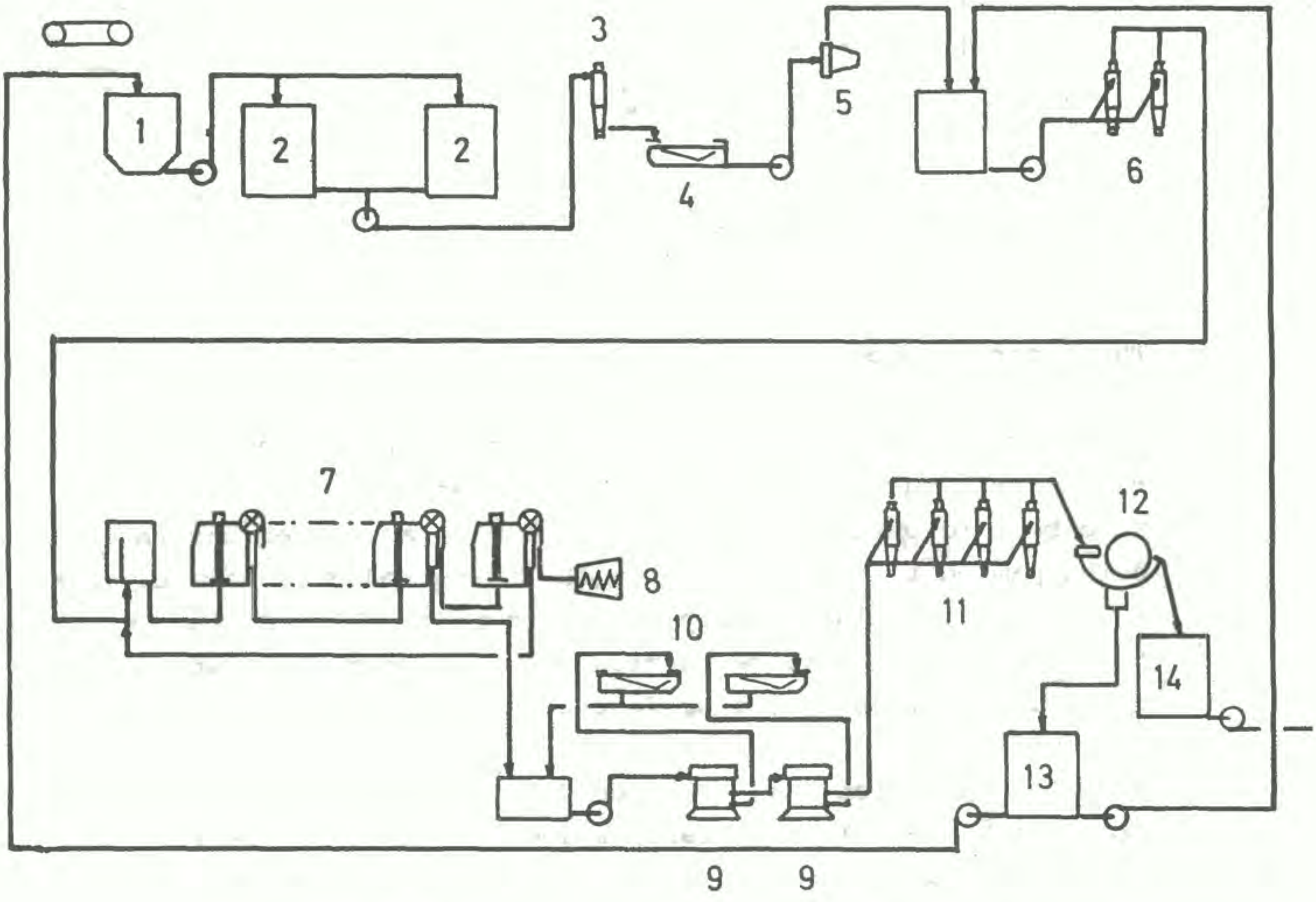


Figure 3.5. Principle flow sheet of the flotation process. 1.Pulper 2.Buffer chests 3.High consistency centricleaner 4.High consistency screen 5.Deflaker 6.Sand separators 7.Flotation cells 8.Centrifuge 9.Pressurized screens with holes and slots 10.Reject screens 11.Centricleaners 12.Thickener 13.White water chest 14.Storage chest

The pulping and screening system is similar in design to the system shown in figure 3.4 but chemicals are usually added to facilitate the pulping. Chemicals are also added to separate the ink from the fibres in the flotation cells where a major portion of the ink is removed.

The final operation in the waste paper system is that of thickening the pulp before storage. The aim is to recycle the white water to the process system and to reduce the carry over of contaminants to the paper mill.

3.7 Paper making

In the paper mill the pulp is converted to paper. An integrated paper mill is situated near a pulp mill and receives the pulp as a slurry directly from the pulp mill. The non-integrated paper mill normally obtains the pulp in dried and baled form and then the first operation is to disintegrate the pulp in water.

The first stage of the paper making operations is the stock preparation. The fibre types to be included in the stock are beaten and mixed. Chemicals and fillers are also added (Figure 3.6).

Many pulps need refining in conical or disc refiners in order to develop suitable strength characteristics. The consistency of the pulps is carefully regulated during the stock preparation operation. White water from the paper machine is preferred for the adjustment of the pulp consistency in order to save the fibre and heat content of the white water. The resulting closing of the white water system also reduces the raw water consumption and the size of possible external effluent treatment installations.

The stock is pumped to the paper machine system where it is screened and then brought to the paper machine itself.

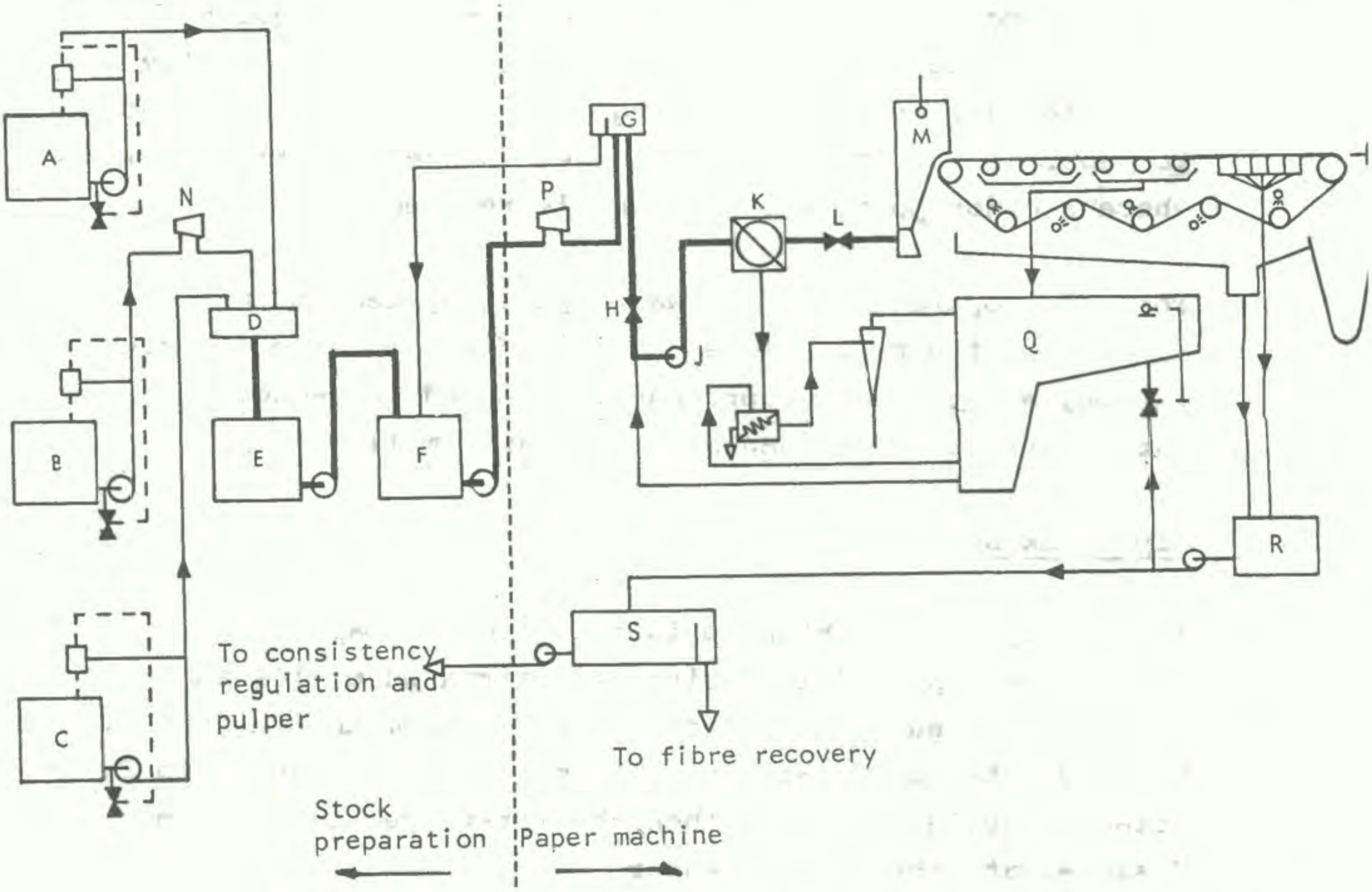


Figure 3.6 Simplified flow sheet of a stock preparation system and part of the paper machine wet end system. A.Groundwood pulp B.Sulphite pulp C.Broke D.Proportioner E.Mixing chest F.Machine chest G.Level box H.Stock valve J.Fan pump K.Machine screen L.Trottling valve M.Inlet box N.Stock refiner P.Machine refiner Q.Wire pit R.Seal pit S.White water chest

The sheet is dewatered on a fine mesh wire, pressed in several roll presses and air dried in a steam heated dryer section. After drying the sheet may be surface treated in a calender or coated before it is wound up on shafts to large reels.

The paper is then finished according to the customer's requirements, including rewinding, cutting to sheets and off machine coating.

A great variety of paper qualities can be fabricated, each requiring its own special manufacturing procedures. In a separate volume the environmental protection techniques available in paper mills will be covered both in general and in the manufacturing of particular paper qualities.

Literature reference list Chapter 3

1. FAO "Waste paper data" 1975-1976

2. Rydholm, S.
   Pulping processes, Interscience Publishers, N.Y. 1965

3. Gonin, C.R. and Venter, J.S.M. (1976)
   Comparison of the influence of various wet bulk storage methods on the pulping quality of sugar-cane bagasse
   CSIR Special report out 127

4. RATIONALE FOR REDUCTION OF MILL DISCHARGES

4.1 Introduction

The fibrous raw materials used in the pulp and paper industry generally consist of less than 50 % cellulose. The remainder is mainly made up of lignin, hemicellulose, mineral fillers, extractives, organic acids and inorganic salts. Part of these substances is generally not reclaimed or recycled and is therefore discharged into receiving water or to the atmosphere.

In addition to the nonusable parts of the fibrous raw materials, some of the process chemicals and the auxiliary chemicals used in paper making cannot be entirely recycled or retained in the product. Therefore, residuals of these chemicals and/or different transformation products may be found in the effluents or in the emissions to the atmosphere.

Finally, a small fraction of cellulose fibres are discharged, mainly resulting from accidental spills.

There is growing recognition that different materials in effluents and/or emissions have considerable resource value. This is one reason why techniques for increasing reclamation and recycling of raw materials and chemicals are gaining interest. Attempts are being made to find new and unconventional uses for by-products, in addition to using the energy value of the organic wastes for steam production in boilers etc.

Parallel with this increasing awareness of the need of saving raw material and making use of formerly unused by-products, there is a firmly established consciousness about the need for environmental protection. As a matter of fact, a long tradition within the pulp and paper industry has clearly shown that it is feasible to fullfil these two objectives simultaneously. This results in i.e. the saving of materials, gaining economic benefits, as well as protecting the environment by minimizing the discharge of pollutants.

Short glossary of terms used

Anaerobic = capable of living in absence of free oxygen
Anoxic = devoid of oxygen
Benthic macrophytes = attached vascular plants
Benthos = the sea bottom or the lake bottom
Euphotic zone = zone where photosynthesis occurs
Eutrophication = an increase of the nutritional standards of water-body and its biological consequences
Heterotrophic bacteria = mainly fungi
Hypolimnion = the water between the thermocline and bottom of lakes
Mutagenic = causes genetic damage
Oligotrophic = low nutrient state, poor
Periphyton = plants attached to surface
Phototrophic zone = zone where photosynthesis occurs
Phytoplankton = planktonic algae (plant plankton)
Trophogenic zone = zone where primary production takes place
Zooplankton = planktonic animals (animal plankton)

4.2 Saving raw material and energy resources

A pulp mill producing pulp for paper should apply the manufacturing process most suitable for the paper quality and maintain a fibre yield as high as possible for that specific paper. Chemical pulp used in high quality paper has a raw material yield of only 40-60 %. The part of the fibre that is dissolved in the cook has had its value reduced to "calorific value" (equivalent to that of coal, oil or gas) while the fibres have a "fibre value" (several times its calorific value). Maintaining a high pulping yield is thus very essential for a pulp mill. Likewise, utilizing the maximum possible part of a log, for sawn products, is of the utmost importance for a saw mill.

Reducing fibre losses from pulp and paper mills is also an important way of economizing with scarce fibre resources. There are still pulp and paper mills loosing 5 to 10 percent of its useful prime fibre to the recipient.

Recovering the chemicals and the calorific value of the spent cooking liquor has been common practice in pulp mills for a long time. However, even if the bark, pith, etc is utilized for steam production the pulp mills must produce part of their steam with expensive coal, oil or gas. The price of these combustibles thus sets the value of the dissolved wood components. Efficient recovery of spent liquor and a cleaner environment is then favoured by the rising energy prices. Technical problems, however, such as silica content of the liquor, sometimes set a limit to the possibilities of closure of the mill systems.

4.3 Polluting discharges from the pulp and paper industry

4.3.1 Air pollutants

The main discharges to the atmosphere from the pulp and paper industry can be classified according to the following table:

Sulphur compounds
Chlorine compounds
Inorganic dust
Organic dust

Sulphur compounds discharged to the air are of two types:

1. Malodorous compounds such as hydrogen sulphide, methyl mercaptan (MN), dimethyl sulphide (DMS) and dimethyl disulphide (DMDS).

2. Sulphur dioxide (SO_2).

The malodorous compounds are formed mainly in the sulphate cooking process. The sulphur dioxide is liberated in the acid sulphite process but also in the neutral sulphite and bisulphite processes. In the sulphate processes some SO_2 is formed in the recovery boiler. The soda process emits neither malodorous compounds nor sulphur dioxide, provided that the chemical system can be kept free from sulphur. This has proved to be very difficult.

Chlorine compounds are emitted in minor amounts from the lignin dissolving bleaching processes. The emissions are mostly of the so-called "diffuse" type which means that the emissions are not located to any particular point source but orginate as fumes from tank vents, wash filters, sewers etc. The gases are chlorine or chlorine dioxide.

Sulphur and chlorine containing gases are toxic to man. Especially hydrogen sulphide must be treated with great caution.

Inorganic dust is emitted from recovery boilers, oil or coal fired boilers and from lime kilns. With efficient filters (especially electrofilters) and scrubbers the atmospheric emissions can be brought down to very low values. The dust consists mainly of sulphates and carbonates.

In the raw material preparation department of the mills some dust of organic nature is often formed, for instance at dry debarking of wood in barking drums; in the dry depithing of bagasse or in dry cleaning of straw. Chipping and handling of bamboo also create large amounts of organic and inorganic dust. In the case of bagasse dry depithing, the dust has been found to cause bagassosis, a respiratory illness (3).

4.3.2 Land pollutants

Land pollution may occur as a consequence of:

- fall out of atmospheric pollutants and emission of harmful gases (especially sulphur dioxide SO_2)
- irrigation with waste water having high salinity
- dumping of sludge.

The emission of sulphur dioxide (SO_2) to the atmosphere may cause adverse effects to the vegetation surrounding the mill. Areas where the vegetation is severely damaged are sometimes found in the vicinity of large SO_2-emitters.

In countries with a serious shortage of water, treated waste water is often used for irrigation. Due to the relatively high salinity of this water (chlorides, sulphates), it has to be used with caution so as not to disturb the ion balance of the soil.

Dumping of sludges and other solid wastes from the mill must be carried out in a way to avoid all risks for leaching of toxic and odorous substances into ground and surface waters.

4.3.3 Water pollutants

The discharges to water may be classified according to the following scheme:

Suspended solids
Slowly biodegradable compounds
Easily biodegradable compounds
Toxic compounds
pH changing compounds
Inorganic salts.

The major part of the suspended solids (SS) in the mill effluents usually consists of fibres or fibre particles. The fibres are of the same type as those in the final products. Fibres are detrimental because they tend to settle in the receiving water forming fibre banks in which fermentation may occur. This may cause oxygen depletion. Suspended not yet sedimented fibres in the water cause turbidity. It also causes stress symptoms to fish and influences their respiration rate, growth rate, blood composition, ability to find food, avoid enemies etc. It has been concluded that low concentrations (below ~ 25 mg/l) of suspended material is not harmful to fish life (25). Mechanical pulp fibres decompose slowly while chemical pulp fibres decompose more rapidly.

The content of easily biodegradable compounds is usually measured by the BOD test (Appendix 3). A considerable part of the wood components dissolved in the pulping and bleaching processes is easily biodegradable. Examples of such compounds are low molecular hemicelluloses, methanol, acetic acid, formic acid, sugars etc.

Slowly biodegradable compounds in the mill effluent mainly consist of high molecular substances of lignin and carbohydrate origin. The amount of such compounds in a mill effluent can be estimated by measuring the COD-value (chemical oxygen demand) and subtracting the BOD-value from it. The lower the ratio BOD/COD the higher is the fraction of slowly biodegradable compounds.

Such compounds are usually coloured and therefore reduce light penetration into the water. They also affect the quality of the drinking water. Living organisms may absorb slowly biodegradable compounds, which may cause them biological changes.

The toxic effects of pulp mill discharges have been studied intensively in recent years. Investigations of the toxicity of effluents from various kraft mill departments have shown that black liquor and the liquor condensates contain the components most toxic to fish. From bleach plants the chlorination and first alkaline extraction stages often account for the largest amounts of acute toxic substances. The chlorination stage effluent contains some free chlorine and is thus subject to rapid chemical changes which makes it difficult to evaluate its toxic effects (22).

A substantial part of the acute toxicity of black liquor is caused by resin acids and by unsaturated fatty acids (26,27). It has been confirmed that accidental discharges of black liquor cause an increase in the toxicity of the mill effluent (21).

The discharges from the pulp industry may have pH-changing effects in the receiving waters. Generally it can be stated that high (over 9) as well as low (below 5) pH-values influence the biological life and reinforce the toxicity of the effluents. In a marine environment the buffering capacity of the salt water drastically reduces any pH-variations.

Dissolved inorganic salts in the effluents originate mainly from the cooking liquor, from the bleach plant (mostly chlorides) and from the chemical recovery area. They are usually harmless to aquatic life. Salts containing nitrogen (N) and phosphorus (P), act as fertilizers in the recipient. The amounts can vary considerably between mills, depending on the raw material, cooking process etc (25).

4.4 Environmental effects of water pollutants

The discharges into the environment by the pulp and paper industry are complex mixtures of substances. Substances discharged into the atmosphere will fall out or be washed out and thus be deposited onto the soil and surface waters. The substances emitted directly into the water are chiefly suspended solids, such as fibres, bark and wood particles and soluble and colloidal material such as wood extractives, lignin degradation products, organic acids, sugars, alcohols, phenolic compounds and inorganic salts.

In this chapter the primary effects of these substances will be discussed in relation to their main characteristics.

4.4.1 Oxygen consuming material

The free water mass is oxygenated through gas exchange with the atmosphere, the inflow of oxygen rich water; and through photosynthesis whereby oxygen is produced mainly by phytoplankton. In stagnant waters (lakes) the diffusion of oxygen from the surface to deeper water layers is limited. Therefore, the amount of dissolved oxygen available is dependent on the thickness of the trophogenic zone, where photosynthesis can take place. This, in turn is dependent on the transparency of the water and also on the presence or absence of nutrients and toxic substances.

A decrease of the oxygen content in water is brought about by oxygen consuming processes taking place in the free water as well as in the contact zone between sediment and water. The extent and rate of these processes, among which the most important are the bacterial breakdown of organic matter originating in the trophogenic zone of the water itself, or being brought into the water from outside sources (e.g. pollution) and the respiration of organisms, depend on a variety of circumstances.

The most important of these factors is of course the amount of oxidizable substances, but also the temperature of the water, especially in the hypolimnion, the deep waters, is of great significance. The rate of respiration and other oxidative processes is doubled or trebled by a temperature rise of 10°C. Thus, in tropical regions where the temperatures of the bottom waters of lakes are about 20°C higher than they are in the temperate region, other conditions being equal, four to nine times as much oxygen will be used per unit of time. The low temperatures in the deep waters of lakes in temperate regions cause a large proportion of the organic matter to be deposited undecomposed in the sediment, whereas the higher temperatures of tropical lakes (or estuaries etc) bring about far more decomposition in the water mass while the material is still settling.

The fact that the solubility of gases in water depends on the temperature is also of great importance to the oxygen situation in tropical waters. The amount of oxygen which may be dissolved in water decreases with increasing temperature, so that at, for example, 30°C only about half the amount of oxygen may be dissolved compared to the amount dissolved at 0°C. This means that in comparison with temperate regions, less oxygen is available in tropical regions for the breakdown of organic substances of industrial or other origin.

In waters affected by the pulp and paper industry the biochemical and total oxygen demand (BOD and TOD) will be increased mainly by four groups of substances of different origin:

a) mud and organic material from erosion caused by logging

b) bark, wood chips and sawdust from preparation of the raw material

c) fibres from pulping and paper making

d) dissolved organic matter such as sugars, organic acids, alcohols, lignin degradation products, phenols etc from the production of pulp.

4.4.2 Oxidizable dissolved and suspended material

With the exception of lignins, most of the dissolved and non-settleable suspended oxidizable material will be relatively rapidly degraded (within one to two weeks) using the oxygen that is dissolved in the water. Upon reaching the receiving water, volatile reduced divalent sulphur compounds will be emitted to the atmosphere or oxidized.

Lignins contribute to the long term oxygen consumption in the water. This was demonstrated for a river receiving waste water from a sulphate pulp mill, in which the BOD of 100 (BOD_{100}) days was found to be only approximately three times greater than the BOD_5 although only about 50 % of the lignins present had been oxidized (42).

It should be noted that biological treatment (with BOD-reduction of 85 %) of bleached pulp mill effluents gives only about 50 % reduction of TOC. The amount of slowly biodegradable compounds in the biologically treated effluents is thus very high (see Table 4.1)(18).

The relation between BOD and COD is a measure of the amount of slowly biodegradable compounds in effluents. The lower the ratio BOD/COD the higher is the fraction of slowly biodegradable compounds.

Table 4.1 Oxygen consumption by some pulp mill effluents. COD and BOD are given as concentrations in mg/l and as fractions of TOD in percent (After NCASI, Tech. Bull. 256 (1972)

	TOD	COD_{Cr}	%	BOD_5	%
Unbleached sulphate (sedimented)	875	800	92	400	46
Unbleached sulphate (bio. treated)	400	330	83	67	17
Bleached sulphate (sedimented)	690	680	98	260	38
Bleached sulphate (bio. treated)	410	290	71	36	9
Kraft liner (sedimented)	1400	1300	93	480	34
Kraft liner (chem. treated)	560	610	109	310	55
Kraft liner (chem. and bio. treated)	180	120	67	14	8
Unbleached paper board (white water)	630	580	92	230	37
Paper board (bio. treated)	180	140	78	32	18

4.4.3 Oxidizable settling material

The discharge of settling and colloidal organic substances into surface waters has in temperate regions resulted in a considerable accumulation of such material in the sediments of many rivers, lakes and coastal areas. Such deposits will often be the most decisive factor for the quality of the receiving water. The degradation of the organic material, e.g. coarse particles such as bark, fibres, and chips, and also finer fragments of fibres and colloidals, will be accomplished both through anaerobic and aerobic processes.

During the microbial respiration in aerobic sediment layers and also during the direct oxidation of reduced material from deeper anaerobic layers, dissolved oxygen in the overlying water is consumed. This may lead to totally oxygen deficient sediments and bottom waters and the formation of methane and hydrogen sulphide, the latter being extremely toxic to higher organisms. Release of organic matter from the sediments into the overlying water will also increase the BOD of the water.

The amount of dissolved oxygen consumed per unit time by polluted sediments is directly related to the extension of the area covered by settled material but fairly independent of the thickness of the layer of deposited organic material.

Investigations of the oxygen consumption of sediments subjected to varying degrees of pollution have been performed almost exclusively in temperate waters. Thus, at a temperature of about 15°C the oxygen demand in polluted sediments may be increased by 1-2 mg O_2/m^2, day compared to uncontaminated sediments. It is unclear, however, how the settleable solids will affect oxygen consumption of sediments in tropical regions. On one hand the rate of oxygen consumption will be increased due to the higher temperatures but on the other hand a larger portion of the settleable material will be oxidized in the water mass and thus never contribute to the oxygen demand by the sediments.

4.4.4 Biological effects

The content of dissolved oxygen in the water and in the sediments is an essential parameter for water quality. The discharge of organic oxidizable matter into surface waters will lead to a number of environmental changes. The details of these are dependent on the type of effluent and on the receiving water. In Figure 4.1 it is shown how in the temperature region, organic pollution may change different parameters and affect benthic algae and the bottom fauna (20).

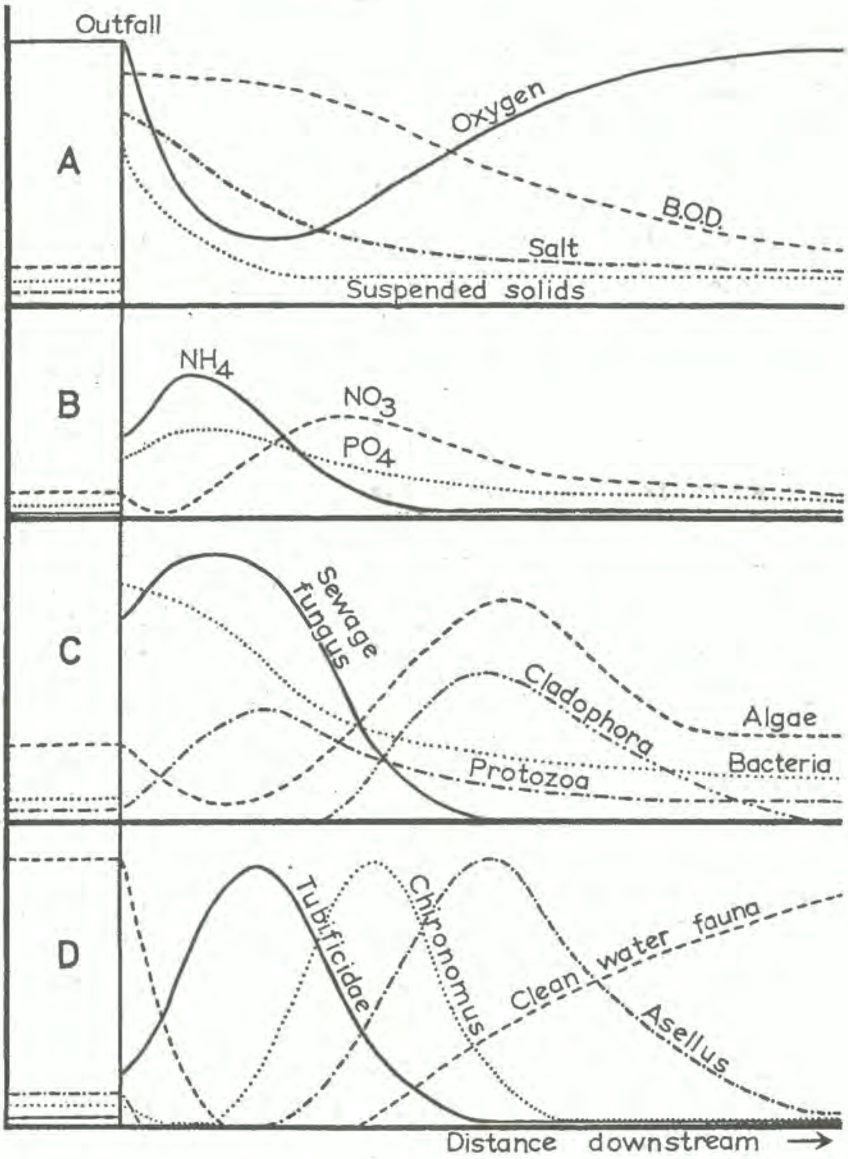


Figure 4.1 Diagrammatic presentation of the effects of an organic effluent on a river and the changes as it passes downstream from the outfall. A & B physical and chemical changes, C changes in micro-organisms and D changes in benthic animals 20)

Also fish and other marine organisms may be severely affected by a reduction of dissolved oxygen. Different species show different sensitivity to decreases of the oxygen content. Table 4.2 shows the reactions of fresh water fish to different levels of oxygen. It is concluded that some reduction in fish production often will occur at 5.6-6.2 mg O_2/l and that some species, viz salmonides, will disappear if the yearly minimum is 4.1-4.4 mg/l or less at 20-25°C (8).

Table 4.2 Illustration of the various "levels of protection" recommended by Doudoroff and Shumway (1970) for dissolved oxygen in freshwater

Level of protection	Acceptable seasonal minimum oxygen concentration mg/l		Percentage reduction in "relative performance index" of fish	Protection to fisheries resources
A	9.0*	7.5*	0	Maximal
B_1	8.3	7.1	1.5	Slight risk to spawning grounds
B	7.7	6.8	3.0	Slight risk to general fisheries
C	6.2	5.6	9.0	Some reduction in fish production will occur often
D	4.4	4.1	20.0	Elimination of some fish species

* These values correspond to the seasonal minimum oxygen concentration prevailing naturally. Thus, level-of-protection "A" allows no lowering in oxygen concentration

Note: In the interest of brevity, the pattern is illustrated with only 2 concentrations of Dissolved oxygen prevailing in a given body of water (i.e. 9.0 and 7.5 mg/l).

4.4.5 Suspended and settling solids

The activities of the pulp and paper industry give rise to emissions of suspended and settleable solids. The actual pulping processes give rise mainly to organic material while in tropical regions logging and side activities such as road construction, may cause heavy land erosion with resultant discharges of large amounts of inorganic material.

Suspended settleable and nonsettleable solids in the free water mass may cause symptoms of stress in fish. Feeding behaviour, ability to avoid enemies, growth, respiration rate etc, may be affected leading to lowered chances for survival.

In the European Inland Fisheries Advisory Commission, EIFAC, a proposal for criteria concerning suspended material and fresh water fish has been made:

a) Concentrations of less than 25 mg/l of suspended solids have not been shown to have negative effects on freshwater fisheries.

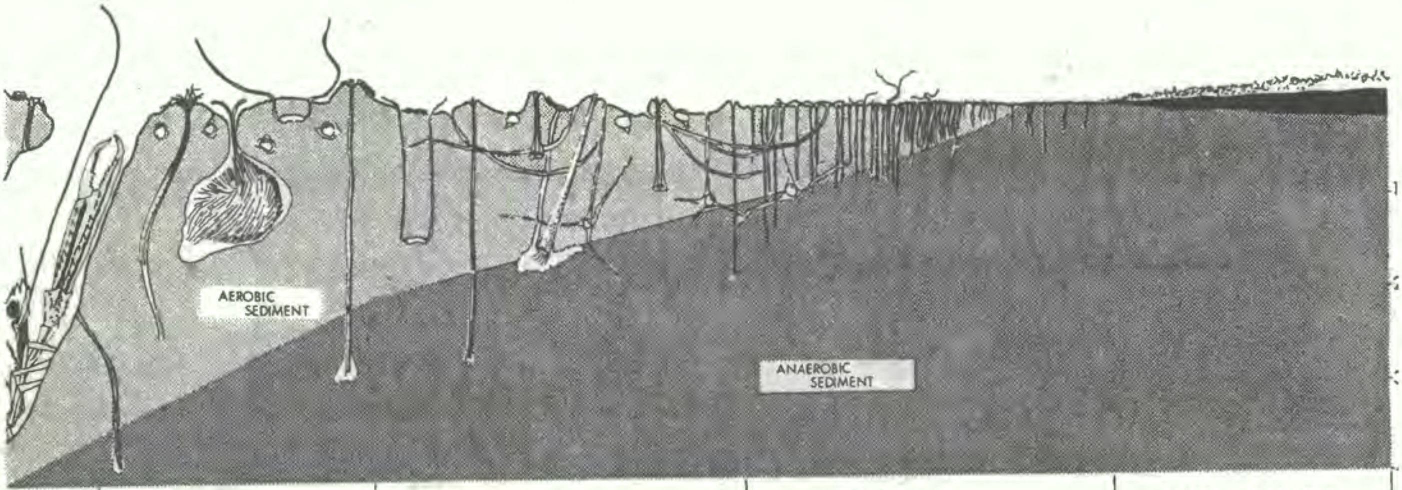
b) It is usually possible to maintain good to relatively good fisheries in waters which normally contain 25 to 80 mg/l of suspended solids.

c) Water containing 80-400 mg/l of suspended solids usually exhibit very poor yields of fish.

d) In 400 mg/l or more of suspended solids only very few fish species will survive.

Even though fish might tolerate several grams per litre of suspended solids for a few hours or days, such levels even for a short period of time should be avoided. The clogging of gills with particulate material has been found to be an important cause of fish deaths. It is recommended that the concentration of suspended solids must not exceed 25 mg/l for an optimal protection of fresh water fisheries (9).

The discharge of easily settleable solids may lead to the accumulation of such material on the bottoms. Thus spawning grounds may be covered and the supply of food organisms may be reduced. In an evaluation of the effects on the aquatic environment caused by settleable solids, the bottom fauna must be taken specially into consideration since these organisms are unable to avoid a polluted area and thus are continually exposed (Figure 4.2)(41).



ZONE	NORMAL	TRANSITORY		POLLUTED	GROSSLY POLLUTED
TYPICAL MACRO-FAUNA DOMINANTS	Nucula	Labidoplax	Chaetozone	Capitella	No MACROFAUNA
	Amphiura	Corbula	Anaitides	Scolelepis	
	Terebellides	Goniada	Pectinaria		Surface covered by Fiber blanket
	Rhodine	Thyasira	Myriochele		
	Echinocardium	Pholoe	Ophiodromus		
	Nephrops				

Figure 4.2 Diagrammatic representation of faunal and sedimentary changes under increasing organic loading. From right to left is seen a "fibre blanket", burrows of polychaetes, bivalves, brittle stars, a sea-urchin and finally a Norway lobster (Nephrops) (41)

It has been estimated that in a temperate lake the elimination of the bottom fauna in an area of approximately 1 km^2 results in a decrease in biomass of about 60 tonnes of fresh weight. This in turn corresponds to a yearly decrease in the production of feeding organisms for fish of approximately the same order of magnitude (44).

Another serious effect caused by water borne solids is siltation and clogging of irrigation canals and deterioration of the quality of irrigation water.

4.4.6 Light absorbing substances

The slowly degradable dissolved organics emitted from the pulp and paper industry mainly consists of residual lignin and high molecular carbohydrates. The residual lignins which are the most resistant to microbial degradation greatly affect the transparency of the water. Their absorption of light waves in the visible region is high and thus lignins reduce the penetration of light into the water and thereby the amount of light available for photosynthesis. Suspended fibres also absorb and scatter a part of the incoming light.

It appears that the most obvious effect on primary producers in receiving waters caused by discharge from pulp and paper mills is a reduction of the depth of the euphotic zone caused by light absorbing matter. A decrease in phytoplankton production is typical near the outlet, whereas more distant areas may show an increase in primary production, especially in nutrient deficient receiving waters. The long term net effect can probably be expected to be detrimental to the ecosystem. Both stimulation and depression of the primary production can change the structure of the phytoplankton populations and affect higher trophic levels, such as zooplankton and fish productivity.

A secondary effect of the decrease of the phototrophic zone and an overall reduction of the photosynthetic activity of the phytoplankton will in turn lead to a decrease of the oxygen content in the deeper water, due to the reduced internal oxygen production.

In lakes, where the water mass is stratified due to sharp temperature or salinity gradients, a decrease of the oxygen production could be serious in cases where the oxygen consumption is high in the bottom water.

Another secondary effect of a reduction of phytoplankton production is a decrease of the biomass and the number of species of zooplankton and eventually a reduction of fish production.

4.4.7 pH-changing substances

The discharges from the pulp industry may have pH-changing effects in the receiving waters. Generally it can be stated that high (over 9) as well as low (below 5) pH-values influence the biological life and increase the toxicity of the effluents.

The effluents from the bleaching department have very variable pH-values (below 2 to over 12). Some sulphite wastes have very low pH-values, 1.2 to 2.0. In some cases alkaline effluents from sulphate pulp mills may raise the pH-value in streams and lakes to a level lethal to fish. Usually, however, the predominant problem is caused by extremely low pH-values occurring in streams receiving some sulphite and bleaching effluents.

In the marine environment the buffering capacity of the salt water drastically reduces any pH-variations.

Table 4.3 gives a summary of effects of different pH-values upon fish. The table refers to long-term exposures. The table shows, for example, that pH-changes even in the pH-range of 6.5-9 may influence the toxicity of other toxicants. Resin and fatty acids have pK_a-values close to 7 and thus their toxic effects may change drastically when the pH-value changes in the pH-range of 6-9 (10,11,15,19, 21,-27,51).

Table 4.3 Summary of the effect of pH-values on fish (10)

Range	Effect
3·0–3·5	Unlikely that any fish can survive for more than a few hours in this range although some plants and inverletrates can be found at pH values lower than this.
3·5–4·0	This range is lethal to salmonids. There is evidence that roach, tench, perch and pike can survive in this range, presumably after a period of acclimation to slightly higher, non-lethal levels, but the lower end of this range may still be lethal for roach.
4·0–4·5	Likely to be harmful to salmonids, tench, bream, roach, goldfish and common carp which have not previously been acclimated to low pH values, although the resistance to this pH range increases with the size and age of the fish. Fish can become acclimated to these levels, but of perch, bream, roach and pike, only the last named may be able to breed.
4·5–5·0	Likely to be harmful to the eggs and fry of salmonids and, in the long term, persistence of these values will be detrimental to such fisheries. Can be harmful to common carp.
5·0–6·0	Unlikely to be harmful to any species unless either the concentration of free carbon dioxide is greater than 20 ppm, or the water contains iron salts which are precipitated as ferric hydroxide, the toxicity of which is not known.
6·0–6·5	Unlikely to be harmful to fish unless free carbon dioxide is present in excess of 100 ppm.
6·5–9·0	Harmless to fish, although the toxicity of other poisons may be affected by changes within this range.
9·0–9·5	Likely to be harmful to salmonids and perch if present for a considerable length of time.
9·5–10·0	Lethal to salmonids over a prolonged period of time, but can be withstood for short periods. May be harmful to development stages of some species.
10·0–10·5	Can be withstood by roach and salmonids for short periods but lethal over a prolonged period.
10·5–11·0	Rapidly lethal to salmonids. Prolonged exposure to the upper limit of this range is lethal to carp, tench, goldfish and pike.
11·0–11·5	Rapidly lethal to all species of fish.

Reference is made to different species on the basis of information known to us; the absence of a reference indicates only that insufficient data exist.

4.4.8 Compounds toxic to aquatic animals

Acute toxicity of effluents from pulp and paper mills to fish and other aquatic organisms has been reported extensively (22,32,50,51).

In spite of the fact that effects at sublethal concentrations are of greater ecological interest than the acute lethal concentrations (LC_{50}), there are still reasons for determining the LC_{50}-values (Appendix 3) of the effluents. This is due to the fact that LC_{50} determinations are technically easy and therefore more convenient for routine works. It has also been possible to establish a fairly constant relationship between the LC_{50}-values and the lowest concentrations where disturbances can be registered (Table 4.4).

Combined effluents from pulp mills, even without treatment, may be classified as "practically non-toxic" according to a system of classification proposed by a joint IMCO/FAO/UNESCO/WHO group.

However, a potential problem of stress to the aquatic ecosystem exists with pulp and paper effluents, because, even if the inherent toxicity is low, the discharge volumes are large.

Early investigators recognized that the volatile constituents of kraft effluents, i.e. hydrogen sulphide, methyl mercaptan, and methyl sulphide, were toxic to fish. They may be rapidly removed, however, by special treatment, such as air stripping and oxidation prior to effluent discharge. Over the past 5 years, most nonvolatile toxicants of importance have been identified and their contribution to acute toxicity has been assessed (Table 4.5).

Investigations of toxicity of unbleached sulphate (kraft) mill effluents showed that black liquor is the most toxic component, followed by the condensates.

Table 4.4 Approximate threshold for sublethal effects for salmon fish in sulphate mill effluents

Function of System Affected	Effects or KME	Species	Size	Temp °C	CONC. TESTED	APPROX. THRESHOLD	COMMENTS	REFERENCE
RESPIRATORY	"Coughing" response elevated	Rainbow	8 - 10 in.	11 ± 1	—	1.1% of full strength KME		Walden, et el. 1970(31)
	" "	Sockeye	207 - 321 g.	10.5 ± 0.5	—	0.1 - 0.2 LC50	Possible adaptation	Davis, 1973(3)
	Ventilation Volume increased	"	" "	" "	—	0.2 LC50	" "	" " (3)
	Oxygen uptake increased	"	" "	" "	—	0.33 LC50	" "	" " (3)
CIRCULATORY	Arterial Oxygen Tension reduced	"	to 2 kg	" "	0.35 LC50	—	No adaptation	" " (3)
	" "	Rainbow	150 g	10	0.33 LC50	—	" "	" " (3)
	White Blood Cell, Thrombocyte Counts reduced	Coho	Juveniles	11 ± 1	—	0.1 TL$_{m}$96	after 21 days exposure	McLeay, 1973 (13)
	Blood neutrophil count elevated	"	"	"	—	0.25 TL$_{m}$96	after 200 days exposure	Howard & McLeay, 1972 (14)
METABOLISM	Plasma glucose elevated	"	"	"	—	0.10 TL$_{M}$96	after 200 days exposure	" " (14)
	Blood & muscle lactate elevated	"	"	"	—	0.25 TL$_{M}$96	" "	" " (14)
	Swimming ability reduced	"	"	13 ± 5	—	0.20 TL$_{M}$96	—	Howard, 1973 (15)
	Muscle glycogen depressed	"	"	11 ± 1	—	0.10 TL$_{m}$96	after 200 days exposure	Howard & MeLeay, 1972(14)
GROWTH	Growth rate decreased	Sockeye	2.4 - 2.8 g	15	—	10-25% FULL strength KME	exoosed over about 8 weeks	Webb & Brett. 1972 (6)
	" "	"	Fingerlings	8	—	0.05 - 0.1 LC50	bleach waste	Servizi, et al. 1966 (5)
	" "	Chinook	Underyearlings	7 - 13	—	0.14 - 0.35 TL$_{M}$96	unbleached waste	Ellis, 1967 (16)
	" "	"	Juveniles	—	—	0.1 - 0.3 TL$_{M}$96	unbleached waste	Tokar & Owens, 1968 (29)
								Tokar, 1968 (25)
					—	6% full strength KME		Warren, 1972 (17)
	" "	Coho	Fingerlings	6	1:169 dilution	—	growth rate reduced after 30 days	Holland, et al, 1964(18)
	Food conversion efficiency reduced	Sockeye	2.4 - 2.8 g	15	—	10.25% full strength KME	8 week exposure	Webb & Brett, 1972 (6)
	Growth rate enhanced	Coho	4 - 10 g	10 - 13	—	0.1 - 0.2 LC50	several weeks exposure	Mason & Davis, 1973(19)
	" "	"	Juveniles	11 ± 1	—	0.1 - 0.25 TL$_{M}$96	70 day exposure	Howard & McLeay. 1972 (14)
BEHAVIOUR	Feed behaviour affected	Coho	4 - 10 g	10 - 13	—	0.1 - 0.2 LC50	response lasted for 2 weeks then disappeared	Mason & Davis, 1973 (19)
	Feeding behaviour affected	Chinook	Juveniles	—	—	0.14 - 0.36	long term study	Ellis, 1967 (16)
	Fish slow & "unreeponsive"	Coho	4 - 10 g	12 - 13	—	0.15 LC50	—	Mason & Davis, 1973 (19)
	"Alarm response" slowed	Sockeye	Fingerlings	8	—	0.4 LC50	Bleach waste	Servizi, et al. 1966 (3)
	Orientation to water current affected	Sockeye	Fingerlings	8	—	0.8 LC50	Bleach waste	Servizi, et al. 1966 (5)
	Fish avoid effluent	Sockeye	3 cm	10	—	0.2 LC50	within 1 hour	Kruzynski - Pers. Comm[1]
	Fish avoid effluent	Atlantic Salmon	7.7 - 14.8 cm	17 ± 0.2	—	10 mm (approx. 006 LC50)	"vague" response	Sprague & Drnry, 1969 (30)
	" "	"	"	"	—	3.77 × LC50	strong response	" " " (30)
	" "	Chinook	Juveniles	—	—	5 - 10% full strength KME	—	Jones, et al, 1956 (20)
								Dimick, et al, 1957 (21)
MORPHOLOGY & PATHOLOGY	Opaque eye pupils, internal hemorr-hages discolored livers	Chinooks	41.3 g	12	1:8.5 dilution	—	"synthesized waste"	Holland, et al (18) 1964 (18)
	40% had opaque eye pupils after 7 days exposure	Chinooks	"	12	1:15 dilution	—	" "	" "
HISTOLOGY	Histological & cytochemical change of liver, kidney, intestine	*Sparus macroocephalus*	25 CM	—	—	field exposure in cages off mill in seawater	12-24 Hr. Exposure (Sublethal)	Fujiya, 1961 (22)
ENDOCRINOLOGY	Plasma cortisol up	Sockeye	168 - 200 g	12.5	0.50 LC50	—	after 2 hr.	Donaldson - Pers. Comm[2]
	Mucous Production increased	"Salmonids"	Juveniles	—	—	2-5% full strength KME	—	Walden & Howard, 1963(23)
IMMUNOLOGICAL	Disease Resistance reduced	Coho	10 g	12.0	0.40 LC50	—	Methemoglobinemia Resistance	Mason & Davis, 1973 (19)

KME = Kraft Mill Effluent

The compounds responsible for the dominating part of the toxicity of the effluent from unbleached sulphate pulping are resin acids and to some extent unsaturated fatty acids (22).

Table 4.5 Compounds toxic to fish in pulp mill effluents (50)

	Toxic Contribution		
Chemical compound(s)	*Major*	*Intermediate*	*Minor*
Resin acids			
Abietic, dehydroabietic, isopimaric, levopimaric, palustric, pimaric, sandaracopimaric, neoabietic	KP D M S		
Chlorinated resin acids			
Mono- and dichlorodehydroabietic		KC	
Unsaturated fatty acids			
Oleic, linoleic, linolenic, palmitoleic		KP	D M
Chlorinated phenolics			
Tri- and tetrachloroguaiacol		KC	
Diterpene alcohols			
Pimarol, isopimarol, dehydroabietal, abietal		M	D
Juvabiones			
Juvabione, juvabiol, $\Delta^{1'}$-dehydrojuvabione, $\Delta^{1'}$-dehydrojuvabiol, dihydrojuvabione			M
Other acidics			
Epoxystearic acid, dichlorostearic acid, pitch dispersant		KC	
Other neutrals			
Abienol, 12E-abienol, 13-epimanool			D
Lignin degradation products			
Eugenol, isoeugenol, 3,3′ dimethoxy, 4,4′ dihydroxy-stilbene		S	

Abbreviations: K=kraft P=pulping D=debarking M=mechanical S=sulfite pulping C=caustic

In the bleachery effluents different neutral toxic substances and chlorinated compounds occur in addition to those previously listed (30). The first chlorination step accounts for the greatest quantity of toxic substances. Different tests of the toxicity of bleachery effluents give very variable results inter alia because of the rapid chemical modification of the chlorination step effluent (22).

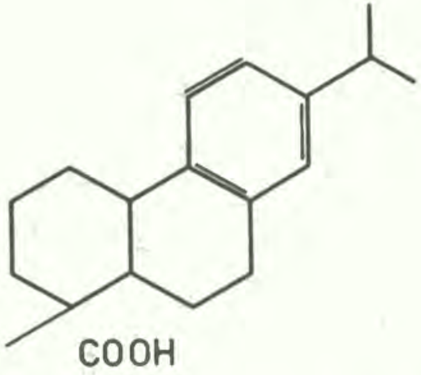
A significant fraction of the acute toxicity of caustic extraction effluent (E-stage) is due to six compounds, mono- and dichlorodehydroabietic acid, 9,10-epoxystearic acid, 9-10-diochlorostearic acid and 3,4,5-trichloro- and 3,4,5,6-tetrachloroguaiacol. The results of a control of caustic extraction effluents from six Canadian sulphate mills are summarized in Figure 4.3 (27,28).

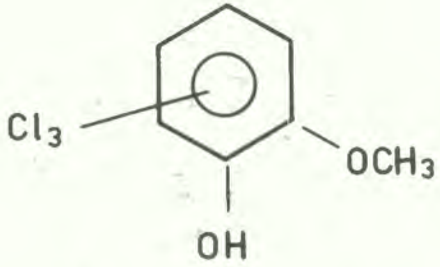
Neutralized bleached sulphate effluents without further treatment commonly have 96 hours LC_{50} values in the range 15-50 % v/v (volume/volume), whereas after biological treatment they are essentially nontoxic (51).

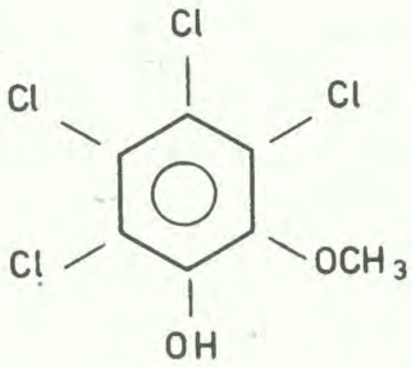
Combined mill wastes are often highly variable in toxicity for reasons not completely understood. Variation of effluent quality can be explained e.g. by variations in the pulping process, the use of combined condensates in the washing department and the frequency and amount of spills. The reasons for variation of toxicity in bleachery effluents are less clear. No useful correlation has been demonstrated between toxicty, BOD and/or TOC.

Because of the high oxygen demand of sulphite mill wastes, it is difficult to measure the acute toxicity of these effluents. The amount of toxicants in the effluents is correlated to concentrations of extractives such as terpenes and resin acids in the liquor. The concentration of these substances depends in turn on the extent of recovery of sulphite liquor.

The presence of resin acids at acutely toxic levels in sulphite mill bleach plant effluents may be due to lower removal of these compounds under the acidic cooking conditions of the sulphite process, compared with their extraction as sodium salts during alkaline sulphate cooks.







	DEHYDROABIETIC ACID		TRICHLOROGUAIACOL	TETRACHLOROGUAIACOL
	MONOCHLORO	DICHLORO		
CONC. MG/L	0,0 - 4,3	0,2 - 2,5	0,3 - 1,1	0,3 - 1,1
96-H LC_{50} (RAINBOW TROUT) pH = 6,4	0,6	0,6	0,75	0,32

Figure 4.3 Chlorinated, toxic compounds in caustic extraction effluent (28)

However, some studies indicate that whole sulphite waste toxicity per se is similar to the toxicity of sulphate effluents. Lignin degradation products, i.e., eugenol, trans-iso-eugenol and 3,3'-dimethoxy, 4,4'-dihydroxystilbene, accounted for about half of the toxicity in one sulphite waste sample. More recently, resin acids were found to be major toxic factors in a number of samples of whole mill effluents from a sodium-base unbleached sulphite mill, an ammonium-base bleached sulphate mill and a calcium/magnesium-base bleached sulphite mill (6,31,51,53,54).

Effluents from caustic extraction (E-stage) in bleaching of sulphite pulp are among the most toxic ones from a sulphite mill.

Resin acids making up the bulk of the acute toxicity of mechanical pulping effluents are abietic, dehydroabietic, isopimaric and palustric acids. Minor toxic components include pimaric, sandaracopimaric, neoabietic and the 18-carbon straight chain unsaturated fatty acids. Neutral materials which accounted for up to 30 % of the toxicity included diterpene alcohols and aldehydes and juvabione and related compounds. The amount of toxicants in effluents is dependent on process conditions, such as pressure and temperature during the disintegration of the wood (17,51).

Softwood debarking wastes contain many of the toxicants present in groundwood effluents, with acid components (mainly resin acids) accounting for about 90 % of the toxicity. Debarker effluents are highly variable in toxicity, normally being essentially nontoxic but sometimes relatively highly toxic at 1-15 % v/v (volume/volume), depending upon process water recycling, water use and particularly wood species (51).

4.4.9 Sublethal effects on aquatic animals

For natural situations the impact of industrial effluents on streams, lakes, estuaries or the sea is highly complex and dependent upon the characteristics of the effluent, the composition of the receiving water, relative flows and the dispersion of the wastes (see even 4.6). Nevertheless, field and laboratory definitions of biologically safe concentrations of various pollutants are important to environmental protection. Much research has been directed towards the development of rapid bioassays to measure the threshold at which sublethal effects occur (16,51). In table 4.5 are summarized different sublethal effects on fish of pulp and paper mill effluents (7).

Recent studies have even shown that the reproduction of fish is affected at concentrations of pulp mill effluents such as occur frequently in discharge areas.

Substantial evidence now exists from different sources, relating to different organisms, which shows a consistent pattern indicating threshold concentrations for various sublethal parameters to be approximately between 0.05 and 0.1 of the 96-hour LC_{50} value. At concentrations of pulp mill effluents in or below this range, no sublethal stresses have been observed (25,51).

Recently it has been demonstrated that chlorinated lignin degradation products could be accumulated in fish living in water areas, which receive bleach plant effluents.

Samples of stationary fish species have been analyzed and found to contain small amounts of chlorinated phenols and guaiacols in their extractable fat. The biological effects of these bioaccumulating compounds, originating from the bleachery effluents, are presently not well known. However, this group of chlorinated phenols is generally known to interfere with energy metabolism in higher animals (23,25).

It should be noted that physical parameters in the aquatic environment may strongly influence the toxicity of pollutants. In tropical regions with high water temperatures toxic effects may differ very much from what is known in temperate regions. The influence of environmental temperatures on the physiology and the ecology of aquatic organisms is well known. For example, toxicants that act on cellular enzymes involved in energy metabolism or that cause changes in uptake rates, such as inhibition of respiratory gas exchange at the gills of fishes, may have their effects intensified by temperature increases. The organisms also may receive greater amounts of the toxicants because of the increased diffusion or the active uptake associated with higher rates of water and solute movement across gills or other cell membranes. Therefore, it is tempting to generalize that temperature rises always increase toxicity to some extent (5).

4.4.10 Toxic effects on algae

Most of the current knowledge concerning effects of mill effluents on productivity and growth of aquatic plants comes from laboratory experiments. Both stimulation and inhibition of the growth of algae have been shown to occur in waters receiving mill effluents. The effects seem partly to be related to the concentration of effluents. Inhibition of photosynthesis can be caused by increased light absorption, altered pH or toxic properties of the effluents. The substances responsible for the latter effect have not yet been identified.

In a study of short term effects of a sulphate mill effluent on the productivity of periphyton and phytoplankton in a receiving freshwater, occasional reduction of photosynthesis was observed at effluent concentrations as low as 0.01 %. Raw effluents at concentrations of 1 % and higher, consistently reduce photosynthesis of both periphyton and phytoplankton. At high concentrations, pH elevation accounted for a significant portion of the inhibiting effect. Since the reduction in available light was insignificant, it was concluded that the depression in photosynthetic rates could be attributed to effluent toxicity.

Condensates and mixed effluents from bleaching have been found to be less inhibitory than effluents from barking and pulp washing (12). Only black liquor was very inhibitory or toxic. The unidentified toxicants were found not to be removed by biotreatment (46). Two marine phytoplankton species were adapted to and exhibited normal growth in relatively high concentrations of pulp mill effluents (48). Of six types of effluents tested, sulphate effluent was most inhibitory to growth, while combined sulphate and newsprint effluent passed through a resin column was least inhibitory. In another laboratory experiment on marine phyhtoplankton, it was suggested that it is possible for phytoplankton to adapt to relatively high effluent concentrations if pH remains normal (47,24). The impact of sulphate mill effluents has also been studied on benthic macrophytes (55). Compared with a control area, the affected area was characterized by reduced benthic macrophyte biomass, reduced species diversity and altered species composition.

4.4.11 Genotoxic properties

The mutagenicity of industrial and laboratory prepared effluents from bleached softwood and hardwood sulphate and sulphite pulps has been tested according to Ames using histidine-requiring mutant strains of Salmonella typhimurium (2,13).

Nearly all of the chlorination stage effluents were found to be mutagenic. The other bleaching effluents were not mutagenic at normal process concentrations. The mutagenicity of the standard C-stage effluent decreased to zero when the effluent was treated for 48 hours with a microflora adapted to this substrate.

Addition of liver microsomes decreased the mutagenic activity of the chlorination stage effluents, indicating that the mutagenic compounds are partly degradable in the mammalian liver.

The structure of the compounds causing the mutagenicity is not yet known. However, they can be extracted with ether and are known to be of small molecular size (< 1000 MW).

Mutagenicity has also been tested on hamster cell cultures. The same type of effluent (chlorination stage) that was mutagenic to bacteria, also had mutagenic effects on hamster cells. The neutral fraction of the chlorination stage effluents was found to have the highest mutagenic activity.

One of the key questions in studies of mutagenic substances in bleaching effluents, is whether they are persistent enough in receiving water to be accumulated in the food chain and thereby constitute a potential danger to man and higher animals.

4.4.12 Growth stimulating substances

Mill effluents have been shown to have an inhibitory effect on growth of plants and animals (see 4.4.3, 4.4.5). The opposite effect has also been found for bacteria and phytoplankton. Dissolved and solid organic compounds are discharged and nutrients (phosphorus, nitrogen and low-molecular growth-promotors) are subsequently released through microbiological decay. The discharge of inorganic phosphorus and nitrogen from pulp and paper industries is significant. It has been calculated that the discharge of phosphorus from a pulp mill producing 250 000 tonnes/year is equal to that contained in untreated sewage from a town with about 20 000 inhabitants (49).

In an investigation of bacterial populations in Lake Superior, receiving the effluents of a pulp and paper industry, elevated number of bacteria were found near the effluent (43). Populations of all bacterial types were higher near the effluent outfall than in other regions of the receiving water. Heterotrophic bacteria were the dominant group with up to 10^6 cells/ml near the outfall. Organic sulphur reducers were the next most numerous and were preponderant to sulphate reducers and sulphur oxidizers. High numbers of Enterobacteriaceae have been found both within the white water system of paper mills (34) and in the effluent discharged (19). Among these bacteria the capacity for nitrogen fixation was widespread.

Growth tests on algae have shown that mill effluents sometimes enhance growth, depending on the amount and variety of the effluents. Biotreated effluents were more stimulatory than raw and lime treated effluents (29). It has also been found that chelating agents in the effluents supplying trace metals to the algae were at least partly responsible for growth enhancement (24).

The content of carbohydrates and organic acids in pulp and paper mill effluents may also act as growth stimulators to colony forming bacteria (Sphaerotilus) or fungi, which can be found as yellow or brownish grey slimy covers on suitable substrates or floating on the surface downstream from an effluent outlet. This often causes increased mortality of fish eggs, anaerobic conditions and difficulties in handling fishing gear.

4.5 Evaluation of impact of pulp and paper mill discharge in the aquatic environment

It is a difficult task to make an evaluation of the overall impact in the aquatic environment caused by combined mill effluents. From the very beginning it is important to remember that no water pollutant acts by itself. It acts and manifests itself as a part of a complex of several other agents, both physical and chemical. The final effect of a water pollutant in the aquatic environment is the result of many factors acting together and of the interactions between them. The nature of these complex interactions is not well understood today. The way towards a deeper understanding of these phenomena is through a better knowledge of the structure and function of aquatic ecosystems.

A first condition for prediction of environmental impact is to know how the pollutants are distributed in the system, i.e. between water, aquatic organisms and bottom sediments. Similarly, a knowledge of the distribution after a few days, a few weeks and a few years is necessary. Furthermore, it is desirable to know the rate of metabolism of the pollutants by microorganisms and higher aquatic animals.

4.5.1 Towards a general system for evaluation of ecological effects

The effects that can be induced in natural waters receiving effluents from pulp and paper industries are thus very diverse and affects all trophic levels in the aquatic ecosystem.

In an attempt to create a common basis for evaluation of different types of detrimental influences, two basic criteria have been suggested for the classification of the effects of all kinds of water pollution. These are

1) extension of effect in time
2) extension of effect in space.

In this context it should be remembered that an "ecological effect" is defined as a departure from an original equilibrium of the ecosystem, i.e. a disturbance of the equilibrium.

The "seriousness" of an effect is judged by the time required from when the disturbance takes place until the original equilibrium is restored.

Effects, causing irreversible changes in the aquatic ecosystem should consequently be regarded as the most serious ones, whereas reversible damages should be regarded as less serious.

The total area affected is also important. Environmental effects in a vast area are considered to be more serious than those affecting a small area.

In Table 4.6 some environmental effects are grouped according to these principles. In the table, the following assumptions are made;

- The local area is defined as having a water mass with a relatively short turnover time and the average turnover time for refractory compounds is not longer than 10 days. However, the turnover time for sediments is more than a year.

- The distant area is defined as having a longer turnover time of its water mass, up to several years and is equal to the area where any effect can be detected.

- Short term effects are reversible within a period of up to a few weeks if the discharges cease.

- Intermediate effects are reversible within a year.

- Long term effects are irreversible for up to a year or more.

Table 4.6

Time Area	Short term, reversible effects	Intermediate effects	Long term, irreversible effects
Local	- Death (fish, plankton) - Decreased light transmission (plants) - Avoiding reactions (fish) - pH-change (fish) - Oxygen deficiency in water mass (fish) - Growth stimulation (heterotrophic organisms)	- Accumulation of toxic substances (fish, molluscs) - Bad taste (fish, molluscs) - pH-change (benthic animals) - Oxygen deficiency in sediment-water-interface (benthic animals)	- Sedimentation of solids, i.e. fibres (benthic animals) - Formation of hydrogen sulphide (benthic animals) - Destruction of fish spawning grounds (fish)
Distant		- Decreased light transmission (plants) - Hampering of photosynthesis (algae) - Avoiding reactions (fish)	- Accumulation of toxic substances (fish, molluscs) - Bad taste (fish, molluscs) - Growth stimulation (algae) - Persistant genotoxic substances in drinking water (higher animals)

4.5.2 Polluting substances causing short term effects

In Table 4.6 a number of examples are given of short term effects, causing rapidly reversible disturbances in the aquatic ecosystems. These effects, according to the basic criteria, might not be considered to be the most adverse ecological effects. However, they are generally very drastic (e.g. fish kills) and have therefore caused much public attention. This is one of the reasons why some of the pollution abatement work in the pulp and paper industry has been concentrated on the elimination of these very obvious, but nevertheless short term, effects.

This group of effects can be caused by a number of substances occurring in the pulp and paper mill effluents, viz:

- substances with high acute toxicity
- light absorbing substances
- substances causing avoidance reactions
- pH-changing substances
- soluble, oxygen-consuming substances
- substances stimulating heterotrophic growth.

4.5.3 Polluting substances causing long term effects

The long term effecs, which cause irreversible disturbances in the ecosystem equilibria are the most adverse ecological effects. Pollution abatement work based on ecological principles should give priority to the reduction or elimination of substances causing this type of effect. Growing awareness for these principles and priorities has led to their being increasingly applied in pollution abatement technologies.

Among the substances which may cause long term effects, the following should be mentioned:

- fibres and other settleable solids
- subtances which show a tendency to bioaccumulate in fish and other aquatic organisms
- substances which through their accumulation may cause chronic toxicity or interfer with reproduction
- substances giving bad taste or odour to fish and shell-fish
- substances stimulating algal growth and thereby cause eutrophication
- persistant substances which have genotoxic and/or other chronically toxic properties and thereby present risks to consumers of drinking water contaminated by these substances.

4.6 Effects related to different types of receiving waters

Most of the research concerning effects on plants and animals caused by pulp and paper mill effluents has been carried out in Canada, USA and the Scandinavian countries. Consequently, very little is known about effects related to receiving waters in other parts of the world. Almost nothing is known about ecological effects in receiving waters in tropical and subtropical areas where these kind of pollutants are discharged. Therefore, it is inevitable that this section to a large extent has to be based on experiences from the northern hemisphere and on theoretical ecological principles.

The need for effect oriented investigations in tropical and subtropical receiving waters, where pulp and paper mill industries are discharging, has to be emphasized.

4.6.1 Rivers and shallow lakes

In spite of the relatively small portion of the earth's surface that is occupied by freshwater, its importance to man is significant. These lakes and rivers constitute the most convenient and cheapest source of water for domestic and industrial needs. Frequently, they also provide the most convenient and cheapest waste disposal systems (36).

Production, standing crop and species diversity of biotic communities in running waters and shallow lakes are to a large extent controlled by a few physical and chemical limiting factors, i.e. temperature, transparency of the water, current, dissolved oxygen, carbon dioxide and inorganic nutrients (phosphorus and nitrogen). Industrial activities always constitute a potential risk that the limiting factors will alter and affect the ecosystem.

Discharges from pulp and paper industries into running water often result in increased average temperature, turbidity and reduced light penetration, lower oxygen concentration and higher concentration of inorganic nutrient. Near the outlet this often leads to anaerobic conditions where heterotrophic organisms, like bacteria and fungi dominate. This may result in fish-kills and production of hydrogen sulphide.

The movements of the water make sedimentation of solids slow. Sedimentation of e.g. fibres is achieved in basins where the flow rate is retarded. Depending on the morphology of the basins, more or less detrimental effects on benthos can be expected. Shallow lakes are generally more susceptible than deep lakes.

Organisms living in fresh waters with low hardness and low concentration of chelating agents, are more susceptible to bioaccumulating and toxic substances.

4.6.2 Deep lakes and reservoirs

Pollutants from pulp and paper industries generally constitute a minor threat to larger lakes than to streams and shallow lakes. This is partly due to dilution of the waste water. Tropical lakes having high surface temperatures tend to exhibit weak density gradients and irregular circulation of the water mass. Lakes in subtropical and temperate regions on the other hand usually have a distinct thermal gradient from top to bottom and effluents are accumulated in the deeper parts where anaerobic conditions usually prevail. This is also to be expected in very deep tropical lakes which tend to be mixed only in the upper layers.

Sometimes heavy loads of fibres cause detrimental effects near the outlets. Settling solids accumulate in deep parts of the lakes where the renewal time is slow. In these areas, benthos is often wiped out and anoxic conditions are created.

4.6.3 Coastal areas

Most of what has been said about conditions and effects in deep lakes is also valid for coastal areas. However, many coastal areas e.g. estuaries, shallow bays, swamps, mangroves and coral reefs are high by productive and diverse and serve as nursery grounds for valuable pelagic fish species. Accumulation of fibres in sheltered bays followed by insufficient oxygen conditions can be a local nuisance. Bioaccumulation of persistent toxicants in fish can constitute a risk for people fishing in polluted areas.

However, marine organisms are generally less susceptible to pollutants than fresh water organisms because of their different physiology and because the medium reduces toxicity of potentially harmful substances.

4.6.4 Waste water disposal by irrigation

In countries with a warm, dry climate, land irrigation by waste water, with or without pretreatment, may be a suitable solution to the disposal problem.

In some cases most of the waste water will be evaporated from the irrigated areas, and in other cases most of the waste water will penetrate the uppermost soil layer. Colloidal and dissolved substances are in this case adsorbed on to the soil surface and attacked by a variety of microorganisms inhabiting the soil and vegetation which break down the organic substances in the waste water.

Before the waste water can be used for irrigation, suspended solids should be removed as completetely as possible especially in cases of spraying in order not to clog the spray nozzles, the pH-value should be increased to within 6.0-9.5 and the temperature should be reduced to a value not exceeding 50°C. In most cases the sodium absorption ratio should be adjusted to a value below 8, at least on permeable soils. The sodium absorption ratio (SAR) is defined by the formula

$$SAR = \frac{C_{Na^+}}{\sqrt{\frac{C_{Ca^{2+}} + C_{Mg^{2+}}}{2}}}$$

where the concentrations (C) are expressed in milliequivalents per litre. In cases where the sodium concentration is too high, ion exchange may take place whereby calcium and magnesium ions are replaced by sodium ions resulting in deflocculation of the soil (especially clay) and decreased permeability to both air and water. Usually, a low enough sodium absorption ratio can be obtained if the pH-value of the waste water is increased by the use of lime.

It should also be mentioned that a general increase of salinity of soils should be avoided as far as possible.

The irrigation method has the advantages of being fairly simple to operate and of having moderate operating costs. On the other hand, there are also some disadvantages, such as the requirement for large areas of land, detailed knowledge and continuous checking of the subsurface conditions, and possible contamination of subsurface water supplies, ground water, wells, streams and lakes. Further, the method is restricted to warm and dry areas as rainy weather reduces the useful area owing to surface drainage and/or reduced evaporation.

As irrigation conditions change with the time of the year, an irrigation system has to be combined with holding ponds for the waste water during seasons when only small amounts of waste water can be used for irrigation, e.g. cold and/or rainy periods.

4.7 Summarizing remarks

Processes designed for saving of raw material, reuse of chemicals, proper treatment of effluents and the choice of suitable areas for location of pulp and paper mills are the most efficient ways for minimizing hazards to the environment and man.

Generally, mills should be located where conflicts with other activities are less likely. Examples of risks that should be considered before decisions are made of suitable areas for mills are:

- pollution of drinking water
- decrease in fish catches
- accumulation of persistent and toxic compounds in animals and people living near mills
- pollution of water for irrigation

- eutrophication of water areas resulting in changes of aquatic habitats and communities
- disturbance of areas important for fish reproduction
- disturbance of tourist areas.

One example of a method for evaluation of ecological effects was described in 4.5.1. Following these principles, the most hazardous long term or irreversible effects can be identified and avoided.

Another approach in assessing risks of pollutants to the environment is to make an over-all cost-benefit analysis where attempts are made to set a correct price on the environment and on the resources that risk being spoiled by the industrial activities. This method is useful when decisions of mill locations are made and when advantages of industrial activities (employment, export of products and import of technical know-how) are compared to inevitable negative consequences for the environment. Those effects that are advantageous to us, benefit from being easily measurable in terms of money, while the negative effects are not. In such over-all cost-benefit anlaysis, the complexity of problems cannot be eliminated, but they can be reduced so as to facilitate the political choices that have to be made.

Literature reference list Chapter 4

1. Alderdice, D.F., Brett, J.R. (1957).
   Some Effects on Kraft Mill Effluent on Young Pacific Salmon
   J. Fish. Res. Bd. Canada 14(5) p. 783-795

2. Ander, P. et al
   Studies on the mutagenic properties of bleaching effluents
   Svensk Papperstidning 14(1977) p. 454-458 (In Swedish, English summary)

3. Atchion, J.E.
Modern Methods of Bagasse Depithing the Key to Large Scale Utilization of Bagasse for Manufacture of Pulp, Paper and Board
Tappi Non-wood plant fibres conference, Rosevelt Hotel, New Orleans, La, Nor 2 (1970)

4. Bohm, P. and Henry, C.
Cost-benefit analysis and environmental effects
Ambio Vol 8(1979), 1

5. Cairns, J., Health, G.A., Parker, B.C.
Temperature influence on chemical toxicity to aquatic organisms
JWEF, Vol 47(1975), No 2

6. CPAR - Identification of the toxic materials in sulphite pulp mill effluents
B.C. Research, Vancouver, 1979
B.C. Progress Summaries No 8 (c)

7. Davis, J.C.
Sublethal effects of bleached kraft pulp mill effluent on respiration and circulation in Sockeye Salmon
J. Fish. Res. Bd. of Canada Vol 30(1973) No 3 p.369-377

8. Doudoroff, P., Shumway, D.L.
Dissolved oxygen requirements of freshwater fishes
FAO Fisheries Technical Paper No 86 (1970)
FAO, Rome 291 pp

9. EIFAC - Report on finely divided solids and inland fisheries
EIFAC Technical Paper No 1 (1964) Food and Agriculture Organization of the United Nations, Rome, 21 pp

10. EIFAC - Water quality criteria for European freshwater fish - Extreme pH-values and inland fisheries
Water Research 3 (1969) p 593-611

11. Eloranta, P.
Pollution and aquatic flora of waters by sulphite cellulose factory at Mänttä, Finnish Lake District
Ann. Bol. Fennici 7(1970), p 63-141

12. Eloranta, V.
Influence of sulfate cellulose effluents on growth of green algae
Vatten (Swedish) 32(1976) 1, 20

13. Eriksson, K-E et al
Studies on the mutagenic properties of bleaching effluents Part 2
Svensk Papperstidning 4(1979) pp 95-104 (In Swedish, English summary)

14. Gall
Referred in Wong, A. and Prahacs, S.
CPAR-project no 228 (1974)

15. Howard, T.E., Walden, C.C.
Pollution and toxicity characteristics of kraft pulp mill effluents
Tappi 48(1965) p 136-141

16. Howard, T.E. and Walden, C.C.
Measuring stress in fish exposed to pulp mill effluents
Tappi 57(1974) 2, p 133

17. Howard, T.E. and Walden, C.C.
Effluent characteristics and treatment of mechanical pulping effluents
Tappi Mechanical Pulping Conference, San Francisco, Calif. 1975

18. Hrutfiord, B.F., Griberg, R.S., Wilson, D.F., Wilson, J.R.
Organic compounds in aerated stabilization basin discharge (1975)

19. Huntley, B.E., Jones, A.C., Cabelli, V.I.
Klebsiella densities in waters receiving wood pulp effluents
J. Wat. Poll. Contr. Fed. , 48, pp 1766-1771

20. Hynes, H.B.N.
The biology of polluted waters
Liverpool Univ. Press (1966)

21. Ladd
Effects of pH on the acute toxicity of kraft pulp mill effluent to Juvenile Coho Salmon
M.S. Theses, Hubolt, St. Coll. Arcata Calif.

22. Landner, L. and Sörensen, L.
Toxic and other effects of bleaching effluents, a critical literature review
SSVL-project 7 (In Swedish)(1975)

23. Landner, L.
Slowly biodegradable toxic substances from paper and pulp mills
Nordforsk 12:e symp., Vattenforskn., 1976

24. Landner, L. and Larsson, T.
Effects of bleaching liquors from kraft pulp mill bleaching on growth and photosynthesis of plankton algae
Svensk Papperstidning (1977) (In Swedish, English Summary)

25. Landner, L., Lindeström, L., Lindén, O.
Effects of forest industry effluents in the receiving waters. Review of today's knowledge
NM 80, IVL-publ. 1977

26. Leach, J.M. and Thakore, A.N.
PRJ 157: Oct. 8, 43 1973

27. Leach, J.M. and Thakore, A.N.
Identificatoin of the constituents of kraft pulping effluent that are toxic to Juvenile Coho Salmon (Oncorhynchus Kisutch)
J. Fish. Res. Board of Canada vol 30, No 4 (1973)

28. Leach, J.M. and Thakore, A.N.
Isolation and identification of constituents toxic to juvenile rainbow trout (Salmo gairdneri) in caustic extraction effluents from kraft pulp mill bleach plants
J. Fish. Res. Board of Canada, p 1249-1257, 1975

29. Lee, E., Mueller, I., Walden, C.
Non-settleable suspended solids: Their impact on receiving waters
Pulp and Paper Canada Vol 79, 10 (1978)

30. Lindström, K., Nordin, J.
Gas chromatography-mass spectrometry of chlorophenols in spent bleach liquors
J. Chromatogr. (1976) In press

31. Lockhart, R.W. and Leach, J.M.
Identification of the toxic materials in sulphite pulp mill effluents
CPAR-report no 408-1 (1976) Can. Forestry Service, Ottawa,Ont.

32. Marier, J.
The effects of pulp and paper wastes, with particular attention to fish and bioassay procedures for assessment of harmful effects
NRCC No 13501 (1973)
Nat. Research Council of Canada

33. Moore, I.E. and Love, R.I.
Effect of a pulp and paper mill effluent on the productivity of periphyton and phytoplankton
J. Fish. Res. Board Can. 34(1977) p 856-862

34. Neilson, A.H., Sparell, L.
Acetylene reduction (nitrogen fixation) by enterobacteriaceae isolated from paper mill process waters
Appl. and Env. Microbiology Vol 32(1976) 2, 197-205

35. Nemerow, N.L.
Liquid waste of industry - theories, practices and treatment
Addison-Wesley Publ. Co., Don Mills, Ontario (1971)
p 365-397. The material industries.

36. Odum, E.P.
Fundamentals of ecology
W.B. Sanders (1971)

37. Oseid, D.M. and Smith, L.L.
Factors influencing acute toxicity estimates of hydrogen sulfide to freshwater invertebrates
Water Research 8 (1974), p 793-746

38. Parker, et al
Some facets of the impact of pulp mill effluent on the Alberni inlet
Pulp and Paper Mag. of Canada 73(10)1972, 89-98

39. Parker & Sibert
Effect of pulp mill effluent on dissolved oxygen in a stratified estuary (1), Empitical Model (2), numvercal model
Water Res. 7, 4, 503-514 (1973)

40. Pearson, T.H., Rosenberg, R.
A comparative study of the effects on the marine environment of wastes from cellulose industries in Scotland and Sweden
Ambio, Vol 5(1976) No 2, p 77-79

41. Raabe, E.W.
Biochemical oxygen demand and degradation of lignin in natural waters
J. Water Poll. Control Fed. 40:R 145-150 (1968)

42. Rokosh, D.A., Rao, S.S., Jurkovic, A.A.
Extent of effluent influence on lake water determined by bacterial population distributions
J. Fish. Board Can. 34, p 844-849 (1977)

43. Rosenberg, R.
Sucession in benthic macrofauna in a Swedish fjord subsequent to the closure of a sulphite pulp mill
Oikos 24, p 244-258 (1973)

44. Seppovaara, O., Hynninen, P.
On the toxicity of sulphate mill condensates
Paperi ja Puu 52:11-23 (1970) (In Swedish)

45. Soniassay, R.N., et al
The effects of BKME color and toxic constituents on algal growth
Pulp Paper Mag Can. 78, 8, p 55 (1977)

46. Stockner, I.G., and Cliff, D.D.
Effects of pulp mill effluents on phytoplankton production in coastal marine waters of British Colombia
Jour. Fish. Res. Bd. Can. 33, 11, p 2433 (1976)

47. Stockner, I.G., and Costella, A.C.
Marine phytoplankton growth in high concentrations of pulp mill effluent
Jour. Fish. Res. Bd. Can. 33, 12, p 2758 (1976)

48. Särkää, M.
Review of several sources of discharge of nutritive salt
Nordforsk miljövårdssekr. Publ. 1875:1, p 161-174, 1974 (In Swedish)

49. Walden, C.C.
The toxicity of pulp and paper mill effluents and corresponding measurement procedures
Water Research 10, p 639, 1976

50. Walden, C.C. and Howard, I.E.
Toxicity of pulp and paper mill effluents
Tappi Vol 60(1977) 1, p 122-125

51. Waldichuk, M.
Some water pollution problems connected with the disposal of pulp mill wastes
Canada Fish Culturist No 31, 1962, pp 3-34

52. Williams, R.W. et al
Toxic effects of sulphite waste liquor on Young Salmon
Res. Bull. No 1, State of Washington Dept. Fisheries, Olympia Wash. Pulp Mill Wastes
Canada Fish Culturist, No 31 (1953) pp 3-34

53. Wilson, M.A. and Chappell, C.I.
Reduction of toxicity of sulphite effluents
CPAR Report No 49-2 (1973)
Can. Forestry Service, Ottawa, Ont.

54. Zimmerman, M.S. and Livingston, R.I.
Effects of kraft mill effluents on benthic macrophyte assemblages in a shallow bay system
Marine Biol. 34(1976) p 297

5. PREPARATION OF FIBROUS RAW MATERIAL

5.1 General

Before cooking or refining the fibrous raw material it is prepared in a section of the mill called the wood yard, wood room etc.

Both the method used in the preparation of the fibrous raw material and the resulting discharges vary widely, depending on the nature of the raw material (softwood, hardwood, bamboo, bagasse, grass, reed etc) and therefore each raw material is treated under a separate heading. Details of the air emissions from the preparation are also given.

5.2 Softwoods and hardwoods

The major source of water pollution from the preparation of softwoods and hardwoods is the debarking operation. The bark constitutes 8 to 17 % of the dry weight of the wood which corresponds to 100 to 400 kg bark/t_{90} pulp depending on pulp type. The debarking operation can be wet or dry.

The bark removed is normally used as fuel in boilers. To increase the fuel value of the bark it is normally dewatered to at least 40 % dry content in presses. This applies to wet as well as dry debarking operations. The effluent from the presses usually contains large amounts of dissolved and suspended solids.

Barking drums are the most widely used debarking equipment. If dry barking is used the drum is perforated from one end to the other. Wet barking drums have closed shells in the inlet side and water (usually warm) is added in the entrance and discharge end. In Figure 5.1 a process diagram for dry debarking is given. The corresponding diagram for a wet debarking plant is given in Figure 5.2.

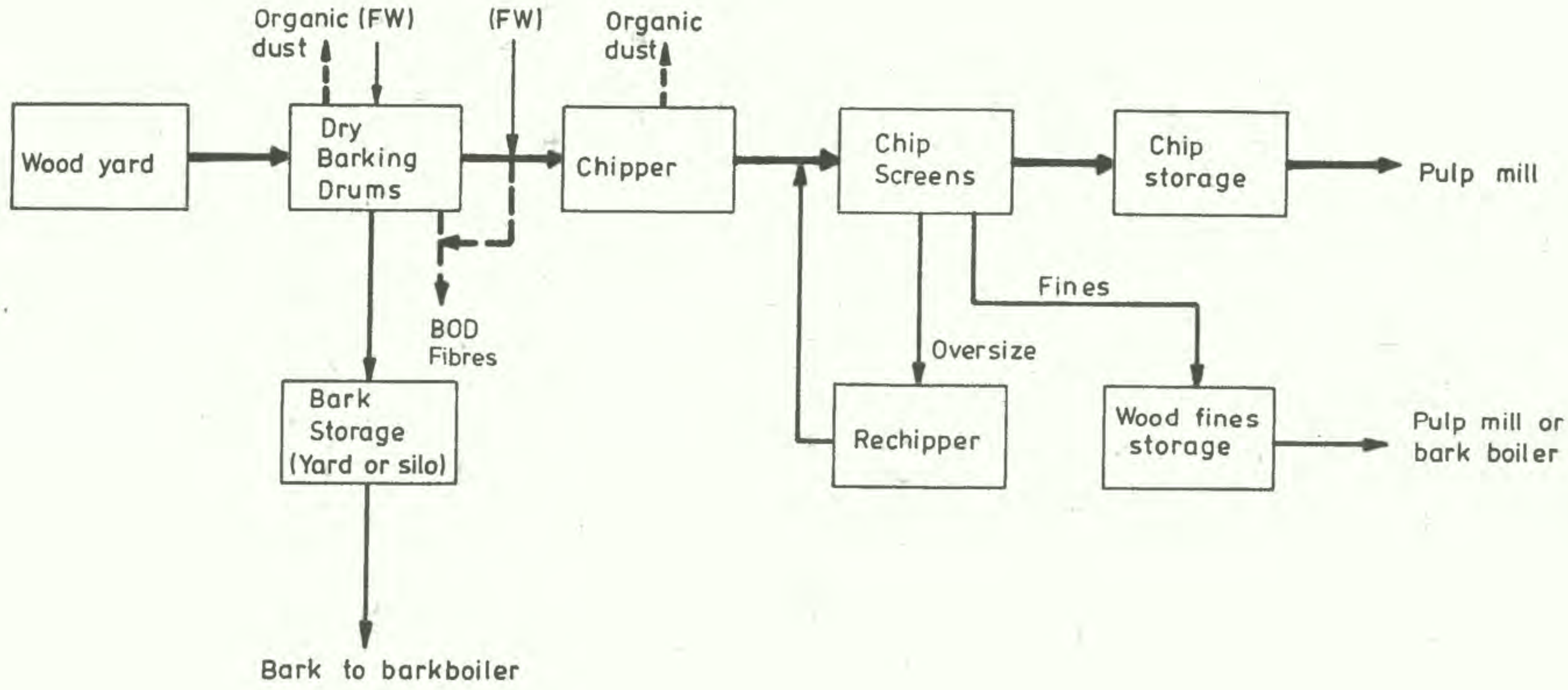


Figure 5.1. Principal flow sheet of dry debarking plant for wood (softwood or hardwood).

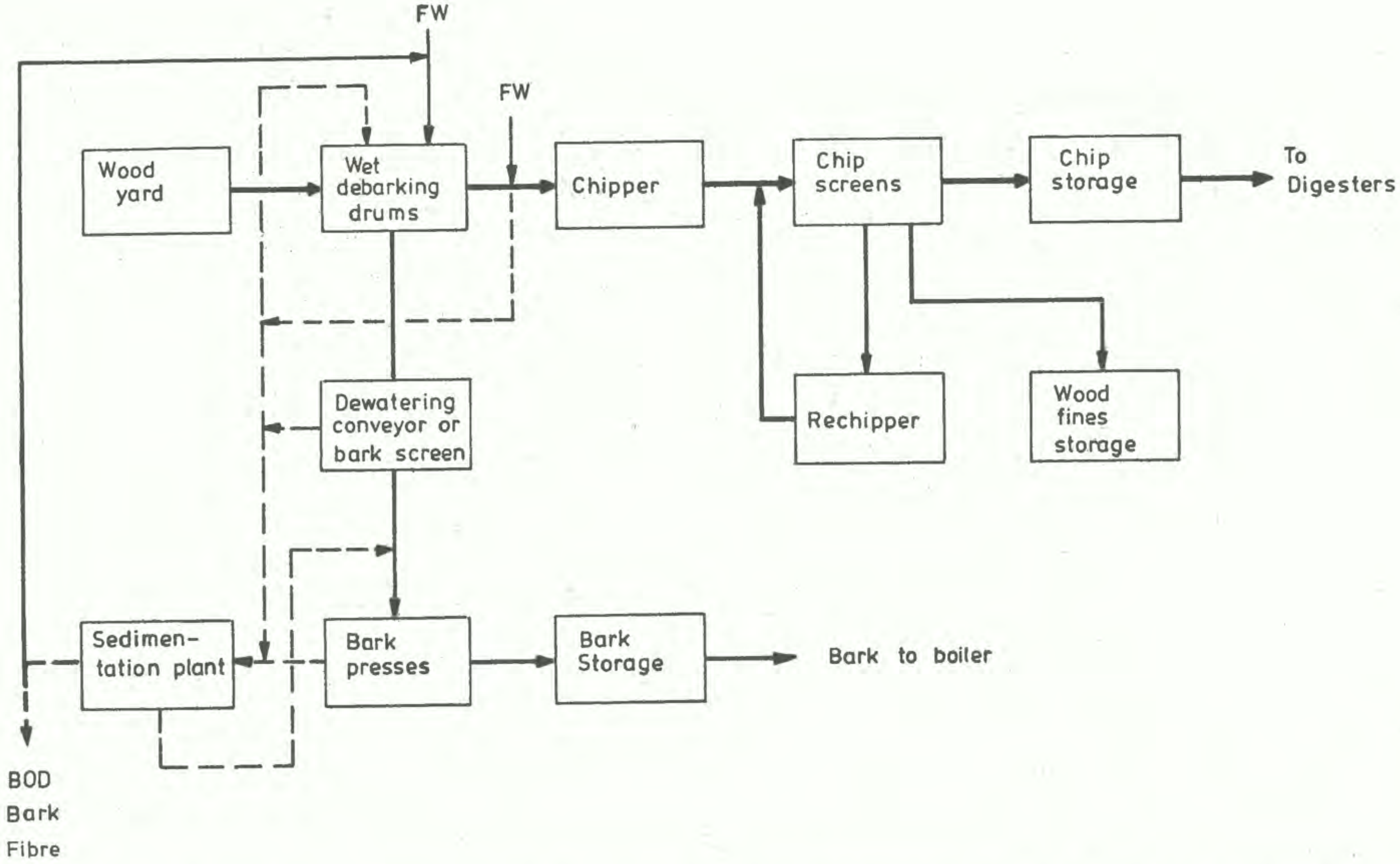


Figure 5.2. Principal flow sheet of wet debarking plant for wood (softwood or hardwood).

Dry and wet debarking of Scandinavian softwoods and hardwoods are given in Table 5.1

Table 5.1 Discharges to water from dry and wet debarking of Scandinavian softwoods and hardwoods. Data given in kg per tonne of dry wood

Debarking	BOD	COD	Colour	Suspended solids[a)]
	kg/t			
Softwoods (dry)	0-3	-	-	-
Softwoods (wet)	4-10	10-25	5-10	5-15
Hardwoods (wet)	5-12	20-40	5-15	5-20

a)The discharge for suspended solids is calculated after mechanical solids removal on medium screens

As can be seen there is great variability in the numbers given mainly due to the factors mentioned previously. Detailed information on the discharges from southern softwoods and hardwoods is not available but there are indications that the effluents have about the same characteristics as given in table 5.1.

By treating the effluent in clarifiers, biological systems and by chemical flocculation the discharges can be reduced. Table 5.2 summarizes the results to be expected from the different methods.

Table 5.2 The approximate reduction in BOD, COD and suspended solids for wet debarking effluents by various treatment methods (3)

Treatment method	Effluent reduction, %		
	BOD_5	COD	Suspended solids
Sedimentation	10	20-40	70
Chemical flocculation	40	60	80
Biological treatment	60-80	50	-

The treatment of debarking effluents will be covered in detail in a separate volume. It must be emphasized, however, that the numbers given here are only indicative. For any detailed calculations or project work, trials have to be made using the actual debarking effluent.

5.3 Bagasse

The storage is dry in bale form or wet, in bulk form (e.g. Ritter storage type). The liquid used in the latter case is reused for slushing or sprinkling the pile. The discharges can thus be kept low. The bagasse depithing, is normally moist or wet. This in turn leads to discharges to water of both dissolved organic substances and suspended solids from this operation (Figure 5.3).

In the Ritter process for wet bulk storage the fermentation of residual sugar is controlled by addition of lactic acid bacteria. In a conventional moist bulk storage (e.g. a pile) the lactic acid bacteria normally dominate but formation of acetic acid (and thus more severe degradation) may occur.

The dissolved organic substance is released when emptying the Ritter storage. The residual substance is washed out on the conveyors or in the depithing operation. The conveyors, the pith presses and depithers are the main sources for the discharges of suspended solids.

The discharges from the preparation of bagasse are given in Table 5.3. The figures are based on a very limited number of investigations and should therefore be regarded as indicative only. Available information indicates that the total release of BOD_5 from a well controlled bulk storage is of the order 20-25 kg/tonne 90 % pulp. In an ordinary pile storage system the release may be up to 50 kg/t bagasse (1,2).

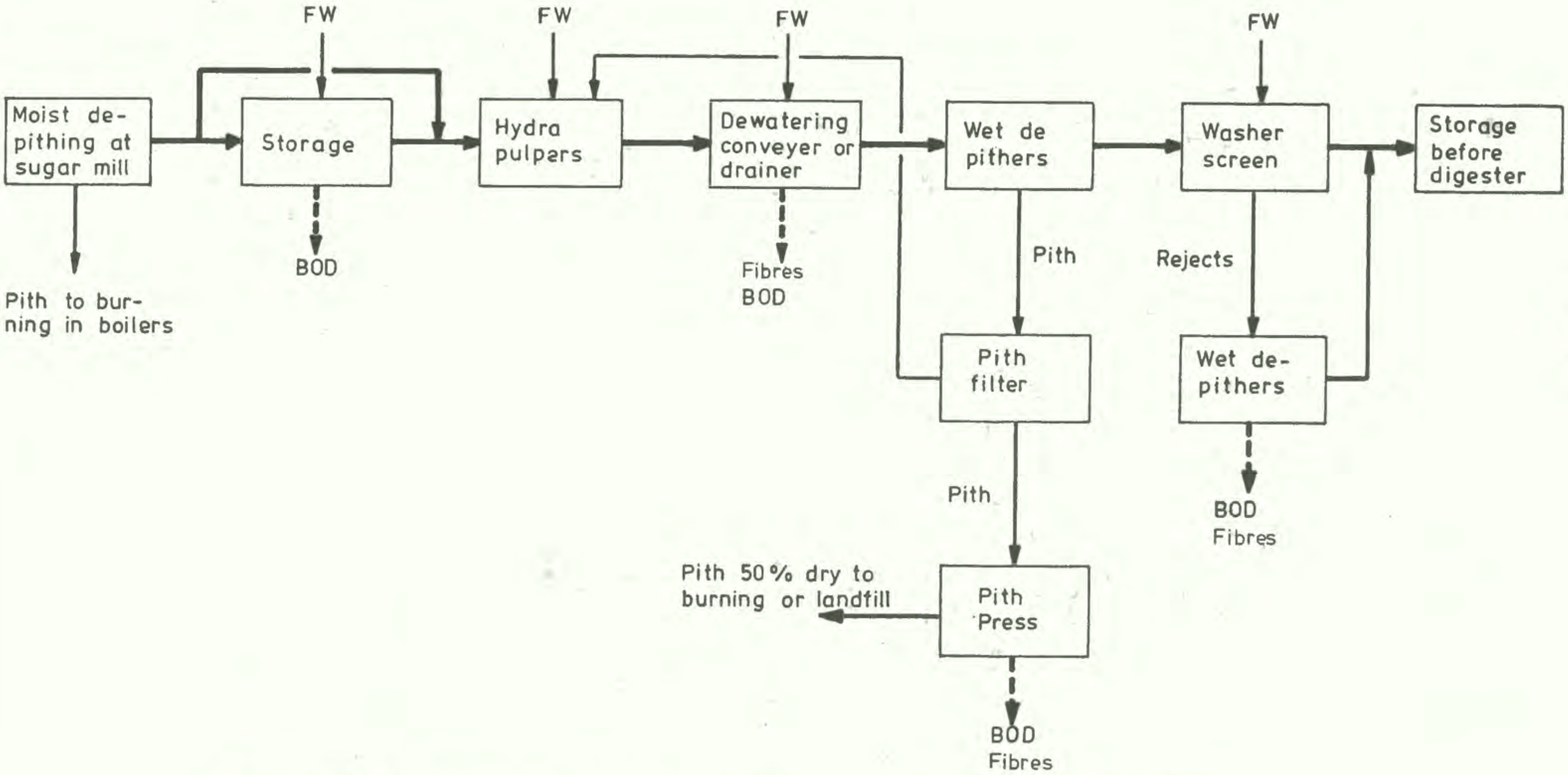


Figure 5.3. Principal flow sheet of preparation plant for bagasse.

Table 5.3 The approximate discharge of dissolved and suspended solids from the bagasse preparation operations. Data are given in kg per tonne bagasse pulp (1,2,4)

Operation	BOD_5	COD	Suspended solids
	kg/t		
Storage, dewatering and dephiting	20-40	60-240	200-400

There is no information available on the BOD and suspended solids reduction obtainable when treating the effluent from bagasse preparation. Since the dissolved organic solids mainly consist of low molecular carbohydrates and acids a biological treatment system can be expected to yield a good treatment result. The suspended solids may, however, present a problem since they mainly consist of small and relatively light particles.

5.4 Bamboo and straw

The operations used in the preparation of bamboo and straw are often dry (Figure 5.4 and 5.5). Water may be used to clean the bamboo prior to chipping and also the chips before the chip storage. The effluent contains particulate material of inorganic and organic origin (stones, grit, fibres).

Literature reference list, Chapter 5

1. Benzinger, H.
   Todays bagasse technology
   PPI, June 1975, p 42-44:57

2. IVL internal data

3. Simon, O., Sörensen, L., Ullman, P., Widell, L.
   Studier av renseriavlopp, biologisk och kemisk rening samt akut toxicitet
   SSVL 9:11, 1977

4. Subrahmanyam, P.V.R.
   Survey of Indian mills made for IVL, 1978

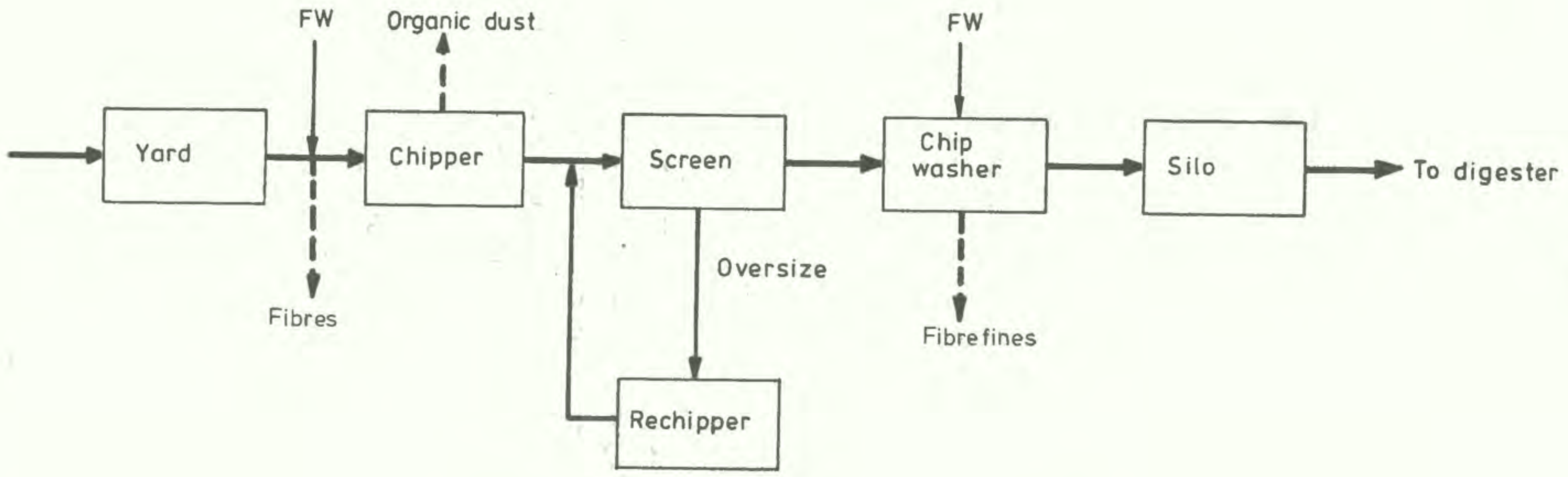


Figure 5.4. Principal flow sheet of preparation plant for bamboo

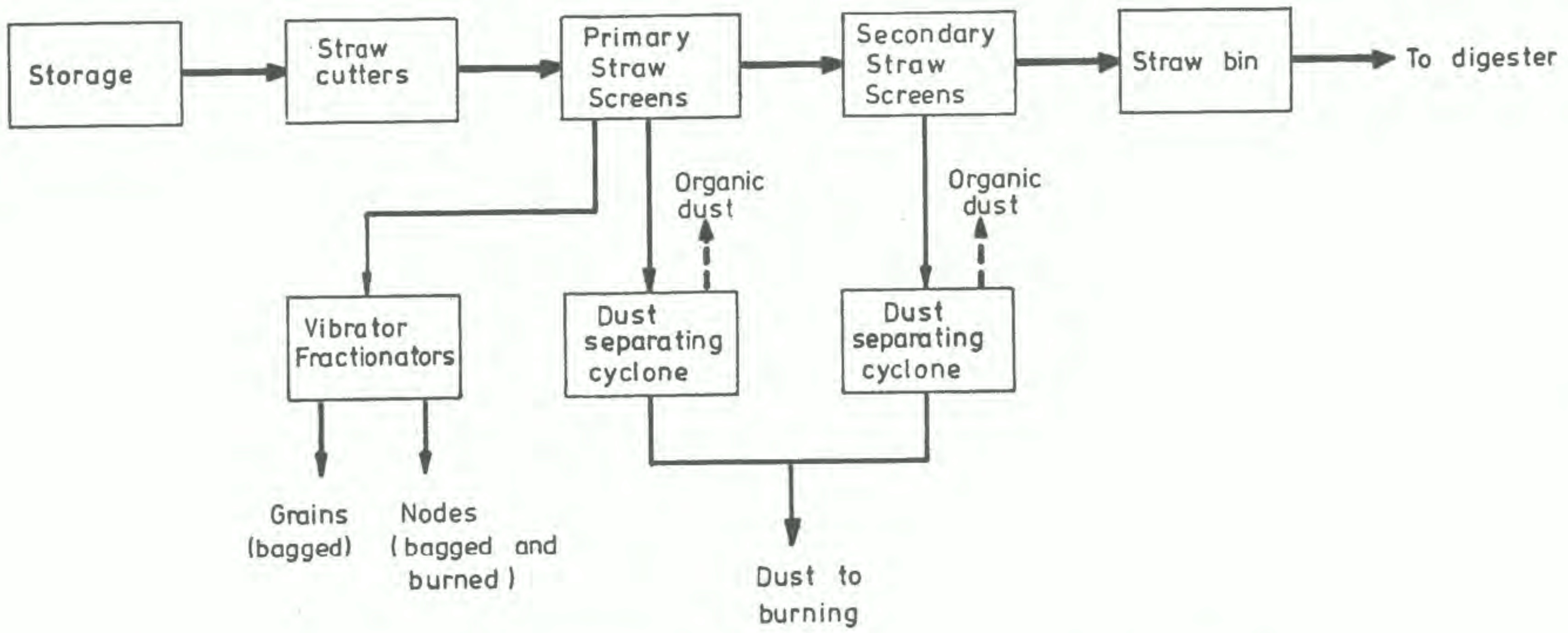


Figure 5.5. Principal flow sheet of dry preparation plant for straw.

6. MECHANICAL AND CHEMIMECHANICAL PULPING

6.1 General

The environmental effects from mechanical and chemimechanical pulping are mainly limited to discharges into water of dissolved organic substance and fibres. The dissolved organic substance has a certain BOD value and may also be toxic to fish. The colour of the effluent is moderate.

In mechanical pulping (including thermomechanical pulping and fibre board manufacture) the amount of substance dissolved is 2.5 to 10 %. The dissolved material is mainly low molecular carbohydrates, lignins and extractives. The yield loss in chemimechanical pulping is normally in the range 5 to 15 %. Not only water soluble material is dissolved but also components that are modified and dissolved by the added chemicals.

A major part of the organic substance is dissolved in the grinding or primary refining stage with only small contributions from secondary refining stages, rejects refining or screening (Figure 6.1). The discharge from the pulping line and the paper mill normally contains only about 70 % of the dissolved substance while the rest follows the paper pulp to drying.

6.2 Mechanical and thermomechanical pulping

The fibre raw material for groundwood and thermomechanical pulps is usually softwoods. Some low density hardwoods e.g. aspen and poplar may also be utilized. At present we have no information on the application of these processes on non-wood fibre raw materials.

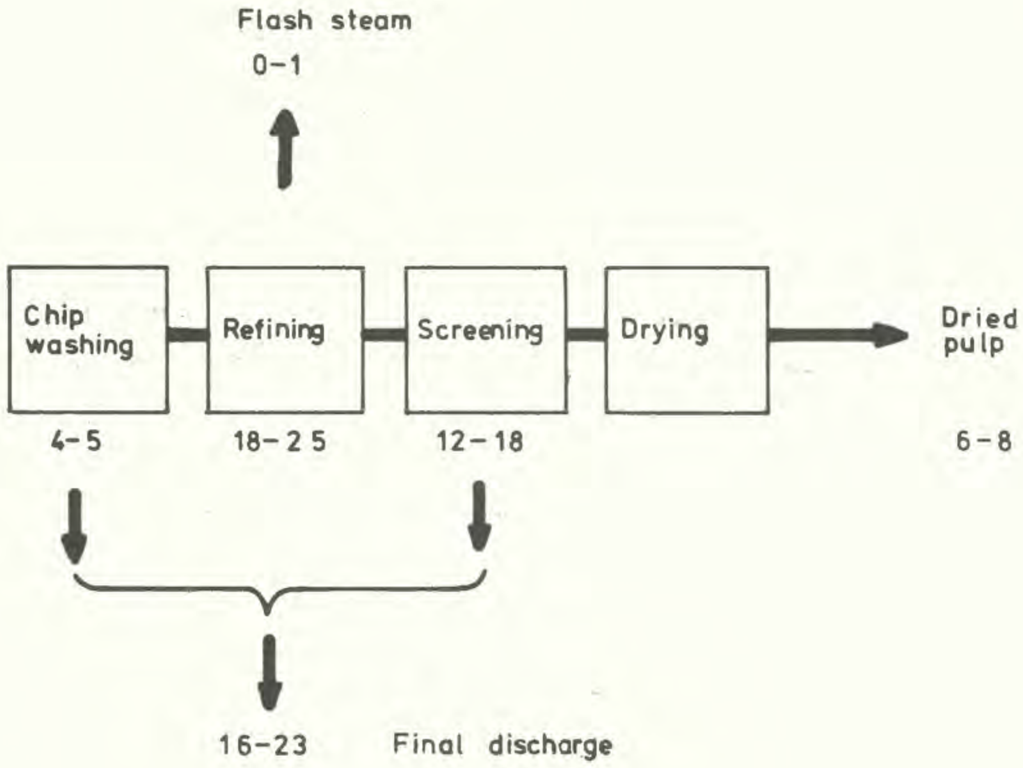


Figure 6.1 The dissolution of organic substance (as kg BOD_7/t_{90}) in thermomechanical pulping of softwoods and the resulting discharges

The discharge of dissolved solids depends upon the wood raw material (wood species, felling season, storage time, amount of bark etc.) and upon process variables, primarily the temperature in the preheating and refining stages. The gross chemical composition of the discharge to water from groundwood and thermomechanical pulping of sprucewood is given in Table 6.1. For both pulping processes the main component is carbohydrates with lignin as the second largest. Extractives contribute 2 to 3 kg/tonne and low molecular acids and methanol are insignificant.

Table 6.1 Chemical composition of substance dissolved in mechanical and thermomechanical pulping of Scandinavian spruce (Picea abies) and in the bleaching of spruce groundwood. All numbers are given in kg/tonne of pulp (1)

Components	GWD	Peroxide bleached GWD	TMP
	kg/t		
Carbohydrates	7	4.0	10
Lignin	4	14.5	6
Extractives	2	1.5	3
Acetic acid	0	9	0.3
Formic acid	-	1.5	-
Methanol	-	0.5	-
Ash	1.5	13.5	9
Not analyzed	2	-	6

The amount of wood substance dissolved increases markedly with an increase in the refining temperature (Figure 6.2). For groundwood and refiner groundwood pulping (100°C) the substance loss is about 25 kg/tonne, for thermomechanical pulps 40 kg/tonne and for hardboard pulps the loss may approach 100 kg/tonne of pulp.

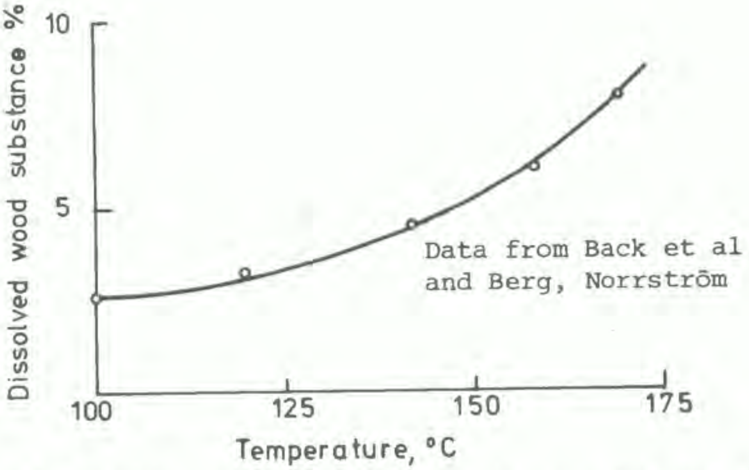


Figure 6.2 Dissolved wood substance during defibration of softwood at elevated temperature

The corresponding BOD-value increases linearly with an increase in defibration temperature (Figure 6.3).

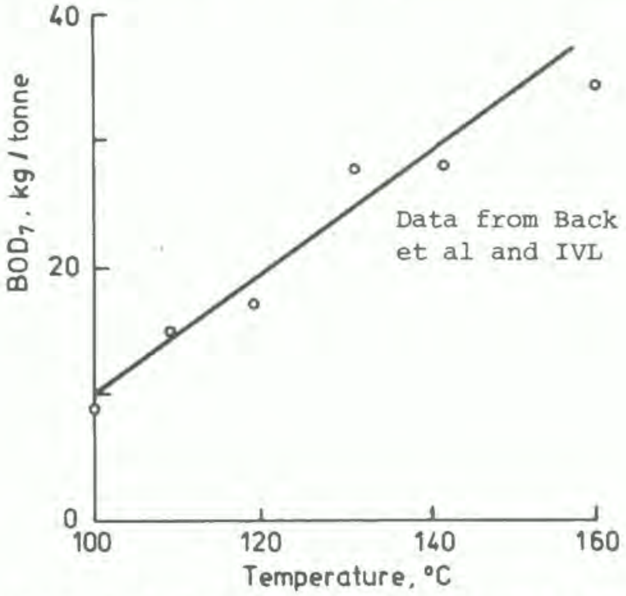


Figure 6.3. The BOD value of the dissolved wood substance as a function of temperature in the defibration of softwood

The discharge of suspended solids from a process line for mechanical or thermomechanical pulping depends mainly on the fibrous raw material, the quality of pulp made and the process configuration. Of great importance is also the amount of accidental spills due to e.g. overflowing tanks and damaged wires. Accidental spills do not, however, affect the total discharge of dissolved solids.

For a well designed process line with adequate buffer tank volumes the discharge of suspended solids can be kept as low as 10-15 kg/t_{90}. An average value would be closer to 20-25 kg/t_{90} and discharges of about 50 kg/t_{90} are not uncommon for old process lines.

A summary of discharges from groundwood, refiner groundwood and thermomechanical process lines is given in Table 6.2.

Table 6.2 Approximate discharges from the process line (excluding the chip wash[a)]) for groundwood, refiner groundwood and thermomechanical pulping (3,5,6,7)

Process	Fibrous raw material	BOD_5	COD kg/t_{90}	SS
Groundwood	spruce	10-22	22-50	10-50
Refiner gwd	spruce	12-25	23-55	"
TMP	spruce	15-30	25-60	"
TMP	pine	10-15	22-31	"

a) The chip wash contributes up to 4 kg BOD_5/tonne

By proper process design the discharges of suspended solids can thus be limited to 10 kg/t_{90}. Further reduction of suspended solids and any reduction of the dissolved substance requires external treatment. The treatment results obtained for some methods are given in Table 6.3.

Table 6.3 Reduction in the discharges from mechanical and thermomechanical pulping by external treatment methods (4)

Treatment alternative	Reduction, % BOD	 COD	 SS
Sedimentation	-	-	60-90
Chemical flocculation	20-30	50-60	85-95
Biological treatment	50-95	30-80	-

The numbers given apply to results normally achieved and the range indicates the variability due to fibrous raw material and process type. From the table it is obvious that very low residual discharges can be realized from a mechanical pulping line equipped with external treatment facilities.

6.3 Chemimechanical pulping

The chemimechanical processes are commonly applied to hardwoods in order to improve the mechanical characteristics of the pulps. Grasses as well as softwood are also pulped in chemimechanical processes.

The chemicals applied are sodium hydroxide ("cold soda"), mixtures of sodium sulphite and alkali (sodium hydroxide or carbonate) or sodium bisulphite ($NaHSO_3$). The pH value in the treatment is around 10 or more for sodium hydroxide or the sulphite mixtures and around 4 for sodium bisulphite.

The fibrous raw material may also be treated with peroxides in the refiner. Although this process may be termed chemimechanical it is included in the section on bleaching of mechanical pulps since the main reason for the treatment is to increase the brightness.

When chemicals are added in the mechanical pulping process, either in a pretreatment stage (impregnation, cooking) or to the chips in the refiner, the result is usually a more marked yield decrease and thus a higher dissolution of organic substances. The higher the chemical charge and the treatment temperature and the longer the treatment time the more substance is dissolved.

Table 6.4 and 6.5 show the BOD, COD and colour of the total amount of dissolved organic material from cold soda pulping and from sulphite chemimechanical pulping.

The numbers given in the tables correspond to the total amount dissolved in the process. The main part of the dissolved material is discharged from the mill with the effluent while a small fraction follows the pulp or the paper.

Table 6.4 The BOD_7, COD and colour of the total dissolved organic substance from cold soda pulping of bamboo, hardwoods and spruce (2)

Fibrous raw material	Pulp yield %	BOD_7	COD	Colour
		kg/t_{90}		
Bamboo	85	110	260	110
Gmelina arborea	88	84	150	60
	84	98	212	-
Poplar	93.5	42	80	-
Birch	89	74	150	-
Eucalyptus globulus	94.5	29	65	115
	92.5	38	93	120
	91	60	130	130
Malaysian mixed hardwoods	89.5	35	138	250
Spruce	88.5	-	153	-
	85	-	205	-

Table 6.5 Some BOD_7, COD and colour values of the total dissolved organic substance from semichemical pulping of hardwoods (2)

Fibrous raw material	Process	Pulp yield %	BOD_7	COD	Colour
			kg/t_{90}		
Gmelina arborea	OH^-/SO_3^{2-}	87.4	77	162	32
	"	86.7	93	186	42
	"	85.5	101	202	44
Asian mixed hardwood	HSO_3^-	80.6	107	290	-
	"	74.3	185	407	-
	"	71.5	203	503	-

It is evident from the table that there is a close correlation between a decrease in yield and an increase in the pollution parameters. The type of fibrous raw material has only little influence on the BOD and COD values while the colour of the effluent is markedly effected by the species. The effluent from pulping of Gmelina arborea and bamboo is relatively light coloured while the Malaysian hardwoods have a very dark coloured discharge.

The yield dependence of BOD and COD values is valid also for sulphite based semichemical pulping (table 6.5). The sulphite addition leads to a lighter colour of the Gmelina effluent.

All numbers given for BOD from semichemical pulping follow a straight line relationship with pulp yield with only minor deviations (Figure 6.4). The figure may thus be used for preliminary calculations and considerations. For more detailed work and design it is always necessary to obtain qualified data by laboratory and pilot runs.

The COD values, if plotted in a corresponding diagram versus pulp yield also follow a straight line showing some minor deviations (Figure 6.5).

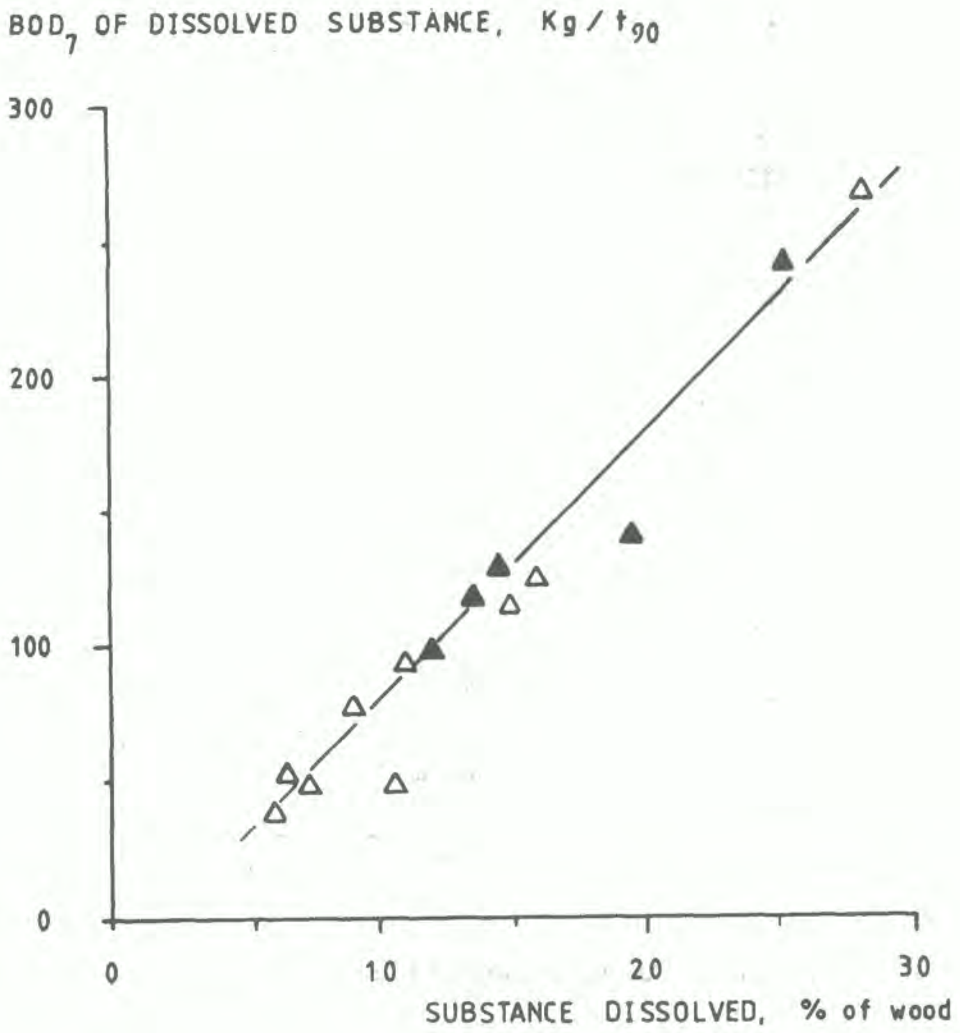


Figure 6.4. The BOD_7 of the substance dissolved during chemimechanical pulping of hardwoods as a function of the total amount of substance dissolved. Open sympols denote cold soda treatment and filled symbols bisulphite treatment (pH 4).

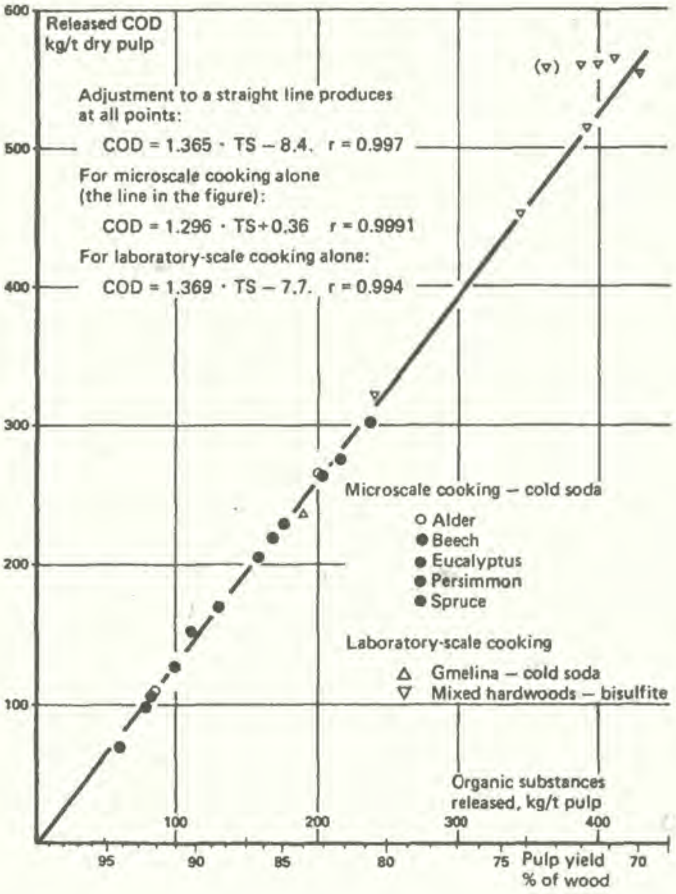


Figure 6.5 Chemical Oxygen Demand as a function of pulp yield (2)

Literature reference list Chapter 6

1. Björklund-Jansson, M.
Kemisk sammansättning hos avloppsvatten från mekanisk massatillverkning före och efter biologisk rening
NM 80 Rapport 2B:11 (In Swedish)

2. Data supplied by Defibrator AB, Stockholm, Sweden

3. Personal communication from Mr J. Betts, Ottawa, Ontario, Canada

4. Simon, O. and Ullman, P.
Biologisk och kemisk behandling av avlopp från mekanisk massa (In Swedish)

5. The t-pulp project final report (In Swedish)
STFI-report B 462 (TM 43)

6. Discharges at the manufacturing of mechanical pulp (In Swedish)
STFI-report B 326 (TM 3)

7. CHEMICAL AND SEMICHEMICAL PULPING

7.1 General

In chemical pulping the fibres are liberated by breaking down and dissolving the lignin by chemical reactions. Semichemical pulping is characterized by a combination of chemical and mechanical attack, to achieve fibre liberation. In semichemical pulping a recovery system for the chemicals is often included.

The chemical reactions in the cook are not entirely selective and thus the carbohydrates and extractives are also attacked and degraded to some extent. After the cook the spent liquor contains the dissolved part of the fibrous raw material and the residual cooking chemicals.

The spent cooking liquor normally contains the largest amount of dissolved organic substance of all process liquors. The chemical composition (both of the organic and of the inorganic part) and the exact amount depend on fibrous raw material, process type and process conditions. A portion of the organic components in the spent liquor is volatile and is released from the liquor phase when blowing the cook or lowering the digester pressure (Figure 7.1).

In the figure a BOD_5-balance typical for softwood sulphate pulping in a continuous digester is shown. The general description is, however, applicable to all types of chemical and semichemical pulping processes. After degassing, the spent liquor is separated from the pulp in the washing operation. The part of the spent liquor that follows the pulp is washed out in a subsequent open process stage e.g. the screening or the first bleaching stage. For normal washing efficiencies (85 to 98 %) the BOD_5 following the pulp may range from about 90 kg/tonne (sulphite viscose) to below 5 kg/tonne of pulp (high yield sulphate pulp).

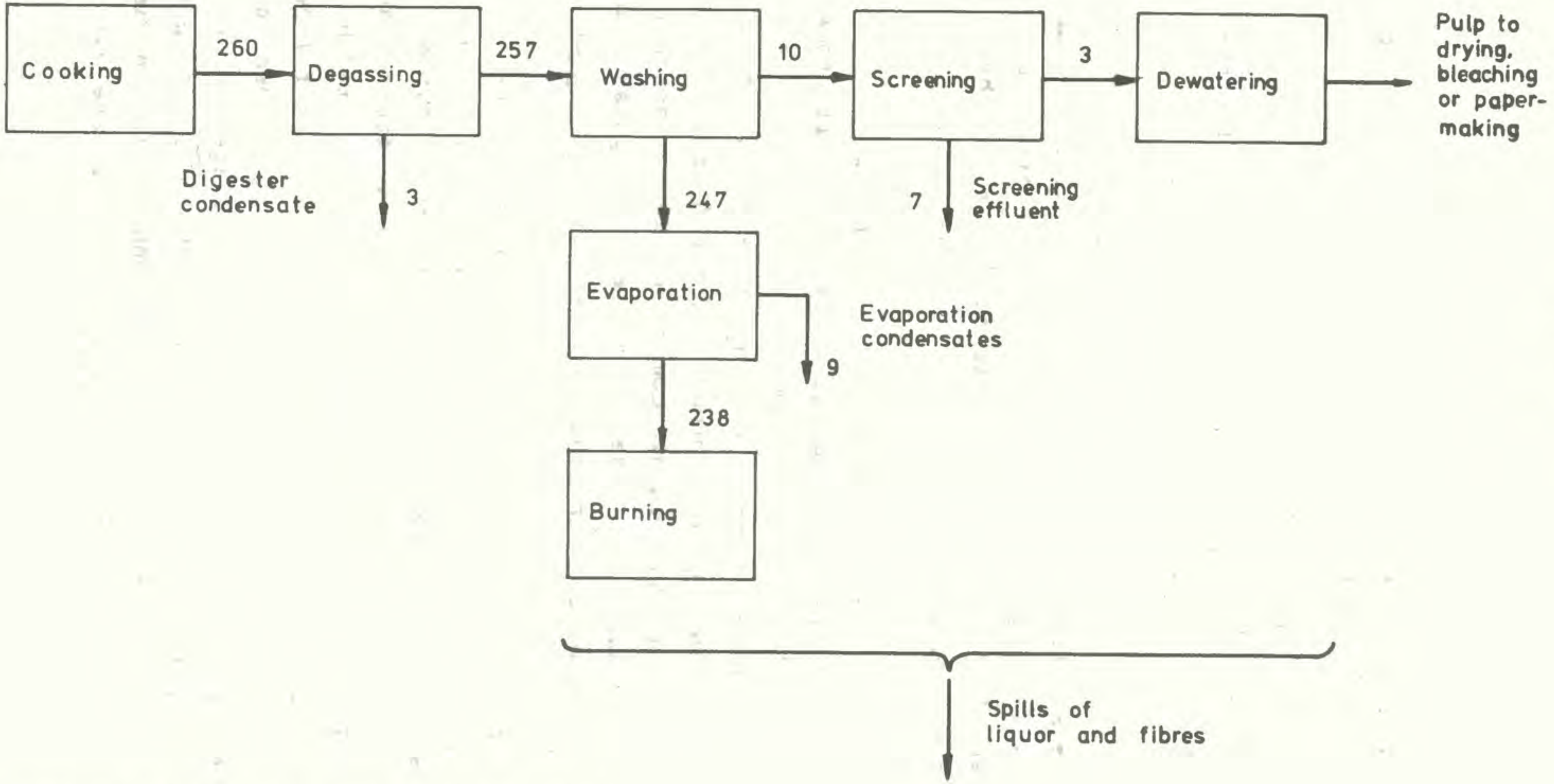


Figure 7.1 BOD_7 balance (in kg/t_{90}) for softwood sulphate pulping line.

For mills with a recovery system or liquor burning the solids content of the spent liquor is increased in an evaporator station. When there is no system for chemical recovery or liquor burning the spent liquor is brought to external treatment facilities (e.g. biological treatment systems) or directly to the recipient. In the latter instance the BOD load is obviously very high ranging from 200 to 600 kg BOD_5 per tonne of product.

In the evaporation station another portion of the volatile organic components of the spent liquor flashes off and combines with the evaporation condensates. The total amount of BOD_5 in the digester and evaporation condensates ranges from around 10 kg/tonne of pulp (sulphate pulping of grasses) to 70 kg/tonne (sulphite pulping of certain hardwoods) (1).

All numbers given refer to normal operating conditions in the evaporation station. When liquor carry-over occurs, e.g. due to foaming, spent liquor solids drastically increase the BOD-values of the condensates.

The discharges of fibres from the pulping process occur with the spent liquor (if there is no recovery system) with the screening effluent and with the effluent from the wet end of the drying machine. Other sources of discharges of dissolved organic material and fibres are spills that occur in the washing-screening system and the spent liquor system.

7.2 Sulphite pulping

The BOD, COD and colour value of the spent cooking liquor from all types of sulphite pulping increases as the pulp yield decreases. In Figure 7.2 information available on the BOD_7 from NSSC and acid sulphite pulping on European softwoods and hardwoods has been collected.

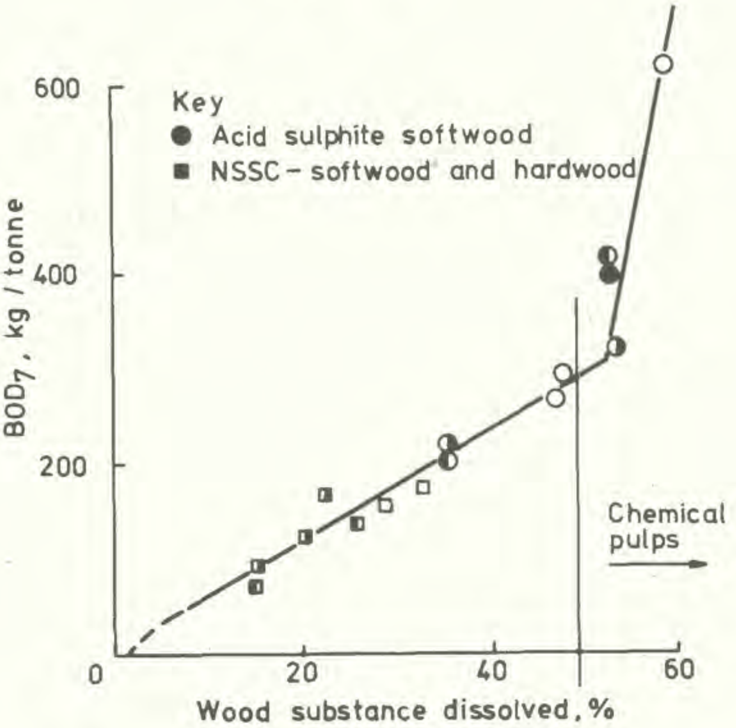


Figure 7.2 The BOD_7-value of the spent liquor from sulphite pulping as a function of wood substance dissolved during the cook (2)

As the pulp yield goes down, the BOD value increases linearly. The same relationship seems to be valid irrespective of fibrous raw material and pulping process. It should also be pointed out that the numbers given earlier for the BOD-value of the discharges from chemimechanical pulping roughly fit the relationship in figure 7.2.

Below 50 % pulp yield the relatively slow BOD increase becomes much steeper. Consequently the BOD_7-value for chemical pulps is 275 to 325 kg/t. Dissolving pulps with a yield around 40 % have a BOD_7-value of the spent liqour of 600 kg per tonne and above.

The spent cooking liquor contains volatile organic compounds that flashes to the condensates when lowering the pressure of the digester or spent liquor, or when evaporating the spent liquor (Table 7.1). In addition volatile furfural is formed by the evaporation of spent liquor. The amount is 6 kg/t_{90} in viscose spent liquor and 2 kg/t_{90} in paper pulping.

Table 7.1 Volatile organic compounds in the spent liquor from acid sulphite pulping of softwood (1)

Component	Softwood, kg/t_{90}	
	paper	viscose
Methanol	7	9
Formic acid	-	0.9
Acetic acid	35	45
Furfural	2	6

The amount of volatile organic compounds that combines with the digester condensates corresponds to about 5 kg BOD_7/tonne. In the evaporation station the condensate BOD depends on the pH-value of the spent liquor. At higher pH the acetic acid is converted to less volatile acetates and the BOD value of the condensate decreases. At pH 7 practically all acetic acid is present as acetate and thus no BOD contribution is obtained.

The BOD, COD and colour values of the total dissolved organic material from sulphite pulping of a number of fibrous raw material are given in Table 7.2. All data originate from mill measurements and there is a good correlation with figure 7.2 which is based both on laboratory and mill data.

Table 7.2 The BOD_7 and COD values of the total dissolved organic material from sulphite pulping of various fibrous raw material (1)

Fibrous raw material	Process	Pulp yield, %	Kappa number	BOD_7 kg/t_{90}	COD kg/t_{90}
Wheat straw	NSSC	48-49	18-20	280	1330
Eucalyptus	Acid	49	12	300	1300
Birch	NSSC	80	-	120	280
Spruce	Acid	51	35	300	1200
Spruce	Acid	60	-	180	800

The approximate discharges of BOD_7 from acid sulphite pulping of softwoods when applying 85 and 95 % washing efficiency combined with spill collection and condensate treatment (for 95 % washing efficiency) are shown in Table 7.3.

Table 7.3 Typical discharge of BOD_7 (in kg/tonne) from acid sulphite paper pulping of softwood

Discharge	Liquor recovery, %		
	0	85	95 a)
Washing loss	300	45	15
Condensates	-	30	15
Spills	-	15	5
Total discharge	300	90	35

a) 95 % liquor recovery combined with condensate treatment (neutralization) and spill collection system

Without any recovery of spent liquor the total BOD_7 is 300 kg per tonne of pulp which can be reduced to 35 kg/t by efficient internal measures. The 85 % recovery case is to be regarded as the average situation for calcium sulphite pulp mills, while the 95 % recovery case is a typical situation for soluble base sulphite pulp mills.

7.3 Sulphate and soda pulping

In the production of chemical pulp not only the lignin but also the hemicelluloses and to some extent the cellulose are degraded and dissolved. The calculated amounts of the various components dissolved by sulphate pulping of some fibrous raw materials are given in Table 7.5.

Table 7.5 Substances dissolved from the fibrous raw material in the chemical sulphate pulping of softwoods and hardwoods. The numbers are in kg/t_{90} (1)

Component	Spruce 50 % yield	Pine 47 % yield	Birch 53 % yield	Eucalyptus 55 % yield
Cellulose	80	85	75	70
Hemicelluloses	380	425	375	290
Lignin	500	530	395	420
Extractives	40	45	35	35

Only a part of the dissolved material is present in the same form as in the fibrous raw material and especially the carbohydrates are severely degraded during the cook. Only about 20 kg/t_{90} of the carbohydrates in the black liquor is present as high molecular material the rest is degraded primarily to saccarinic acids but also to formic acid, acetic acid, lactic acid and glycolic acid.

All substances in Table 7.6 contribute to the COD-value of the black liquor. The colour of the spent liquor is mainly due to the high molecular lignin fraction. The main source for BOD, however, is the low molecular fraction i.e. the acids mentioned above and the low molecular degradation products of lignin. Major substances are phenols and phenolic carboxylic acids (~ 80 kg/t_{90}), vanilla and derivatives (~ 20 kg/t_{90}), methanol and ethanol (15-20 kg/t_{90}).

Table 7.6 The organic composition of the black liquor from sulphate pulping of pine (3)

Component	Amount, kg/t_{90}
Lignin, high molecular	500
low molecular	30
Carbohydrates, high molecular	20
low molecular	500
Extractives	40
Organic sulphides	2

The most volatile components in the black liquor are methanol, ethanol, organic sulphides and terpenes. The digester condensate contains methanol, organic sulphides and terpenes. The evaporation condensates also contain methanol and sulphides and in addition higher alcohols, sesquiterpenes and guajacoles.

Basically the same compounds and in about the same amounts are found in soda pulping. The major difference is that less organic sulphides are formed. If the cooking liquor could be kept free of sulphur compounds there would be no odour emitted from soda mills. However, sulphur is introduced in various ways into the process, for instance with the wood raw material and with the oil into the lime kiln. Therefore even soda mills smell.

Table 7.7 presents the BOD-value of digester and evaporation condensates from the sulphate pulping of softwoods. The relative distribution between digester and evaporation condensate BOD depends to a large extent on the equipment and process conditions in the individual mill. Few reliable data exist on the total condensate BOD of hardwoods but available figures indicate values around 20 kg/t_{90}.

Table 7.7 The BOD_7-value (in kg/t_{90}) of digester and evaporation condensates from the sulphate pulping of softwoods and Eucalyptus (Globulus and Saligna)(2)

Position	Continuous cooking		Batch cooking
	Softwood	Eucalyptus	Softwood
Digester condensate	2.6	5.5	4.9
Evaporation condensate	9.0	13	5.5
Total	11.6	18.5	10.4

A simplified process scheme for a mill for bleached sulphate or soda pulp is shown in Figure 7.3. The main discharge as well as the main pollutants are given in the figure. For soda pulping the emissions of sulphur compounds are low.

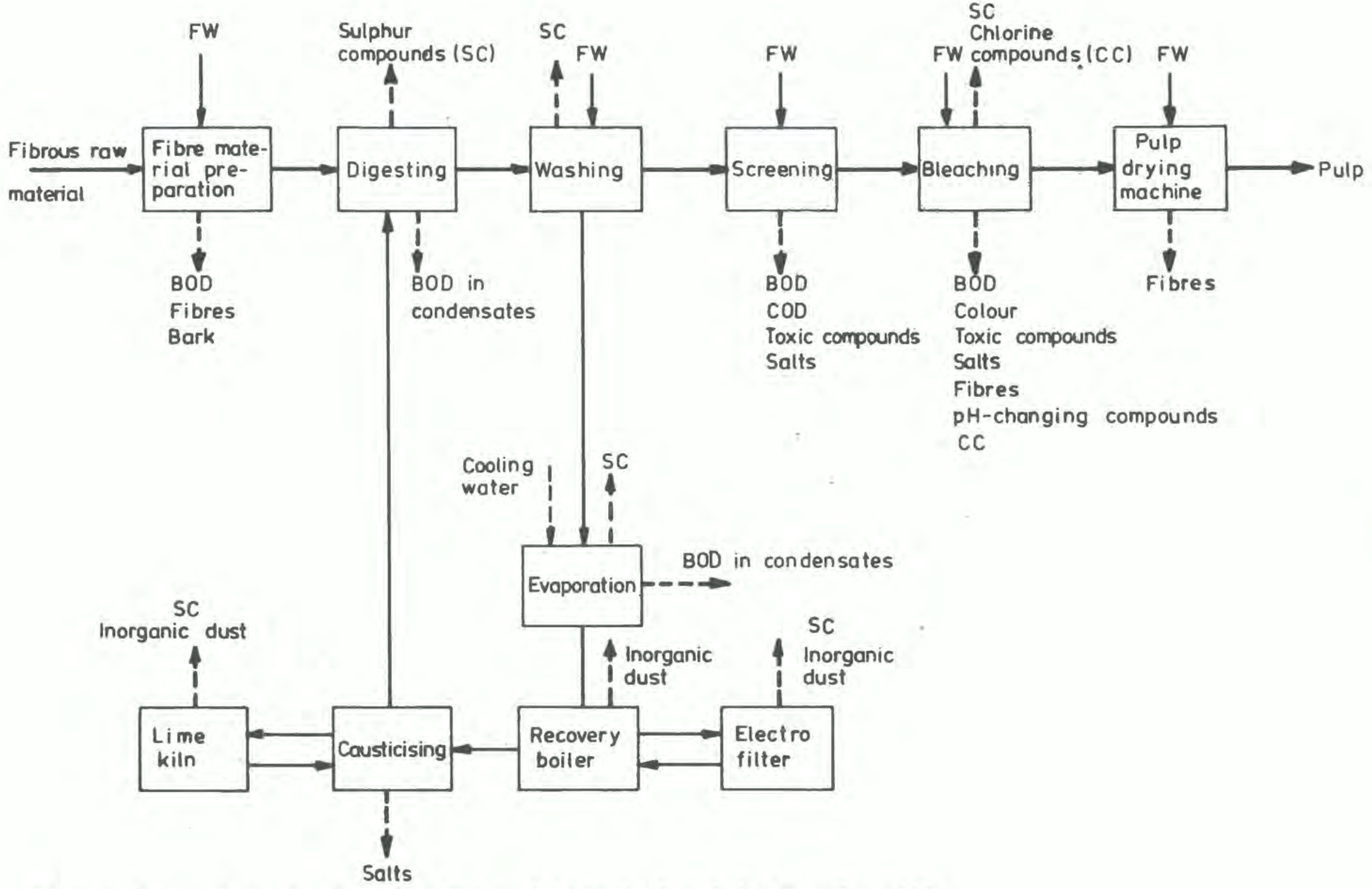


Figure 7.3. Principal flow sheet of bleached sulphate pulp mill.

The BOD, COD and colour values of the organic substance dissolved in chemical sulphate and soda pulping are given in Tables 7.8 and 7.9.

Table 7.8 The BOD_7, COD and colour of the organic substance dissolved in soda pulping

Fibrous raw material	Pulp yield	Kappa number	BOD_7	COD	Colour
				kg/t_{90}	
Cotton	55	-	340	970	2050
Straw	60	85	350	940	900
"	50	20	250	930	1050
Bagasse	80	-	265	750	-

Table 7.9 The BOD_7, COD and colour values of the organic substance dissolved in sulphate pulping

Fibrous raw material	Pulp yield	Kappa number	BOD_7	COD	Colour
				kg/t_{90}	
Bamboo	46	30	295	1300	1190
Bagasse	48	15	350	1340	950
Birch	58	26	190	-	-
	53	20	270	-	-
	50	17	300-350	-	-
Eucalyptus globulus	53	18	270	1190	-
	53	17	350	1550	2150
Pine	48	35	280	1350	1400

The discharges from chemical sulphate pulping of Eucalyptus using different in-plant abatement techniques are given in Table 7.10. No external treatment has been assumed but the spills are contained and eatcontribute only 15 kg BOD_7/t_{90}.

A more efficient spill collection system is assumed at the 95 % washing efficiency level and a condensate treatment with 80 % efficiency on BOD_7.

Table 7.10 The BOD_7, COD and colour values for chemical sulphate pulping of Eucalyptus (1)

Process	Washing efficiency %	BOD_7	COD kg/t_{90}	Colour
Direct discharge	0	270	1190	1650
Spills retained	85	75	270	180
Condensate treatment, efficient spill collection	95	25	90	115

From the fibre line of sulphate mills discharges of suspended solids originate mainly from the washing and screening operations. Normal discharges range from 25 to 35 kg/t_{90}. With a closed screening systems and a well designed spill collection system values around 15 kg/t_{90} may be obtained.

Literature reference list Chapter 7

1. IVL internal data

2. Norrström, H.
   Pure and appl. chem., Vol 45, pp 181-186

3. Pettersson, B.
   Sammansättning hos avlopp från sulfatblekerier
   NM 80 Rapport nr 2B:6, 1976 (In Swedish)

4. The SSVL Environmental Care project 1970-73,
   Stockholm 1974

8. WASTE PAPER PROCESSING

8.1 General

Waste paper is an increasingly important raw material for production of newsprint, tissues, printing and writing papers magazines and boxboard. The greatest portion of waste paper is not chemically treated but is pulped mechanically. Processing with chemicals (deinking) is, however, necessary for newsprint and writing paper. There are two main methods of deinking; flotation and washing. Flotation deinking in 1978 accounted for about two thirds of all deinked fibres produced worldwide. The washing deinking method is used mainly in the United States, while flotation deinking remains the dominant process in all other areas.

The important distinction between these systems is that in flotation deinking essentially all of the fillers and dissolved contaminants remain with the fibres while ink particles, hot melts, and other substances lighter than water are removed. In washing deinking fillers, dissolved solids and suspended solids are to a large extent removed with consequent lower yields.

The major sources of emission from waste paper processing are the deinking stage and the screening stage. Others are accidental spills and white water, floor drainage, wash-up, cooling and sealing water.

Organics present include additives, products of hydrolysis and fibres lost in the process. Inorganics derive from mineral fillers, ink pigments and other materials separated from the fibre in waste paper, as well as chemicals if used in the process.

8.2 Discharges of waste paper effluent

The effluent can be kept at a low level in a modern integrated waste paper process. Depending upon the quality of the product and the equipment used the effluent flow will vary from a few m^3 per tonne of waste paper processed to more than 100 m^3 per tonne for an old deinking process employing the washing system (Table 8.1).

Table 8.1 Emission of water from the process

Process	Flow, m^3/t average numbers
Mechanical treatment only	1 - 3
Deinking by flotation	5 - 20
Deinking by washing	50 - 100

Normally the white water from the waste process is recirculated from the dewatering stage to dilution before the screening and cleaning operations or to the flotation cells. Remaining process water follows the pulp to the paper mill. This quantity must be replaced in the waste process. Clarified white water from paper making operations may supply the greater part.

A considerable yield loss of the raw stock occurs in waste paper processes, especially if deinking is involved. This loss appears in the waste water primarily as BOD_7 and TSS. The loss for common grades of waste paper is shown in Table 8.2.

Table 8.2 Average yield loss for common grades of waste paper raw stock (1,2,3)

Paper type	Ash, %	Yield loss, %
Corrugated board	5	5-10
Bond	2	10
Newsprint	2	15
Ledger	5	15
Offset	12	19
Book	20	34
Gummed	10	40
Coated	30	50

If a bleaching operation is involved in the waste paper process the yield loss will further increase in the range of about 2 to 3 percent.

The major pollutants of waste paper effluent, as discussed above, are dissolved and suspended solids. Colour can be a factor in deinking and bleaching operations although it is a minor one in comparison with the colour values which result from manufacture and bleaching of chemcial pulps.

Table 8.3 gives a range of values for the BOD_7, COD and total suspended solids of the effluent from waste paper processing and bleaching.

Table 8.3 Approximate BOD_7, COD and TSS (in kg/tonne) in pulping of waste paper including deinking and bleaching (2)

Types of treatment	BOD_7	COD	TSS
		kg/t_{90}	
Mechanical pulping only	15	40	50$^{x)}$
Pulping including deinking	20-40	50-90	150-200
Bleaching	10-20	20-40	-

Part of the surprisingly high COD values in waste paper deinking originates from non-settleable fines, fibre fragments and ink particles cleaned out in the deinking operation.

The amount of ink sludge produced in the deinking operation is about 50 to 100 kg per tonne of pulp produced from waste paper. This sludge should be separated from the main effluent and dewatered. It can then be disposed of together with the other solid wastes in a land fill or be burned in bark boilers. In the latter case it might cause an emission of dust to air. Table 8.4 shows an example of the amounts of metals which such an ink sludge may contain.

Table 8.4 Average values of the amount of metals per kg of dry sludge from Scandinavian waste paper processing (2,3)

Metal	mg/kg
Cu	250-400
Mn	200-300
Mo	10-50
Ni	10-50
Cr	10-100
Co	traces
Pb	100-300
	traces

Apart from the treatment of the ink sludge, the treatment of the effluent from a waste paper mill are much like the treatment of paper mill effluent (Table 8.5). About 60 to 70 % of the BOD can be removed in a biological treatment plant. This indicates that the effluent from a waste paper mill is degradable to about the same extent as the effluent from a newsprint mill.

Table 8.5 Treatment results on an effluent from a (household) waste paper treatment plant (1)

Treatment	Reduction, %		
	BOD_7	COD	SS
Sedimentation	10	10	70-80
Chemical flocculation (20 kg alum/t_{90})	20-30	20-40	80-90
Biological treatment (2-3 kg BOD_7/m^3, day)	60-70	20-30	-a)

a) biological treatment must be combined with sedimentation or flocculation to obtain SS-reduction

Literature reference list Chapter 8

1. Anderson, R.
   Environmental impact at treatment of recycled paper
   SSVL-project 24 DP 11, Stockholm

2. IVL internal data

3. United States Environmental Protection Agency (EPA).
   Development document for effluent limitations. Guidelines and proposed new source performance standards for the bleached kraft, groundwood, sulphite, soda, deink and non-integrated paper mills
   Vol. 1 and 2, January 1976 (EPA 440/1-76/947-a Group I, phase II

9. BLEACHING OF MECHANICAL AND CHEMICAL PULPS

9.1 General

The aim of the bleaching operation is to increase the visual qualities e.g. the brightness or whiteness of the pulp or to obtain a pulp suitable for the manufacture of regenerated cellulose. Pulps in a high yield (and with a high lignin content) are usually bleached using peroxide or dithionite in such a way that the yield is retained (lignin preserving bleaching).

When bleaching chemical pulps the dark coloured lignin residues are removed by applying chlorine containing chemicals (chlorine, chlorine dioxide, hypochlorite) and alkali. To produce dissolving pulps the low molecular carbohydrates have to be removed. To achieve this, treatment with strong alkali is used.

Using conventional bleaching technology all of the dissolved organic substance is discharged from the bleach plant. The amount and composition of the discharged material depend upon the type of pulp to be bleached and the conditions in the bleaching. Any dissolved material that is brought to the bleach plant with the incoming pulp (e.g. black liquor residues) is also discharged.

Using oxygen bleaching or bleaching sequences starting with an extraction stage the effluent from those stages may be recycled to the recovery system. According to the closed mill concept developed by Rapson and Reeve all of the bleach plant effluent is brought to a sulphate recovery system and the chlorides in the system are removed by the Salt Recovery Process.

9.2 Bleaching of mechanical and chemimechanical pulps

Bleaching with peroxides and dithionites (hydrosulphites) is called lignin preserving bleaching. In spite of the name a certain dissolution of organic material occurs. The chemical composition of material dissolved during peroxide bleaching of groundwood is given in Table 9.1.

Table 9.1 Approximate BOD$_7$, COD and colour of the discharges from the pulping and bleaching of Scandinavian groundwood pulps

Bleaching process	Bleached brightness % SCAN	BOD$_7$	COD kg/t$_{90}$	Colour
Dithionite	67	20	-	-
Peroxide	80	30	60	40

Low molecular compounds account for more than 50 % of the dissolved organic material and acetic acid alone for 40 % in peroxide bleaching of spruce groundwood. The BOD$_7$-value of the dissolved substance varies between 10 and 30 kg/t$_{90}$ depending on the alkali charged in the bleching (Figure 9.1).

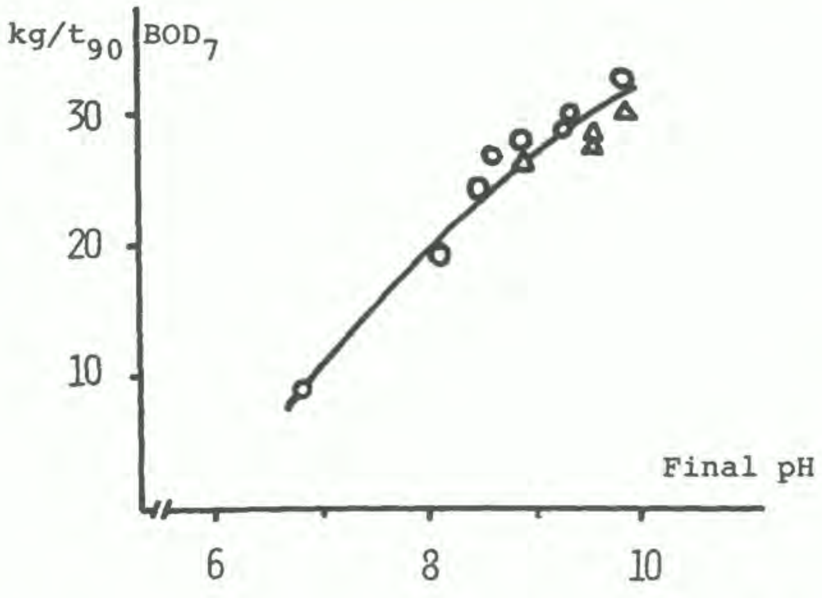


Figure 9.1 Dissolution of BOD$_7$ (as kg/t 90 % dry pulp) in peroxide bleaching versus final pH. The material includes both groundwood pulps and thermomechanical pulps

Very few measurements exist on the discharge from dithionite bleaching. For normal brightness increases on softwood mechanical pulps (around 5-7 units SCAN), the discharge is of the order of 5 kg BOD_7/t_{90}. It should be pointed out that not all of the material dissolved in peroxide or dithionite bleaching is discharged with the effluent. As in mechanical pulping part of the dissolved material follows the pulp to drying or to the paper mill

The total discharges of BOD_7, COD and colour from the pulping and bleaching of softwood groundwood pulp are given in table 9.1. It has been assumed that the dissolved substance in the pulping stage has a BOD_7-value of 5 and 15 kg/t_{90}, respectively, in the dithionite and peroxide bleaching stages.

In production of TMP and RMP the system can be simplified when the bleaching is carried out in the same refiner as is used for the pulping. The chemicals are then charged into the refiner, where the main reaction occurs and sometimes extra reaction time is provided for in a retention tank. The total amount of dissolved solids (measured as COD) in thermomechanical pulping and refiner bleaching of poplar and two softwoods is shown in Table 9.2.

Table 9.2 Total amount of dissolved COD in thermomechanical pulping and refiner bleaching (1)

Fibrous raw material	Charge of chemicals, kg/t_{90} peroxide	Charge of chemicals, kg/t_{90} alkali	COD kg/t_{90}	Brightness % SCAN
Poplar	0	0	31	-
	7	9	52	-
	12	9.5	56	-
	32	12.5	58	-
Pinus massoniana	0	0	64	-
	17	16	97	-
	33	27	122	-
Pinus densiflora	0	0	59	54.7
	15	10	118	69.0
	21	13	137	70.9

9.3 Influence of process parameters in the bleaching of chemical pulps

The following factors are of importance for the discharge of pollutants from bleaching plants;

1. Lignin content of the unbleached pulp
2. Extent to which the unbleached pulp has been washed
3. Bleaching conditions such as
   - degree of delignification of unbleached pulp
   - bleaching chemicals and charges used
   - bleaching sequences
   - temperature and pH
   - final brightness and strength requirement.

The extent to which the various systems have been closed and the recirculation pattern of the filtrates are other important factors.

During the bleaching process lignin, carbohydrates and extractives are dissolved from the pulp. Through laboratory bleaching trials of different pulp types the dissolution of various components can be estimated. An example is given in Table 9.3.

Table 9.3 Substance loss in the bleaching of various types of pulp (kg/t_{90}) (3)

	Sulphate pulp		Sulphite pulp, softwood	
	pine	birch	paper[a)]	dissolving[b)]
Lignin	50	20	35	12
Carbohydrates	19	22	12	70
Extractives	1	3	8	8
Total	70	45	55	90

a) unbleached kappa number 20
b) unbleached kappa number 8. Final brightness ~ 92 % SCAN

For all paper pulps the major dissolution of substance takes place in the prebleaching (C+E). When bleaching sulphate pulps the major part of the dissolved substance appears in the E_1-stage effluent. However, in the bleaching of sulphite pulp the major part is dissolved already in the chlorination stage. For viscose pulps the major dissolution takes place in the hot alkali refining stage. The dissolved substance consists mainly of carbohydrates and degradation products of carbohydrates.

The colour of the effluent is linearly related to the amount of lignin dissolved, which is directly proportional to the lignin content of the original pulp. The variation of the discharge of colour form stages C and E with the kappa number of the original pulp is shown graphically in Figure 9.2.

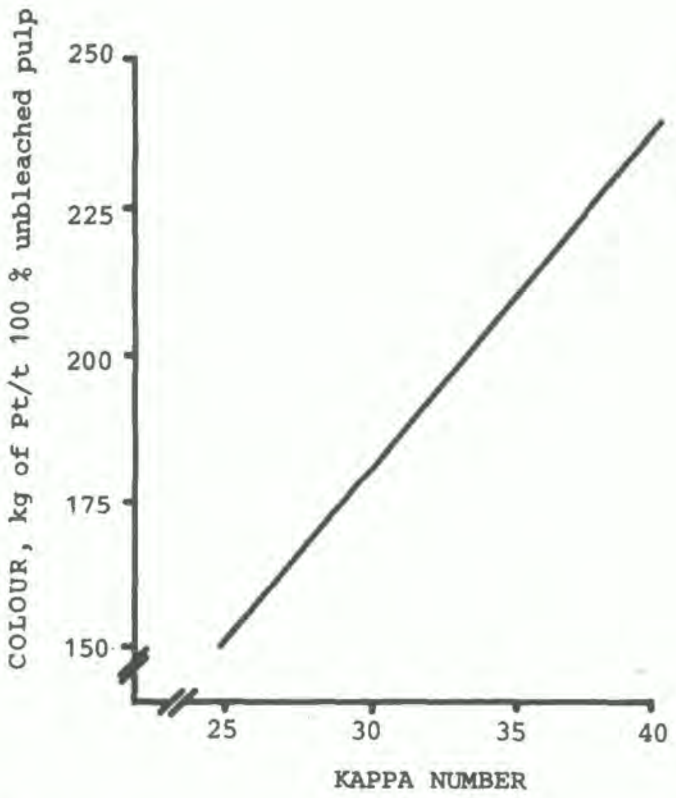


Figure 9.2 The colour from prebleaching (C+E) of pine sulphate pulp versus kappa number of unbleached pulp

The BOD content of the effluent (stages C and E) is also linearly dependent on the amount of lignin dissolved. A plot of the total BOD_7 against the initial kappa number is presented in Figure 9.3.

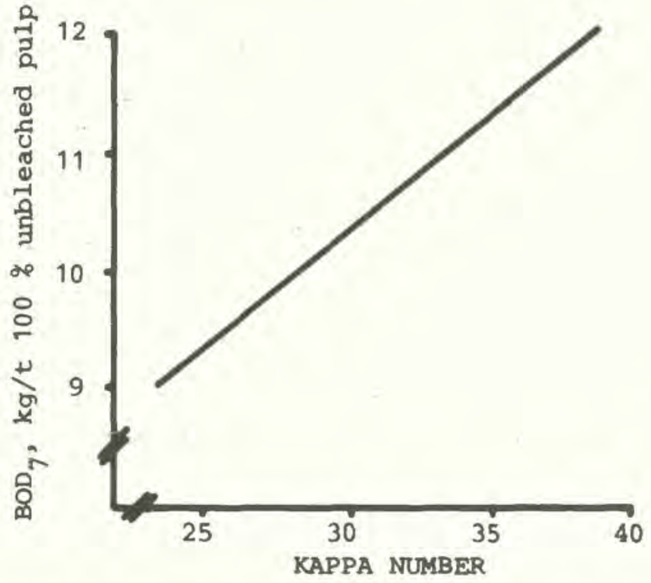


Figure 9.3 Total BOD_7 from prebleaching of pine sulphate pulp versus kappa number of unbleached pulp

A high washing loss of the incoming pulp leads to a higher discharge of BOD and colour from the first two bleaching stages. In Figure 9.4 the colour of the effluent from fully bleaching of a birch sulphate pulp is shown. Normally the total colour from the C and E-stages is around 50 kg/tonne.

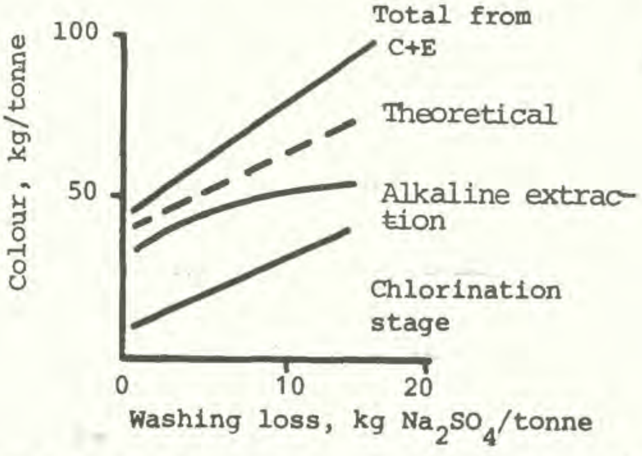


Figure 9.4 The colour of the chlorination and alkaline extraction stages effluent as a function of the degree of washing of the unbleached pulp. Birch kraft pulp with a kappa number = 16

When the washing loss increases the colour increases in both the chlorination and alkaline extraction stage. In these laboratory bleaching experiments the washing loss was simulated by addition of black liquor. It is interesting to note that the increase in colour is higher than could be expected from calculations when the colour of the black liquor was added to that of the effluent (the line "theoretical"). Components in the black liquor thus react to more coloured compounds during the chlorination.

Both the charge of chlorine in the chlorination and the charge of alkali in the extraction stage influence the pollution load (Figure 9.5). An increase in the charge of chlorine at higher temperature leads to a marked increase in the effluent BOD_7. The effect is small, however, at normal temperature and especially when chlorine dioxide is added.

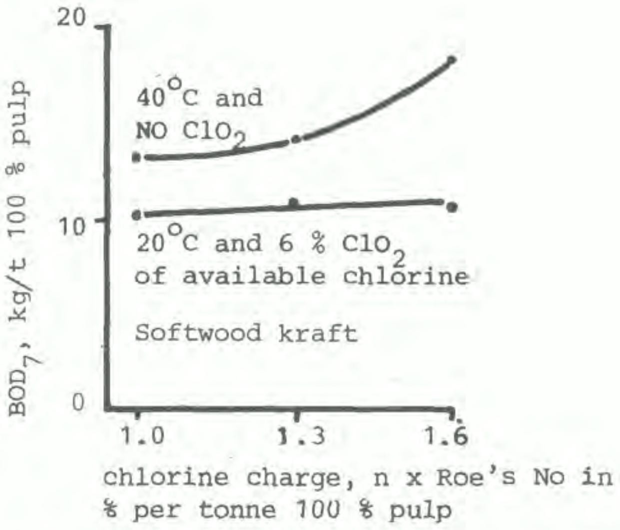


Figure 9.5 The BOD_7-value of the chlorination and alkali stage effluent as a function of the charge of chlorine. Bleaching of softwood sulphate pulp.

The final pH of the alkaline extraction stage is in most instances kept above 10 (Figure 9.6). At lower pH-values the dissolution of chlorinated and degraded lignin from the pulp rapidly decreases. This leads to an increased bleaching chemical demand in the later stages. Within the operating range there is, however, a clear effect of the alkali charge on the colour in the effluent.

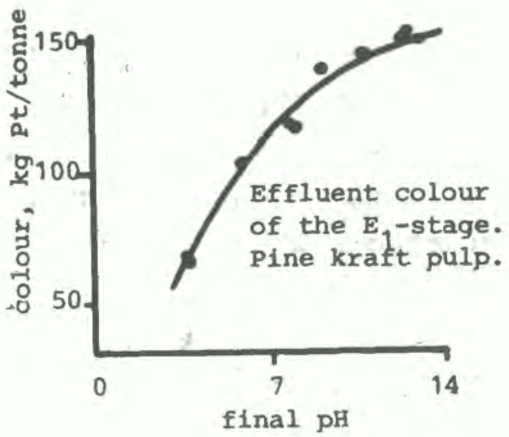


Figure 9.6 The colour of the alkaline extraction effluent as a function of the final pH in the stage

9.4 Discharges from the bleaching of chemical sulphite pulps

The main fibrous raw material for the production of bleached chemical sulphite pulps is softwoods. In addition various hardwoods, primarily birch and beech are used. In Table 9.4 the BOD$_7$, COD and colour values for the discharge from the bleach plant are summarized.

Table 9.4 The BOD$_7$, COD and colour values of the discharge from the bleaching of chemical sulphite pulps (2)

Fibre	Pulp type	Process	Kappa number	BOD$_7$	COD	Colour
					kg/t	
Softwood	Paper	Acid	30	15	60	100
	Paper	pH 4	30	15	-	-
	Viscose	Acid	12	30-40	-	40-50

Depending on the great variability in process conditions, kappa number and washing loss of the unbleached pulp, there is a great variation also in the discharge of pollutants.

The high BOD and COD values of the discharges from the in the alkali extraction stage.

Table 9.5 shows the contribution of BOD_7 and colour from the individual stages in the bleaching of softwood sulphite pulps. The washing between the bleaching stages has been assumed to be complete (i.e. no carry-over of bleaching chemicals between stages) and likewise the carry-over of dissolved substance with the unbleached pulp has been assumed to be negligible. The kappa number of both pulps is in the range of 10-12.

Table 9.5 The BOD_7 and colour values (in kg/t_{90}) from the individual bleaching stages in softwood sulphite paper and viscose pulp bleaching (3)

Bleaching stage	Paper pulp		Viscose pulp	
	BOD_7	Colour	BOD_7	Colour
C stage	6	25	2	25
E stage	6	45	26	45
Final stages	2	5	2	5

9.5 Discharges from the bleaching of chemical sulphate and soda pulps

Sulphate and soda pulps from a variety of fibrous raw materials are utilized to produce bleached pulp. The discharges of BOD_7, COD and colour are summarized in Table 9.6.

Table 9.6 The BOD_7, COD and colour values (in kg/tonne) of the discharge from the bleaching of sulphate and soda pulps at a normal washing loss (for a modern mill) (2)

Fibrous raw material	Pulping processes	Kappa number	BOD	COD	Colour
Bamboo	Sulphate	-	17[a)]	90	-
Straw	Soda	12	16[a)]	60	70
Eucalyptus	Sulphate	20	14[b)]	60	70
Birch	Sulphate	20	14[b)]	60	70
Scotch pine	Sulphate	33	15[b)]	80	160
	Sulphate+O_2	20	12[b)]	50	100

a) BOD_5-value
b) BOD_7-value
c) Kappa number of O_2-bleached pulps

There is relatively little variation in the BOD and COD values between species while the colour values show a wider range. Besides the traditional effluent characteristics (BOD, COD, colour) the amount of chlorine bound to organic molecules in the bleach plant effluent is significant. The chlorinated organic compounds often show only a slow degradation by biochemical oxidation and some tend to accumulate in organic tissues.

The amount of organically bound chlorine for some bleaching sequences is shown in Table 9.7. By substituting chlorine with chlorine dioxide and by oxygen bleaching the organic chlorine can be reduced from about 13 kg/t to values below 5 kg/t. These modifications, however, require changes in process equipment and will increase the investment and the operating costs.

Table 9.7 The BOD, colour and amount of organically bound chlorine generated in various bleaching sequences for softwood sulphate pulp (3)

Bleaching sequence	Kappa number	D[a)] %	BOD_7 kg/t	Colour kg/t	Org. chlorine kg/t
C_DEHDED	35	10	16	175	13
(C+D)EDED	25	25	12	100	6
	25	75	12	75	4
	25	100	11	60	2
O(C+D)EDED	17	15	11	85	6
	17	50	11	60	3
	17	100	10	40	1

a) D denotes the amount of chlorine dioxide added in the chlorination stage

The same process modification also reduces the BOD and colour discharges. Most marked is the colour reduction (up to 75 %) while the BOD reduction is a less spectacular 35 %. It should be pointed out that the delignification in the cook has been extended to kappa number 25 for the bleaching sequences with high amounts of chlorine dioxide.

Appart from process modifications the dissolved organic material in the bleach plant effluent can be reduced by external treatment methods. Some alternatives are given in Table 9.8. Colour reductions of more than 90 % can be achieved while the BOD reduction by these methods usually is limited to below 50 %. Of the methods indicated in the table only oxygen bleaching can be considered fully commercially available and proven.

Table 9.8 Reduction in bleach plant pollution by process modifications or external treatment methods. Softwood sulphate pulp bleaching (2)

Process modification or treatment	Reduction, %	
	BOD_7	Colour
Oxygen bleaching	30	50
Chlorine dioxide	30	60
Oxygen + dioxide	35	75
Adsorbing resins[a)]	20	90
Ultrafiltration[a)]	20	90

a) the values given refer to treatment of E_1-effluents

Literature reference list Chapter 9

1. Data supplied by Defibrator AB, Stockholm

2. IVL internal data

3. SSVL
   Chloride in recovery system, 1974-1976
   Stockholm 1977 (In Swedish)

10. PAPER MAKING AND PULP DRYING

10.1 General

Paper making needs large quantities of water. However, the volume of polluted effluent varies from mill to mill with the degree of white water system closure; the paper grade produced; size of the mill; raw material used and other local conditions. The pollutants consist of suspended solids (fibres, fibre fragments, inorganic fillers) as well as dissolved substances (dissolved wood components, paper making additives). Generally the main part of the dissolved substances is generated in the pulp mill and follows the pulp to the paper mill.

Pulp drying is less water consuming and less polluting than paper making.

10.2 Paper machine white water system

Closing the white water system means using less fresh water by recycling used white water. The main reasons for reducing the water consumption are

- to reduce the economic loss due to lost fibre. Fibre losses are strongly related to the volume of discharged effluent
- shortage of fresh water of good quality
- to cut the costs for building and running an external treatment plant. These costs mainly depend on the volume of water to be treated.

Usually anyone of these reasons is enough to motivate investment in internal measures to reduce the water consumption.

Water is needed in paper making for diluting the stock, as shower water on the wire and in the press section, as cooling water and as sealing water in pumps, screens and agitators. A total of about 200 m^3 of water is needed per tonne of paper produced.

In a completely open white water system (Figure 10.1) fresh water is used in all these positions. The only white water recycle is the short circulation where the water in the wire pit is partly used for final stock consistency regulation before the head box. Fibre losses may be as high as 50-150 kg/tonne of paper. Such a system is very uncommon today.

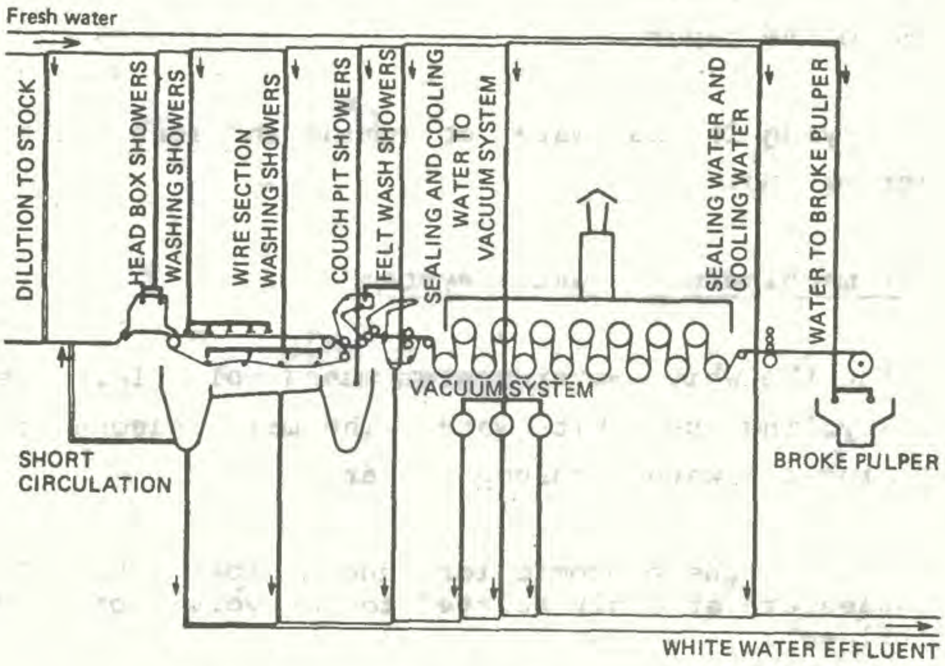


Figure 10.1 A completely open system

About ten years ago the white water system design shown in Figure 10.2 was very common. There are still mills built with such a system, however. The most heavily contaminated white water from the wire section is reused for diluting the stock. Excess white water, 100-200 m^3/tonne of paper is discharged for external treatment. The losses of fibres and fillers are in the range of 25-50 kg/tonne.

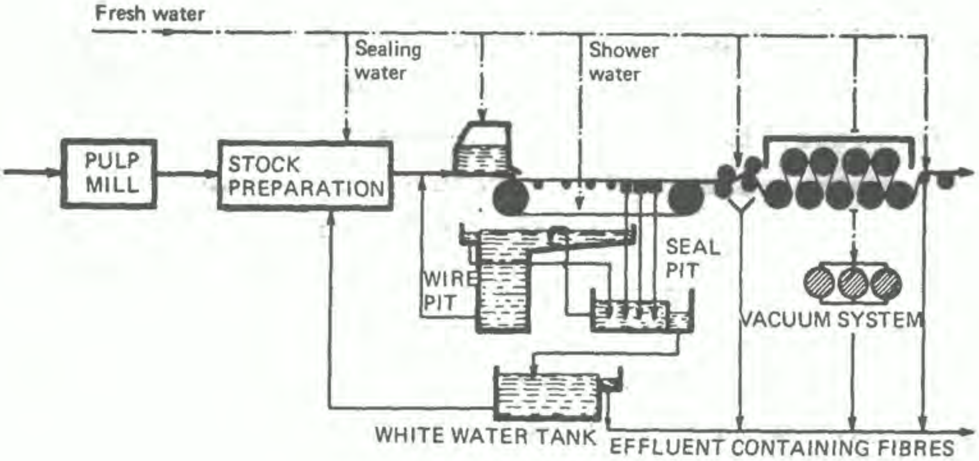


Figure 10.2 A white water system with recirculation

Further reuse of white water for example as shower water instead of fresh water calls for internal cleaning devices to remove fibres and fines from the white water. The usable fibres are then recovered and converted to paper. Figure 10.3 shows the principle for such a white water system. This is the most common system on new paper machines. Uncontaminated process waters are sewered separately. Only cleaned excess white water 10-50 m^3/t is discharged to the external treatment plant. Fibre losses range from 5-25 kg/t. However, there are paper mills which have taken very advanced internal measures to reduce the water consumption and fibre losses below these figures.

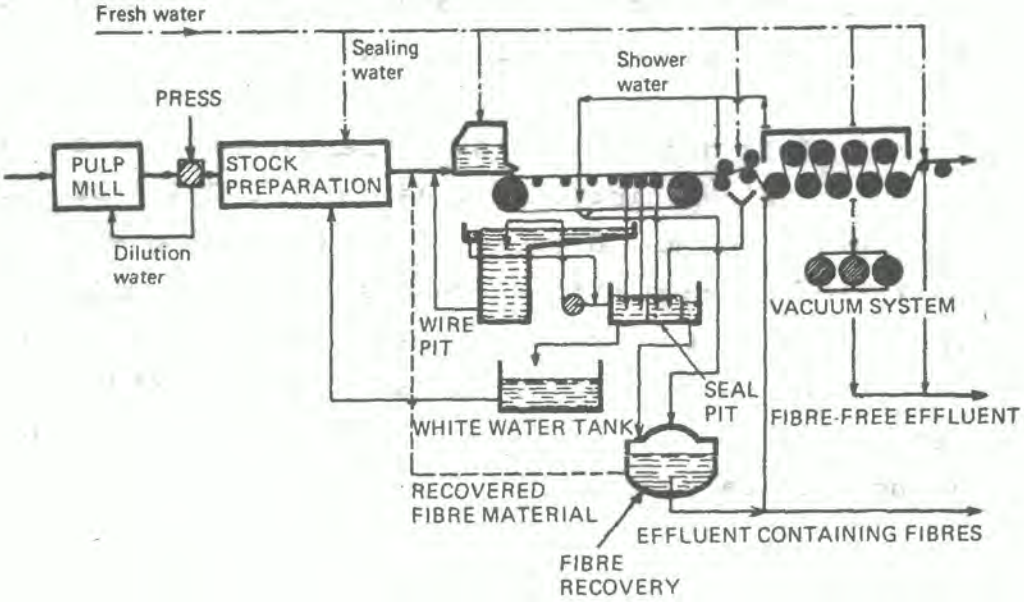


Figure 10.3 An almost closed white water system with fibre recovery

Operating difficulties and quality deterioration (for example due to build up of dissolved substances in the white water) limits the white water system closure. Some of the problems observed are reduced retention, slower dewatering, foaming, bad sizing, picking, linting, deposits on machine components and deterioration of paper strength and printability. The configuration of the optimized white water system depends on many factors which have to be investigated in each individual case.

10.3 Paper mill discharges

The discharge of suspended solids from paper mills is almost entirely determined by the water consumption i.e. the degree of white water system closure. The amount of filler and the mean fibre length of the pulp is also important since small particles are more difficult to keep within the processes.

The discharges of dissolved substances from paper mills consist of dissolved wood components and paper making additives. The main part of the dissolved organic components is generally transferred from the pulp mill. Consequently environmental measures implemented in the pulp mill, such as closure of the screening room, improved washing etc, greatly affect the situation in the paper mill.

In paper mills dissolution of fibre material as a rule only occurs in the refining stage. As much as 2-4 % of certain high yield pulps may dissolve during refining while the dissolution of conventional chemical pulps is very low. Normally only 1 to 5 kg BOD_5/t is generated in the paper mill. Depending on the paper grade the discharge BOD may increase due to other added substances such as paper dyes, coating chemicals etc.

The discharge of dissolved substances (BOD) should theoretically not be affected by system closure. However, as a secondary effect the discharged BOD from paper mills is generally to a minor extent decreased with water consumption.

Table 10.1 shows discharges from US paper mills in 1972. The discharged water volume and the suspended solids for different paper grades, in Sweden, for the same period are shown in Figure 10.4A (1). In Figure 10.4B the estimated emissions of dry solids after system closure assuming known technology are shown. Depending on demands for environmental protection and other local conditions it may be possible to achieve lower figures in some cases.

Table 10.1 Discharges from US paper mills 1972 (2)

Manufactured quality	Water, m^3/t		BOD_5, kg/t		Susp.solids, kg/t	
	average	range	average	range	average	range
Newsprint	93	52-115	20.4	19-22	45	20-70
Carton board	42	5-130	11.2	4-18	28	3-80
Fine paper	63.4	26-130	10.7	7-19	30.8	18-20
Tissue	95	45-150	11.5	7-23	34.0	10-70

Closing of white water systems of paper machines hardly ever completely solves an environmental problem. It must be supplemented by an external treatment plant, usually a sedimentation basin. Sedimentation has little effect on the BOD and in future the authorities may require the waste water to be purified from the BOD. This may require either chemical flocculation or biological treatment or a combination of these two methods. For some types of paper mill effluents from 40-70 % of the BOD can be removed by a fairly low cost chemical treatment.

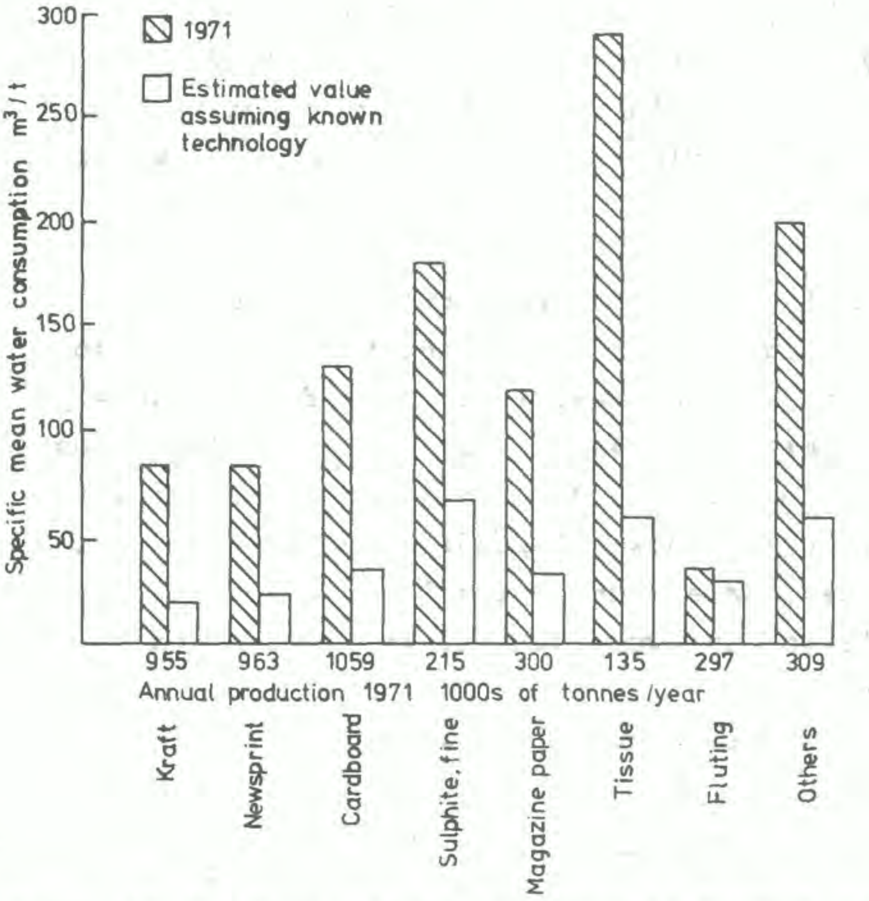


Figure 10.4A Mean water consumption in Swedish paper mills

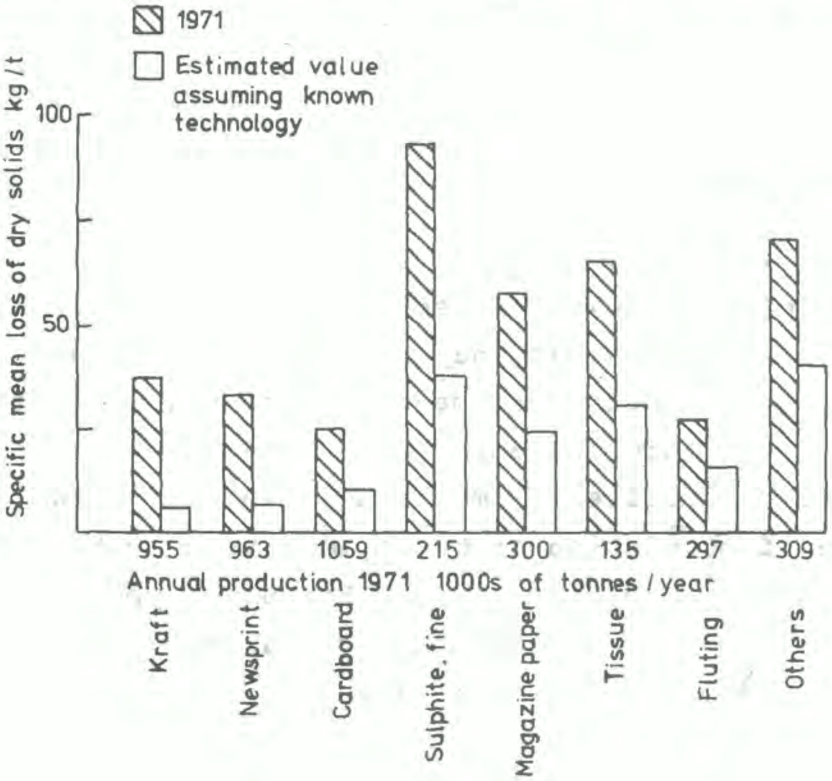


Figure 10.4B Mean solids in Swedish paper mills

However, there are mills where the internal system has been closed so far that a further external treatment would be pointless from an environmental point of view. In such mills spill collection systems have been installed to take care of accidental discharges for recycling to the process or for a slow controlled discharge. This is very important since accidental discharges may contribute 25-50 % of the earlier given figures for discharges. The accidental discharges should be reduced by proper design of the storage capacities for pulp, broke and white water.

10.4 Pulp drying

10.4.1 Water requirement

Water requirement for the pulp drying operation varies widely depending on the system employed and the type of pulp to be treated. Besides shower water, which is the main process water addition, cooling water, sealing water and scrubber water are also used in this operation.

Flash drying operation

The only water added in the flash drying operation is for the cleaning of exhaust gases in the scrubber (washing tower). The amount of water added is in the range of 4-10 m^3/tonne all depending on the flash drying system utilized and the type of pulp to be treated. A certain amount of the water added is recirculated.

Cylinder mold machine

The cylinder mold machine requires shower water for cleaning the cylinder wire. Generally fresh water is applied but also warm water or recirculated white water from the drying operation, cleaned or uncleaned, is used. The amount of shower cleaning water ranges approximately from 1 to 4 m^3/tonne of pulp.

Hot or warm shower water is also applied onto the pulp web to attain a relatively low viscosity of the pulp water and thus improve the drainage properties of the web. Particularly chemical pulps need this type of shower water, the quantity required depending on the type of pulp and other circumstances. A normal range is 1-4 m^3/tonne of pulp. When mechanical pulp is treated, shower water on the web is very uncommon. Sealing water is also used on the pumps for pulp and white water, and on the vacuum pumps.

Thus, the total amount of fresh water required on a cylinder mold machine is 2-7 m^3/tonne of pulp.

Fourdrinier machine

A fourdrinier machine requires almost the same types and amounts of water as does the cylinder mold machine. The shower cleaning water of the cylinder wire on the cylinder mold machine corresponds here to the cleaning water on the breast roll and wire return rolls.

10.4.2 Effluent discharges

The discharge from the pulp drying machine depends on the equipment, degree of white water reuse and type of pulp. Often the effluent from this operation is reused in other departments of the mill and the discharge from the pulp drying operation can be transferred. The main emission is suspended solids and normally there are only marginal amounts of BOD, COD etc being generated here. However, if there are high washing losses the amount of oxygen consuming material emitted can be high and reuse of the effluents may be difficult.

Flash drying operation

Assuming that the consistency of the pulp is increased from 10-15 % to 90 % in this operation, an excess of white water of 5-8 m^3/tonne of pulp is discharged or reused and 1.0-1.5 m^3/tonne of pulp leaves the system as vapour through the cyclones.

The contribution of the scrubber (washing tower) is 4-10 m^3/tonne.

Cylinder mold and fourdrinier machines

The consistency of the pulp at the inlet of the pulp drying machine is about 1.0 % but can sometimes be as low as 0.5 %. The pulp is dewatered and pressed to 40-50 % before the steam drying operation takes place. There is an excess of white water the main part of which is used for the dilution of the pulp before the drying machine. The net discharge from the operation is thus 7-20 m^3/tonne of pulp as white water and 0.8-1.3 t/t of pulp as vapour.

Bleached chemical pulps cause the least polluted effluents as regards BOD and COD due to the stringent requirement for clean pulp to the bleaching operation. In case of unbleached pulps the washing and screening operations decide the amount of washing losses being transferred to the pulp drying operation causing increased contents of BOD, COD etc in its effluent.

When drying mechanical pulps the effluent from the operation sometimes has a relatively high content of suspended solids due to the finest wash out of the pulp. The degree of system closure must be taken into account as this influences the discharges of water and fibres to a large extent.

Literature reference list Chapter 10

1. SSVL
   The SSVL Environmental Care Project. Technical Summary
   Stockholm 1974

2. United States Environmental Protection Agency (EPA) 1976 Development document for effluent limitations. Guidelines and proposed new source performance standards for the bleached kraft, groundwood, sulphite, soda, deink and non-integrated paper mills. Vol 1 and 2 January 1976 (EPA 440/1-76/047-a Group I, phase II

11. EMISSION OF AIR POLLUTANTS

The pulp and paper industry emits several compounds to the atmosphere. In Table 11.1 the main emissions to air are indicated for the different types of production.

Table 11.1 Emissions to the atmosphere from the pulp and paper industry

	Odorous compounds	SO_2	Cl-compounds	NO_x	Particulates
Fibrous raw material preparation	-	-	-	-	x
Sulphate and soda pulping	x	x	-	x	x
Sulphite and NSSC pulping	x	x	-	x	x
Semichemical pulping	x	x	-	x	x
Mechanical pulping	-	-	-	-	-
Bleaching	-	x	x	-	-
Pulp drying and paper making	-	-	-	-	-
Steam generation	-	x	-	x	x

- nil or insignificant
x main emission

11.1 Preparation of fibrous raw material

Inorganic and organic dust constitutes the only atmospheric emission from the preparation. The amounts and charcter of the dust emitted largely depends on the raw material and equipment utilized. As a rule, however, the dust has only a local distribution which makes it a minor environmental problem. The working environment may be heavily affected though and the dust must be regarded as a potential hazard to the health of the labour force.

The emission from the chipping and chip screening of softwoods and hardwoods is in the order of 1 kg dust per tonne of wood. The main part of the dust is removed in cyclones and often used as fuel.

In a wet or moist pretreatment system for non-wood raw materials the air emissions can be expected to be of the same order as for wood. From a dry preparation system the dust emissions are considerable (reliable data is lacking). There are also health problems relating to the handling of silicious grasses e.g. the lung disease bagassosis.

11.2 Sulphate and soda pulping

11.2.1 Major air pollutants from sulphate and soda pulping

The major air pollutants from sulphate and soda pulping are given in Table 11.2. Providing that the soda pulping chemical system can be kept reasonably free from sulphur the emission of sulphur compounds is very low.

Table 11.2 Air pollution emissions from various parts of the sulphate and soda pulping processes

Emission source	Reduced sulphur compounds	Sulphur dioxide	Nitrogen oxides	Dust
Cooking	x	-	-	-
Washing	x	-	-	-
Evaporation	x	-	-	-
Recovery furnace	x	x	x	x
Causticizing	x	-	-	x
Lime kiln	x	x	x	x
Tall oil cooking	-	-	-	-

- nil or insignificant
x main emission

11.2.2 Emission of odorous compounds

Emission of odorous volatile reduced sulphur compounds is the major air quality problem in sulphate and also partly in soda pulping.

The most important odorants emitted from the sulphate and soda processes are hydrogen sulphide, methyl mercaptan, dimethyl sulphide and dimethyl disulphide. Other reduced sulphur compounds such as alkyl sulphides have been detected but in far lower concentrations than those mentioned above (5). In Table 11.3 typical emissions of reduced sulphur compounds from the main sources are summarized. Emissions from the soda pulping process mainly correspond to the lower figures in the table.

Table 11.3 Main emissions of reduced sulphur compounds from sulphate and soda pulping (1,30,32)

Emission source	Emission rate, kg S/t_{90}			
	H_2S	CH_3SH	CH_3SCH_3	CH_3SSCH_3
Digester, batch	0-0.15	0-1.3	0.05-3.3	0.05-2.0
Digester, continuous	0-0.1	0.5-1.0	0.05-0.5	0.05-0.4
Washing	0-0.	0.05-1.0	0.1-1.0	0.1-0.8
Evaporation (indirect)	0.05-1.5	0.05-0.8	0.05-1.0	0.05-1.0
Recovery furnace (with direct contact evaporation)	0-25	0-2	0-1	0-0.3
Recovery furnace (without direct contact evaporation)	0-1	0.01	0.01	0.01
Smelt dissolving tank	0-1	0-0.08	0-0.5	0-0.3
Lime kiln	0-0.5	0-0.1	0-0.1	0-0.1
Tall oil cooking	0-0.5	0.01	0.01	0.01
Settling basin	0-0.5	0-0.2	0.01	0.0.02

The main sources of formation and emission of reduced sulphur compounds are the cooking, the evaporation, the recovery furnace and the lime kiln. The emission from the different processes can vary within a wide range depending on equipment, operation parameters and control techniques.

Beside the major discharge points, minor sources such as the washing, the smelt dissolving and black liquor tanks and the waste water treatment basins have been found to give essential contributions to the total emission.

The odour threshold for all major reduced sulphur compounds from the pulping process is unfortunately low and has an order of magnitude of 1 ppb (1 µg sulphur/m^3). In Table 11.4 odour thresholds are given for some compounds.

Table 11.4 Absolute odour threshold values for reduced sulphur compounds from sulphate pulping

Compound	Odour treshold ppb	Reference
Hydrogen sulphide H_2S	0.2-4.7	(15,17,34)
Methyl mercaptan CH_3SH	0.8-2.1	(15,34)
Dimethyl sulphide CH_3SCH_3	1.0-3.9	(15,17,34)
Dimethyl disulphide CH_3SSCH_3	5.6	(34)

Although reduced sulphur compounds in the ambient air represent the main odorants in sulphate pulping, there is no simple relationship between the concentration of these compounds and the odour around a sulphate mill.

11.2.3 Sulphur dioxide emission

Sulphur dioxide is emitted from the recovery furnace and the lime kiln. Moreover, in many odour control systems the reduced sulphur compounds are converted to sulphur dioxide in incinerators.

The emission of sulphur dioxide from a recovery boiler is dependent on process parameters, such as the sulphur to sodium ratio in the black liquor and the heat value of the black liquor. The SO_2-emission from a recovery furnace can be decreased by installing a flue gas scrubber working with alkali or oxidized white liquor as scrubbing agent. The scrubber chemicals can be recovered, mostly as Na_2SO_4, and recycled to the recovery system.

In mills with low sulphur to sodium ratio the SO_2 emissions are very low. In soda processes with very low sulphur to sodium ratio normally no SO_2 is emitted from the black liquor burning.

From the lime kiln the SO_2-emission is mainly caused by the sulphur in the fuel. Still, most of the sulphur dioxide is absorbed in the lime and transferred to the white liquor. Measurements in Sweden indicate that 50-100 % of the sulphur in the fuel is absorbed. The efficiency of adsorbance is influenced mainly by the amount of sulphur.

11.2.4 Emission of nitrogen oxides

Nitrogen oxides are formed during all types of thermal combustion. This formation occurs either through reaction between the atmospheric nitrogen and oxygen, or through a reaction between nitrogen in the fuel and atmospheric oxygen. The major compound resulting from the combustion is nitrogen monoxide. Smaller quantities of nitrogen dioxide, normally less than 5 %, are also formed.

The amount of nitrogen oxides formed, depends on several factors, the most essential being the flame temperature and the oxygen concentration in the flame. The formation of nitrogen oxides increases rapidly with temperatures above about 1300°C, particularly when the oxygen concentration is above 2 %. In addition to these two parameters, the nitrogen content of the fuel and the configuration of the combustion unit influence the nitrogen oxide formation.

In recovery furnaces the water content in the black liquor reduces the flame temperature and consequently the NO_x-formation. The low content of nitrogen in the black liquor (< 0.5 %) and the reducing conditions in the lower part of the furnace will further limit the formation of nitrogen oxides when compared to other combustion processes (9).

In the lime kiln a fuel with a high heat value is mostly used (e.g. oil), this gives higher flame temperatures and thus more NO_x is formed (9).

The emissions of nitrogen oxides from incinerators for odorous gases have not been investigated.

In Table 11.5 typical emissions of nitrogen oxides are given.

Table 11.5 Emissions of nitrogen oxides from recovery furnaces and lime kilns (9)

Process unit	NO_x-concentration ppm by vol. (average)	(range)	Emission rate kg NO_x/t_{90} pulp (average)
Recovery furnace	30	0-53	0.2
Lime kiln	200	113-260	0.2
Power boiler	200	161-232	5-10[a]

a) kg NO_x (as NO_2) per ton of oil

11.2.5 Dust emission

The recovery furnace, the smelt dissolving tank and the lime kiln are main emission points for dust in a sulphate or soda mill. Minor emission sources are lime slakers, chip filling etc.

In the flue gas from a recovery furnace particulate concentrations between 5 and 20 g/m^3 (on dry gas) have been measured. The dust consists mainly of sodium sulphate (Na_2SO_4) and sodium carbonate (Na_2CO_3) with smaller quantities of sodium chloride (NaCl). The carbonate content decreases with increasing sulphur to sodium ratio in the black liquor.

The particles of the primary emission have a size range of 0.1 µm to 1000 µm (23,32).

In recovery furnaces with direct contact evaporation the dust is partly collected in the evaporator. Modern recovery furnaces are mostly equipped with electrostatic precipitators from which the dust is recovered and recycled to the furnace. A flue gas scrubber is sometimes used after the precipitator. Table 11.6 contains data on typical dust emissions from recovery furnaces.

Table 11.6 Typical dust concentrations and emissions from sulphate and soda pulp mills

Emission source	Concentration (mg/m^3)	Emission rate (kg/t)
Recovery furnace		
- after electrostatic precipitator	10-1000	0.1-7
- after direct evaporation[a)]	900-5000	7-60
Smelt dissolving tank	40-2500	0.01-2
Lime kiln after dust removal	10-1000	0.01-1

a) before an electrostatic precipitator, if any

When the smelt from the recovery furnace is dissolved in the dissolving tank, steam is evolved and drops containing sodium compounds are emitted. Sometimes the tank vent is equipped with a demister.

In lime kilns most of the dust originates from the lime. The amount of particles emitted depends on the kiln design (length and diameter). The gases emitted from the lime kiln will contain fairly high concentrations of dust, 5-30 g/m^3 on dry gas have been measured. Concentrations after dust removal are given in table 11.6.

11.2.6 Organic compounds

Organic compounds, other than those containing sulphur, are emitted from various sources in the process. The major types of compounds include terpenes, hydrocarbons, alcohols and other organic compounds released from the wood or the black liquor. The emission rate and significance of these compounds has not been very well investigated, although it is well known that some of them can act as odorants and that the terpenes and hydrocarbons are photochemical reactants.

The flue gases from the recovery furnace and the lime kiln contain minor amounts of polyaromatic hydrocarbons (PAH). Polyaromatic hydrocarbons form a group of compounds containing several aromatic rings and many of the compounds are known to cause cancer.

11.3 Sulphite and NSSC pulping

11.3.1 Emission of sulphur dioxide

The main air emission from sulphite mills is sulphur dioxide. The potential for release of sulphur dioxide from the digesters, washing and evaporation is dependent on the pH of the liquors used. A low pH increases the sulphur dioxide emission.

The relief gases are normally recovered in the acid preparation system. The blow gases from the batch digester cause considerable emission in some mills. The SO_2-emission can amount to between 1 and 50 kg per tonne of pulp. The SO_2 losses depend mainly on the design of the acid preparation system and the operation of the gas relief from the digesters. In bisulphite and neutral sulphite cooking, the SO_2-emission normally is less than 2 kg per tonne of pulp.

The emission of SO_2 from the washing depends on the washing system. Typical values of SO_2-emission from the washing is 1-10 kg per tonne of pulp.

The evaporation of sulphite spent liquor results in release of SO_2 from the liquor. If the vent gases are recovered this emission is small.

At mills with calcium base there is normally no SO_2 recovery from the spent liquor burning. Most of the process sulphur is emitted as SO_2. This means that the SO_2 emission may amount to 80 kg SO_2 per tonne of pulp, normal values are 50 kg per tonne of pulp (24,32).

For mills with other bases (magnesium and sodium) most of the sulphur dioxide is retained in the recovery system and used for making new liquor. The emissions can be kept low (less than ~ 20 kg SO_2 per tonne of pulp for magnesium base). Because of the solubility of sodium compounds it is easier to maintain a low emission with sodium base.

11.3.2 Emission of odorous compounds

Sulphite mills will not cause an odour problem similar to sulphate pulp mills. Magnesium and ammonium based sulphite mills will,however, give a characteristic odour in their vicinity. Furfuryl mercaptans and furfuryl methyl sulphides are compounds which cause the typical magnesium base odour (12,31). Pyrimidines are odorous compounds found in the emissions from an ammonium base mill (13).

In some cases hydrogen sulphide emissions have occurred from recovery furnaces due to incomplete combustion. Some of the sodium based processes give H_2S emission from the raw acid preparation.

11.3.3 Emission of nitrogen oxides and hydrocarbons

Very few data exist on the emission of NO_x from sulphite pulp mills. The emission of NO_x from sulphite spent liquor combustion will probably be of the same order as from sulphate recovery furnaces. One exception is probably ammonium base recovery furnaces where the nitrogen content in the liquor increases the NO_x formation. One series of tests indicates NO_x emissions ranging from 200-500 ppm with peak values up to 1000 ppm (32).

No data is known regarding emissions of hydrocarbons.

11.3.4 Dust emissions

In calcium based mills the flue gases from the burning of spent liquor are normally treated in cyclones with a dust removal efficiency of about 75-85 %. The remaining emission is in the range of 10-25 kg per tonne of pulp.

From magnesium and sodium based liquor burning, the dust is recovered by electrostatic precipitators or cyclones and the flue gas subsequently passes through the recovery system. The remaining dust emission is normally less than 1 kg per tonne of pulp.

Minor particulate emissions occur also from the burning of ammonium sulphite spent liquor (e.g. potassium compounds originating from the wood).

11.4 Semi-chemical pulping

Semi-chemical and high yield pulp is produced by a variety of different processes. However, the recovery system and liquor combustion can be classified under the sulphate-soda or sulphite-NSSC headlines. The emissions from these processes are discussed in sections 11.2 and 11.3.

11.5 Bleaching of chemical pulps

Chemical pulp is normally bleached by treatment with chlorine containing chemicals e.g. chlorine, chlorine dioxide and hypochlorite. The major air pollution is caused by chlorine compounds from C, H and D stages and SO_2 from SO_2 treatment.

The supply system for chemicals includes the preparation of chlorine dioxide and hypochlorite and the gasification of chlorine. In the preparation of chlorine dioxide SO_2 is used.

Some emission values are summarized in Table 11.7.

Table 11.7 Emission values from bleaching of chemical pulp

	Cl_2	ClO_2	SO_2
Emission, kg/t	0.1-3	0.1-1	0.1-1

The emission can be reduced by scrubbing with an alkaline liquid for Cl_2 and SO_2 and with chilled water, peroxide or SO_2-water for ClO_2.

11.6 Pulp drying and paper making

In the pulp drying water is removed from the fibres by pressing and heating. The only emission to the air is normally water vapour, except when flash drying is used. Then SO_2 and a certain amount of fibres also are discharged. The amount of SO_2 depends on the sulphur content of the oil used.

In paper making no emission except water vapour is discharged to the atmosphere. However, if volatile additives are used in the process, emission of such compounds may occur.

11.7 Steam generation

11.7.1 Processes

The steam for the processes is generated from burning of spent liquor, waste products and oil, gas or coal. Oil, gas and coal are normally burned in specially designed power boilers, but also together with liquor and waste.

Waste products from the forest industry are often burned in order to reduce a disposal problem and/or to utilize the energy content of the material. Bark, sawdust, sludge and pith are examples of waste products which are burnt.

Mostly the waste is burned in a boiler, often in combination with other fuels such as oil, gas or coal.

Burning of waste can be carried out by pile burning, inclined grate, fluidized bed, spreader stoker or cyclone burning (16). The ash content of waste varies from less than 1 to about 5 %.

11.7.2 Bark and waste burning

The main emission from waste wood boilers is particulate matter. Particle size distribution analysis shows that most of the particles on a mass basis have diameters larger than 50 μm. The particles consist of ash and residue of unburnt material. The amount of unburnt material varies mostly between 10 and 50 percent.

Spreader stoker and cyclone burning have a high carry-over of particulate matter. Normally modern waste boilers are equipped with cyclones for dust collection. A typical efficiency for cyclone equipment is 85 % and typical emissions are 1-5 g per kg of dry waste. New waste boilers are often equipped with electrostatic precipitators. With such equipment a cleaning efficiency of above 95 % is achieved.

No data on the emission of nitrogen oxides from wood waste burning have been found. Usually the high moisture of the fuel will lower the temperature and thus the NO_x emission. The lower temperature will favour the formation of PAH. However, very little is known of the emissions of polyaromatic hydrocarbons. Only two investigations from wood fired boilers are known. One of these shows a total PAH emission of 10-30 g/tonne of dried wood and 0.2-0.7 g of benz-pyrene per tonne of dried wood at far from ideal combustion conditions. The other shows lower values at better combustion conditions, but the same PAH-spectrum is found.

11.7.3 Oil combustion

Particles emitted from oil combustion consist of partly uncombusted oil drops (cenospheres) and particles formed at the combustion. The ash content in oil is low, 0.01-0.1 %.

For this reason the emission of unburnt material at good combustion conditions is low. For particle control, cyclones are commonly used. However, many boilers have no control equipment. The particle size distribution is not very well studied but will, of course, vary with the operating conditions. The ash contains relatively large amounts of vanadium and nickel.

The main emission from oil combustion is sulphur dioxide. The magnitude of the emission depends on the sulphur content of the fuel oil used.

Nitrogen oxides are emitted as a result of oxidation of nitrogen in the fuel and reaction between nitrogen and oxygen in the combustion air. The latter reaction is favoured by high temperatures. The magnitude of the emissions depends on the nitrogen content in the fuel oil, the combustion temperature and other operating conditions. The emission normally varies between 4 and 15 kg NO_x (as NO_2) per tonne of oil.

The formation of polyaromatic hydrocarbons is favoured by low combustion temperature and poor combustion conditions. The formation processes and their dependence on combustion conditions are, however, not very well known.

11.7.4 Gas burning

Gas is a clean fuel. The only emission of importance is that of nitrogen oxides. The emissions depend very much on the combustion conditions, furnace design etc, but may be considerably higher than that from oil combustion. Emissions of up to 70 kg NO_x (as NO_2) per tonne fuel have been reported.

11.7.5 Coal combustion

The ash content of coal is relatively high, usually betweer 5 and 20 %. Of the ash produced in stokers and cyclone-fed boilers about 50 % or less will be found as fly ash, while the rest is retained in the boiler as bottom ash. In pulverized coal-fired boilers about 90 % will be found as fly ash. Electrostatic precipitators or bag filters are used to control the emissions. A high collection efficiency is necessary. With a collection efficiency of 99.5 %, the particle emission is in the order of 400-500 g per tonne of coal used.

The particles contain relatively large amounts of trace elements. Some of these elements, such as cadmium, zinc, lead etc are enriched on the finer particle fraction due to volatilization and resorption processes. Trace elements such as mercury, halogens, sulphur and selenium are emitted mainly or partly in gas phase.

About 90 % of the mercury in coal will be emitted to the atmosphere.

The emission of SO_2 depends on the sulphur content of the coal, usually between 0.5-2 % and is of the same order of magnitude or larger than the sulphur dioxide emission from oil combustion.

The emission of nitrogen oxides from coal combustion is (as from oil combustion) a result of oxidation of nitrogen in the fuel and the reaction between nitrogen and oxygen in the combustion air. The emission depends on the nitrogen content in the fuel and combustion technique and conditions.

Normally it is in the same range as for oil combustion and varies between 5 and 20 kg NO_x (as NO_2) per tonne of coal used.

The emissions of polyaromatic hydrocarbons (PAH) has not been thoroughly studied. Difficulties with sampling and analytical procedures make many reported values unreliable.

Literature reference list Chapter 11

1. Andersson, B., Lövblad, R. and Grennfelt, P.
   Diffuse emissions of odorous sulphur compounds from kraft pulp mills
   Swedish Water and Air Pollution Research Laboratory (1973) IVL B 145, Göteborg

2. Berglund, B., Berglund, U. and Lindvall, T.
   Perceptual interaction of odour from a pulp mill
   Proc. 3rd Int. Clean Air Congress A 40- A 43 (1973)
   VDI Verlag Düsseldorf

3. Bhatia, S.P., de Souza, T.L.C. and Prahacs, S.
   Removal of sulfur compounds from kraft recovery stack gases with alkaline suspension of activated carbon
   Tappi 56(12) p 164-169

4. Borg, A. and Warnqvist, B.
A mathematic model for sulphur emissions from recovery furnaces
Svensk Papperstidning 77(1974), 4 (In Swedish)

5. Borg, A., Nilsson, K., Teder, A. and Warnqvist, B.
The influence of the process conditions on the emission from recovery furnaces
STFI report B 203 (1973)
Swedish Forest Products Research Laboratory, Stockholm (In Swedish)

6. Boström, C-Å and Grennfelt, P.
Carbon monoxide as an environmental control parameter in recovery furnaces
Nordmiljö 80 project report 1:6
Swedish Water and Air Pollution Laboratory, Göteborg (1978) (In Swedish)

7. Chamberlain, R.E., Lofkranz, J.E., Norris, R.G., Smith, A.R. and Wostradowski, R.A.
Eliminate recovery furnace H_2S emissions by controlling CO
Pulp and Paper Canada 79(1978) T44-T48

8. Cooper, H.B.H
Black liquor oxidation with molecular oxygen in a plug flow reactor. Ph. D. Dissertation
University of Washington. Department of Civil Engineering, Seattle, Washington

9. Galteano, S.F. and Leopold, K.M.
A survey of emissions of nitrogen oxides in the pulp mill
Tappi 56(1973) No 3, 74-76

10. Galeano, S.F. and Amsden, C.D.
Oxidation of weak black liquor with molecular oxygen
Tappi 53(1970) 2142-2146

11. Grennfelt, P. and Lindvall, T.
Is hydrogen sulphide a suitable odour index for flue gases from soda recovery furnaces
Svensk Papperstidning 79(1976) 389-393

12. Grennfelt, P.
Investigation of the emission of odorous compounds from a magnefite pulp mill
Swedish Water and Air Pollution Research Laboratory. Report, Göteborg (1976) (In Swedish)

13. Grennfelt, P.
Investigation of the emission of odorous compounds from a semi-chemical ammonium base pulp mill
Swedish Water and Air Pollution Researach Laboratory, Report, Göteborg (1975) (In Swedish)

15. Leonardos, G., Kendall, D. and Barnard, N.
Odour threshold determinations of 53 odorant chemicals
J. Air Poll. Contr. Ass. 19(1969) 91

16. Lindskog, A.
The emission of polyaromatic hydrocarbons
Report to the Swedish Energy Commission (1978)
Swedish Water and Air Pollution Research Laboratory, Göteborg (In Swedish)

17. Lindvall, T.
On sensory evaluation of odorous air pollutant intensities
Nord. Hyg. Tidskr. 1979, Supplementum 2

18. Morrison, J.L.
Collection and combustion of non-condensable digester and evaporator gases
Tappi 52(1969), 2300-2301

19. Mulik, J.D., Stevens, R.K. and Baumgardner, R.
An analytical system designed to measure multiple malodorous compounds related to kraft mill activities
Conf. on methods in air pollution and industrial hygiene studies, Los Angeles, Calif. April 6-8, 1971

20. Murray, J.S.
Tappi Environmental Conference, San Fransisco, May 15, 1973

21. NCASI
Identification and control of total reduced sulphur gaseous emissions from the lime kiln stack
National Council of the Paper Industry for Air and Stream Improvement.
Atmospheric quality improvement technical bulletin no 80 (1975), New York

22. NCASI
Investigation of the feasibility of the use of chemical oxidation systems for the removal of odorous gases from high volume low concentration kraft mill sources
National Council of the Paper Industry for Air and Stream Improvement.
Atmospheric quality improvement technical bulletin no 86 (1978), New York

23. NCASI
A study of particulate size distribution in emissions from controlled sources in the kraft process
National Council of the Paper Industry for Air and Stream Improvement.
Atmospheric quality improvement technical bulletin no 94 (1978), New York

24. OECD
Pollution by the pulp and paper industry, Paris 1973

25. Oloman, C., Murray, F.E. and Risk, J.B.
Selective absorption of hydrogen sulphide from stack gas
Paper Trade Journal 153(1969) 92-94

26. Smith, A.D.
Bark burning
Pulp and Paper Canada 74(1973) 9, 98-102

27. SSVL
The SSVL Environmental Care Project
Technical Summary, 1974
IVL-Consulting Ltd, Stockholm

28. SSVL
Lime kilns
Final report from SSVL project No 11, 1976
IVL-Consulting Ltd, Stockholm (In Swedish)

29. SSVL
Computor control of a recovery furnace
Final report from SSVL project No 4, 1977
IVL-Consulting Ltd, Stockholm (In Swedish)

30. Statens Naturvårdsverk
Air pollution problems of the Swedish forest industry
Swedish Environment Protection Board
Publication 1969:3 (In Swedish)

31. Thorn, P.A., Gardner, H.S and Hrutfiord, B.
Odorous compounds from magnefite pulping
Pulp and Paper Canada 78(1977) 9, T215-T217

32. US Environmental Protection Agency
Environmental pollution control pulp and paper industry
Part I Air EPA 625/7-76-001

33. Verein Deutscher Ingenieure
Wood treatment and wood pre-processing VDI 3462
Düsseldorf (1974) (In German)

34. Wilby, F.V.
Variation in recognition odour threshold of a panel
J. Air Poll. Contr. Ass. 19(1969) 96

12. SURVEYS OF MILL DISCHARGES

12.1 General considerations

Surveys of mill discharges to air and water may have two basic aims:

1) to be used externally e.g. in contacts with authorities

2) to be used to improve the operation of the mill.

Surveys according to 1) may have to be made to obtain data for discussions with authorities on permits for increased production, they may form part of a regular check-up from the authorities etc. Surveys according to 2) may be profitable since high discharge levels of fibres and chemicals represent a significant loss of value.

Basic elements in mill surveys are flow rate measurements and sampling techniques. In this section aspects of these techniques will be discussed as well as the planning and presentation of the surveys. The main emphasis here is on discharges to water, but these aspects of planning are also applicable to measurements of discharges to air.

12.1.1 Planning of surveys

Thorough preparation must be made before surveys are carried out.

1. Literature studies. Establish what can be regarded as normal discharge levels.

2. Flowsheets. Make a survey of the sewer systems of the mill and establish the discharge points. Detailed flowsheets of the processes are also required.

3. Resources. Analyse the actual resources of personnel, equipment and laboratory work needed to carry out the survey and if necessary adjust the measurement to the available resources.

For a survey to be of practical value, it should consist of both flow measurement and sampling for analysis and it is of the utmost importance that this is carried out according to a thoroughly planned measuring programme. The programme must be adjusted to specific needs, and should cover items such as duration of measurement, measuring and sampling points, methods of flow measurement, sampling technique for analysis etc.

The analyses must be chosen according to the actual resources of the laboratory and other requirements. A simple survey will only call for a few parameters and analyses. For more extensive programmes, many samplings and analyses may have to be carried out. The number and type will depend on the type of mill. Analyses should always be carried out according to standard methods.

The extensive survey will be used when surveying a mill or when big discharges cannot be explained by simple measurements. The extensive survey should provide comprehensive information on the processes and discharges from the mill so that appropriate measures can be taken to minimize losses etc. The result of such a survey should also assist in the planning of the simpler routine preventive measures.

Where a mill has not been previously surveyed it is recommended that a start be made with a very simple spot check to obtain approximate discharge levels. This will facilitate the organisation of a more extensive measuring programme.

12.1.2 Presentation and use of the results

The result of the measurements should be presented as soon as possible to the responsible personnel of the different mill departments. If anything is observed, measures to check it can then be taken in good time.

The results of extensive measurements should be reported in detail and evaluated thoroughly as these will form the basis for comprehensive measures.

12.2 Flow rate measurements of liquids

12.2.1 General

There are several methods used for the measurement of flow rates and which one to choose will depend on the type of sewer (channel, pipe etc), the accessibility for installation of measuring equipment and the properties of the effluent, especially corrosiveness and the presence of suspended solids. The methods may be divided into two groups according to the type of system. Open systems include open channels, floor channels etc, and closed systems are mainly pipes. For the relevant calculations of flow in either case, reference is made to the literature.

12.2.2 Flow rate measurements in open systems

There are three main methods of flow measurements in open systems:

1) Methods based on the change of water level

2) Methods based on the determination of the area and the velocity of the liquid

3) Methods based on dilution.

Flow rate measurements based on water level change

The most commonly employed methods in the first group are weirs and venturi or parshall flumes which are placed in a channel etc as a dam or constriction causing changed level and velocity of the water.

The use of a weir is one of the most accurate methods for measuring flow rate. A weir is a dam placed in a channel, flume or pipe outlet and over which the water flows freely (Figure 12.1). The flow is calculated from the geometry of the weir and the water level upstream of it. Weirs are made of steel plate, planed wood or plastic material. The edges of the weir plates in contact with the flowing medium should be sharp and cut so as to form an angle of 45° to the direction of flow.

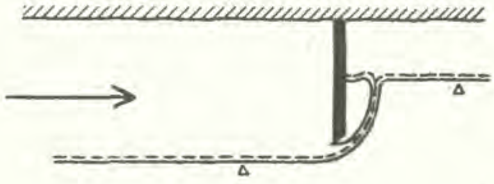


Figure 12.1 Flow over a weir

The choice of a suitable weir is made on the basis of the channel width, the accessible dam height and the range within which the flow is expected to vary. Rectangular weirs without end contractions (Figure 12.2) have their edge extending across the entire width of the channel. This type is used for high flow rates.

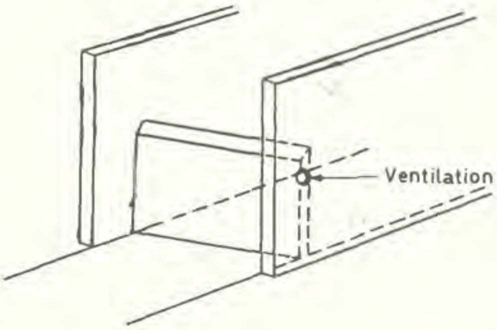


Figure 12.2 Rectangular weir without end contractions

Rectangular weirs with end contractions (Figure 12.3) are weirs being combined with a contraction of the channel. This type is used for moderate flow rates. V-notched weir (Thompson weir) (Figure 12.4) consists of a V-shaped notch in the dam. This type is normally used for varying flow rates.

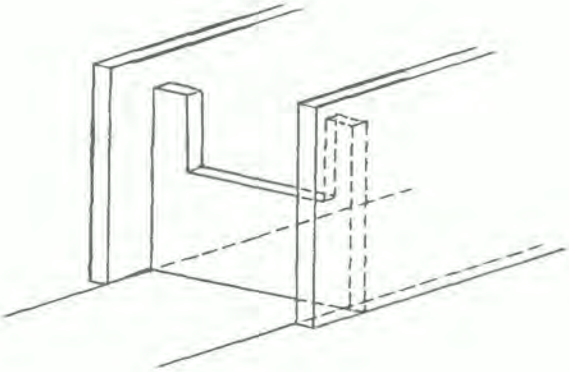


Figure 12.3 Weir with end contraction

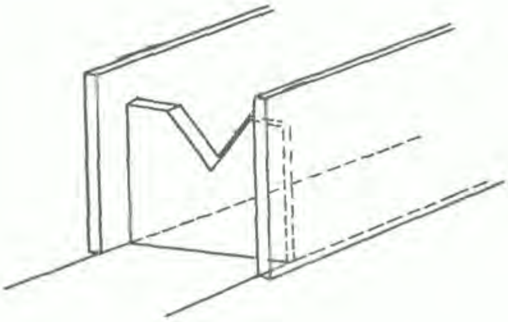


Figure 12.4 Thompson weir

Because of the simple mounting, weirs can be recommended for temporary installation in channels, flumes and pipe outlets. Provided that sedimentation and microbial growth are controlled and that the sensing device is protected against corrosion, weirs are extremely reliable in their operation. See also Appendix 4.

A constriction in a channel causes an increase in the water level. For a suitably shaped constriction, the flow rate can be obtained with sufficient accuracy by measuring the level upstream of the constriction.

A <u>Venturi flume</u> (<u>Figure 12.5</u>) is the open channel equivalent of a Venturi tube. No international standards are available for Venturi flumes.

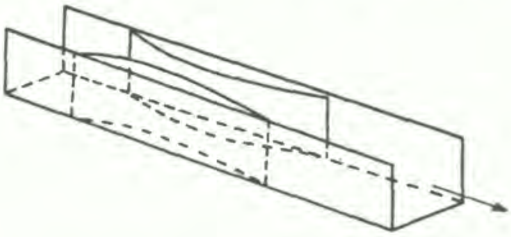


Figure 12.5 Venturi flume

The <u>Parshall flume</u> (<u>Figure 12.6</u>) is a modified Venturi flume of standardized dimensions.

Measuring flumes are usually cast in concrete on the site, but standardized flumes are made of stainless steel or plastic. When designing the flume, attention should be given to any future increases in flow, for instance as a result of a rise in production. The measuring device should be mounted in a separate measuring chamber.

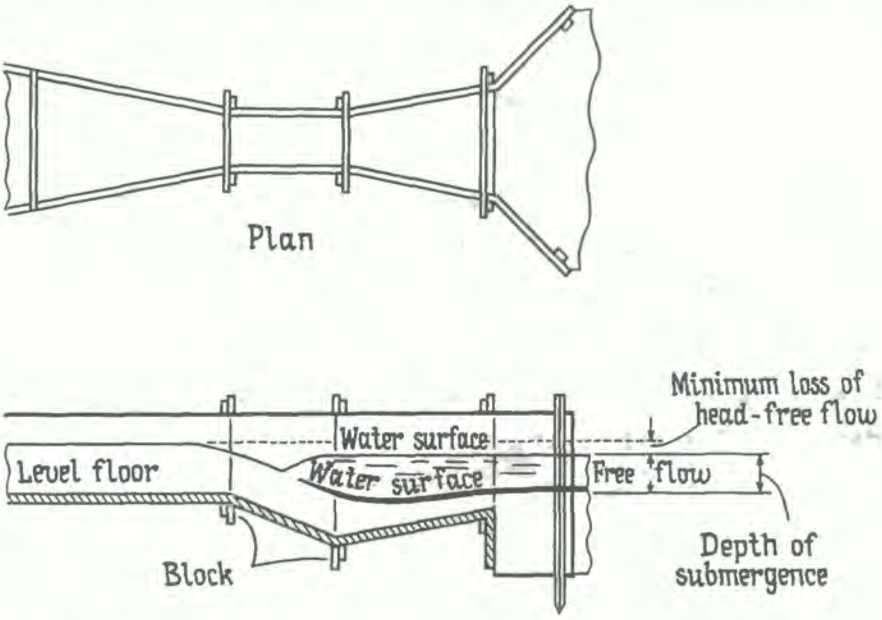


Figure 12.6 Parshall flume

As they are self-cleaning, flumes are reliable in their operation and little maintenance is called for. For waste water systems conducting fibres, flumes are preferred to weirs. For satisfactory operation flumes require a slightly smaller drop in level than weirs, but they are more expensive to install, especially in already existing channels.

To calculate the flow rate, the water level relative to the weir edge or the bottom of the flume must be measured. To achieve this a gauge is placed upstream of the measuring device.

For permanent installations it is preferable to place the gauge in a separate cylindrical measuring chamber close to the channel and communicating with it; when the channel is accessible for inspection the water level can be measured directly. This method is suitable for temporary installations where for some reason automatic recording is not arranged for.

A bubble tube for measuring the water level consists of a narrow vertical tube submerged in the channel. The tube is fed with compressed air via a reduction valve, so that there is a steady air flow from the orifice. The pressure in the tube is measured and, after conversion, transmitted to a recording instrument. The bubble tube can be recommended for temporary installation because it can easily be mounted directly in the channel, or in case of measuring flumes in a separate chamber communicating with the flume.

Measurement of electrical capacity is another method of measuring the water level. This type of gauge is sensitive to microbial growth and deposited debris. In certain cases, it may also record the conductivity of the water and thus give a false signal.

Measurement of level by means of a float should always be carried out in a separate measuring chamber. The level is transmitted by a cable to a meter or, preferably, to a recorder. With a mechanical transmission system a float will be sensitive to corrosion. Provided that there is no interference from growth in the measuring chamber or from corrosion, the float yields reliable and accurate measurements.

The echo sound is also employed for the measurement of the water level. This method has the advantage of no direct contact between the measuring device and the fluid.

Measurement of water level may also be carried out by means of pressure plates. This method is based on the principle that the height of the water column is directly proportional to the hydrostatic pressure caused by the water column.

Flow rate measurement based on velocity

If the flow area is known, the flow rate can be calculated from the velocity of flow, as measured with a velocity indicating instrument. Since the velocity varies over a cross section of the flow, it is necessary to know the approximate velocity distribution across the section. From the velocity distribution the mean velocity is calculated.

For estimating the order of magnitude of a flow it will suffice to measure the velocity at one point, preferably in the centre of the flow where normally the velocity is a maximum. The approximate mean velocity is then calculated.

The velocity can be measured with a pitot tube, which measures the difference between dynamic and static pressure in the system. The pitot tube is connected to a differential manometer.

Pitot tubes are inexpensive and can often be mounted at connection points or pipe joints, but they are very sensitive to deposition of solid particles, which tend to clog the tube.

Flow measurements with current meters may be employed for the accurate determination of the velocity of flow provided that the content of suspended particles is not too high.

Current meters are expensive and their sensitivity is low at both low and high velocities of flow. The accuracy is affected by corrosion and growth.

If a salt solution or an isotope is injected and the time for it to reach a given point or to pass between two given points is measured, the flow can be calculated from the result.

Flow rate measurements based on dilution

A concentrated solution of a substance (inorganic salt, isotope or dye tracer) that can easily be determined in low concentrations, is injected into the medium at a constant, known rate. The concentration of the tracer is then measured far enough downstream for complete mixing to have taken place.

12.2.3 Flow rate measurements in closed systems

Several methods have been developed for flow rate measurements with a good degree of accuracy in closed systems. The methods may be divided into three main categories.

1) Measurement of a pressure difference

2) Determination of the velocity and area of the liquid

3) Methods based on dilution

In addition there are some miscellaneous methods.

Pressure difference methods

The most common types of measuring devices used for continuous flow measurement are orifice plates, flow nozzles, and venturi tubes. Constriction of a pipe results in an increase in the speed of the flowing medium and a corresponding drop in its static pressure. The pressure difference is measured manometrically.

A standardized orifice plate consists of a thin plate with a central, sharp edged hole which is mounted perpendicularly to the direction of flow (Figure 12.7). The flow rate is highest and the contraction greatest just below the orifice.

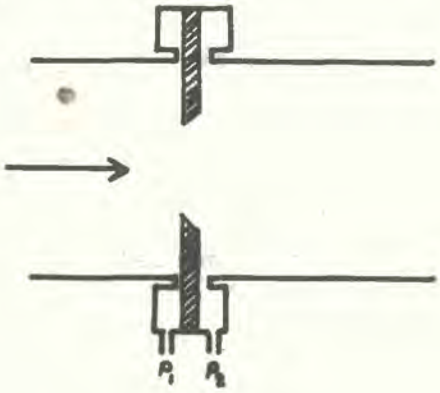


Figure 12.7 Orifice plate

Orifice plates give a high level of accuracy but at the expense of a large pressure drop, which increases the pumping costs. They do not function satisfactorily in the presence of suspended particles and are therefore unsuitable for permanent installation in systems with fibres. The fact that orifice plates can sometimes be easily inserted at pipe flange connections in existing systems renders them suitable for temporary installations.

The Venturi meter(Figure 12.8) is inserted in a line of pipe and consists of three parts:

1) the inlet cone in which the diameter of the pipe is gradually reduced

2) the throat or constricted section

3) the outlet cone (diffuser), in which the diameter increases gradually to that of the pipe in which the meter is inserted.

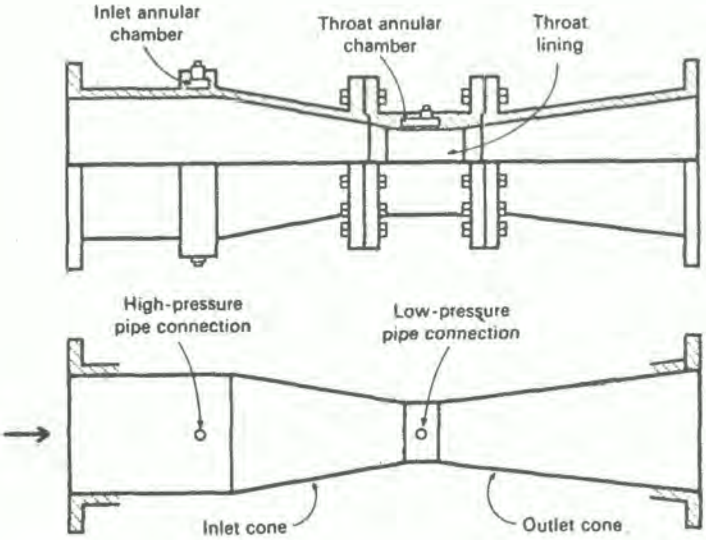


Figure 12.8 Typical Venturi meter

The inlet cone can be conical or of the nozzle type. No standards are available for conical Venturi tubes. Venturi meters are selfcleaning and well suited for permanent installations in waste water systems. Because of its small dimensions and the availability of relevant standards, the Venturi nozzle is preferable to the conical Venturi tube. Like orifice plates, the pressure pipes of the Venturi meter also tend to be clogged by suspended particles. The Venturi nozzle is preferable to the conical Venturi tube. Like orifice plates, the pressure pipes of the Venturi meter also tend to become clogged by suspended particles.

Nozzle flow meters make use of the Venturi principle but employ a nozzle inserted in the pipe instead of the Venturi tube. Flow nozzles are as sensitive as orifice plates to deposition of solids and are thus unsuitable for permanent installation in waste water systems. For temporary installation they offer no advantages over orifice plates.

Direct measurement of velocity

A rotameter consists of a transparent vertical conical tube, increasing in diameter upwards, in the direction from which the flow occurs. The tube is constricted by a rotating body, which is forced upwards in the tube as the flow increases, thus increasing the discharge area.

The liquid in a pipe can be measured by a magnetic flow meter which consist of a straight pipe section fitted with standard flanges. An electric coil around the tube imposes a magnetic field which changes with the velocity of the liquid. Magnetic flow meters are resistant to corrosion and unaffected by the presence of suspended particles.

The supersonic meter is based on the measurement of the velocity according to the Doppler principle, i.e. the frequency of the sound wave is changed by reflexion on air bubbles or particles in the fluid.

There are electrical methods used for measuring the quantity of water flowing in a stream such as conductivity cells and anemometers. Although some of these methods have been used they are not ideally suited for making flow measurements in waste water from pulp and paper mills because the floating and suspended materials commonly found in the waste water interfere with their operation.

Methods based on dilution

The dilution methods used (chemical, radioactive and dye tracers) can be applied to flow rate measurements also in closed systems.

Miscellaneous measuring methods for flow rate

When, as is often the case, the flow cannot be measured directly, usually because the system is inaccessible for the installation of measuring equipment, other methods must be resorted to.

If the system includes vats or containers where the level can be measured the flow can be calculated from the rate at which the level rises on closing the outlet valve.

Where feasible the effluent may be diverted to a suitable container and the time required to fill can be measured.

If the concentration of the liquor before and after e.g. an evaporator and either the inlet or the outlet flow can be measured by any suitable method, the other flow can be calculated. Foaming introduces an error.

If no other method is possible the flow of pulp suspensions can be calculated from the pulp concentration before and after a thickener or filter unit and the rate of pulp output. The largest source of error is the determination of the inlet pulp concentration. If water is added to the system between the sampling points, the flows must be measured.

12.3 Liquid sampling methods

12.3.1 General considerations

The choice of a sampling device must take into account the characteristics of the system. Waste water systems of pulp and paper mills call for a corrosion-resistant sampler, where operation is not influenced by microbial growth or by the presence of suspended materials. Furthermore, it should be easy to assemble and to dismantle for inspection and maintenance.

Representative samples are sometimes difficult to obtain from automatic sampling of waste water containing oil, dense suspended particles or other not easily dispersed constituents.

12.3.2 Sampling in flumes and channels

A very simple way to collect samples from waste water is manual sampling. It is essential, however, that the manual sampling is performed with accuracy.

A scoop-type sampler consists of an endless chain or a wheel to which one or more sampling scoops are attached.

The lower part of the chain is submerged in the channel. By adjusting the speed of the wheel or chain the sampling interval may be changed. Growth and sedimentation in the scoops may occur. Scoop-type samplers do not function very satisfactorily.

In pneumatic samplers the sample is collected in a chamber which is then closed. The sample is forced through a tube to a collection vessel by means of compressed air. The opening and closing of the chamber is operated by a magnetic valve or, more reliably, by compressed air.

Pneumatic samplers which stay open between the sampling periods are not to be recommended because of the risk of disturbing microbial growth and accumulation of suspended material in the sampling chamber.

A vacuum sampler is another alternative for collecting samples.

12.3.3 Sampling from pipes

There is at present no commercially available pneumatic sampler suitable for sampling from a tube under pressure.

It is, however, possible to sample from a diverted flow. When the disposal of the excess part of the diverted flow, say to a flume, is inconvenient, sampling may be effected through a valve mounted on the pipe and opening at intervals. Sealing difficulties can arise through a build-up of suspended material on the pressure side. The volume removed will vary with the pressure in the pipe. In pipes containing pulp it is necessary that the sampling pipe is extended to a distance (30 % of the pipe diameter) inside the transport pipe in order to avoid wall effects.

12.3.4 Installation and operation of samplers

If the medium carries much suspended material it may be difficult to obtain representative smaples. Care should be taken to mount the sampler at a point where the sampled water is well mixed. This applies especially to sewer systems which receive waste waters of widely varying densities. The sampler should be mounted so as to be easily accessible for inspection and maintenance. For sampling water containing much sand the distance of the sampler from the bottom of the channel should be such as to prevent the sand particles from entering the sampler. Sampling in corrosive waters calls for careful selection of the material from which the sampler is made.

For permanent installation in waste water systems where the variations in flow or concentration are moderate, cumulative samples may be collected for each shift or for each 24 h. In sewers from production units, in which there may be sudden discharges of strongly polluting material, cumulative samples should be taken during each shift.

The volume removed in the sampling process should not be so large that the total volume collected in a sampling period is difficult to handle. On the other hand, the sample should be large enough for the loss during transport to the collecting vessel to be negligible. The volume of the sample will also be dependent on the type of analysis to be carried out.

Sampling at constant intervals can be recommended only where the flow and the composition of the effluent varies only moderately as may be the case for e.g. main outlets. Sampling at intervals depending on the flow rate should otherwise be carried out.

12.4 Flow rate measurements of gases

Flow rate measurements of gases can be performed by a Prandtl pressure head (pitot tube) and a micro manometer (pressure gauge) (Figure 12.9 A) provided that the flow rate is not too low and the water content of the gas is not too high. At high water contents in the gas a so called S pitot tube (Figure 12.9 B) can be used.. The measurements have to be performed at a number of points in the measuring area which is in the cross direction of the gas flow. In some cases it is difficult or impossible to carry out the measurements with satisfactory accuracy and it is then more reliable to calculate the flow from available process data.

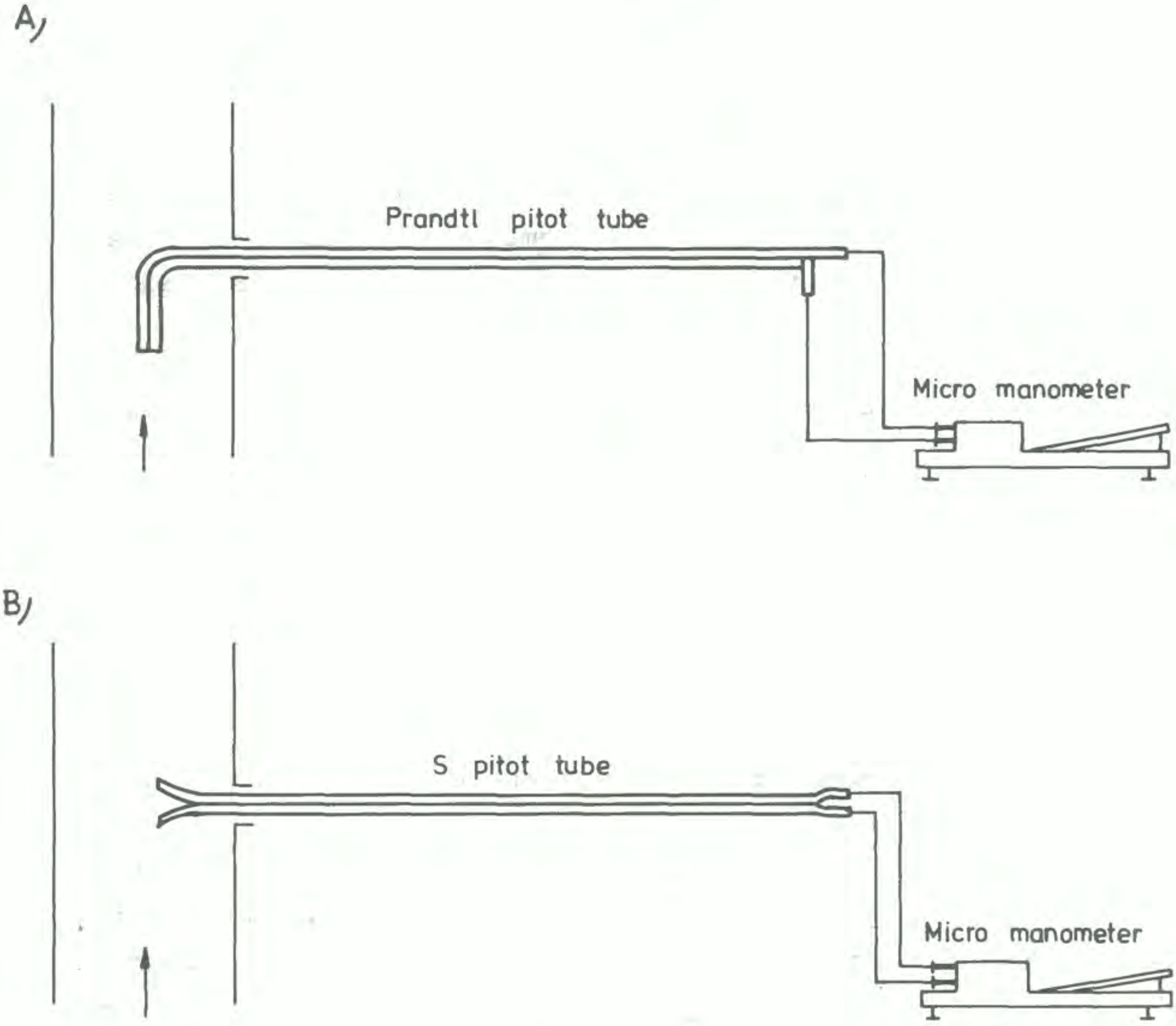


Figure 12.9 Methods for flow rate measurements A) with Prandtl pitot tube B) with S pitot tube

12.5 Gas sampling methods

12.5.1 General considerations

The concentration of the components in the gas is normally related to dry (water free) gas. It is, therefore, often necessary to determine the water content of the gas. This can be done according to the following methods:

1) Condensation of the gas by means of a cooling system

2) By means of a wet and dry thermometer

3) By calculation from the partial pressure at the actual temperature provided that the gas is saturated.

Compared to sampling in water, where often one sample of water is sufficent to determine several parameters, the sampling methods in gaseous emissions have to be chosen according to the specific gaseous component desired. Two main principles can here be distinguished:

1) Sampling of dust and other solid particles or aerosols.

2) Sampling of gaseous components.

12.5.2 Dust and solid particles

It is essential that the sampling be carried out isokinetically, i.e. the velocity of the gas in the sampling device has to correspond to that in the duct.

To obtain representative samples, the sampling in the gas has to be performed at several points in a cross section of the duct. Preferably, the duct should be in a vertical position. The choice of sampling points is based on the type and size of the duct and on the length of the straights before and after the sampling section.

Some guidelines for the choice of sampling positions are as follows:

- Circular duct; the length of the straight section before the sampling point should be at least 5 times the diameter of the duct, and the length of the straight section after the sampling section should not be less than the diameter of the duct.

- Rectangular duct; the length of the straight section should here exceed 2.5 (L+W) before the sampling point and 0.5 (L+W) after it. (L and W are the lengths of the sides of the inner cross section area of the duct.)

The sampling of particulate matter in gases can be carried out in two different ways depending on the moisture content and the composition of the gas:

1. In cases with low moisture content in the gas, e.g. at oil fired boilers, a suitable filter for removing the dust is used. The amount of the dust collected on the filter can then be determined gravimetrically. Figure 12.10 A shows a schematic sketch of the equipment needed for this sampling method.

2. For the determination of the dust content of particulate matter in gases where the main part of the dust exists in the form of inorganic salts, it is often advantageous to use a wet chemical method.

   The dust is dissolved in a liquid after which the analysis of the desired component can be performed. The wet chemical method generally is applied with gases from sulphate recovery boilers and lime kilns. Figure 12.10 B shows the principle.

12.5.3 Gaseous components

For collecting samples of gaseous components, the sampling procedure should in principle comprise an adequate number of sampling points so as to obtain a representative value of the average concentration of the component. If this concentration can be considered as constant in the sampling section it is not necessary to collect samples at more than one point.

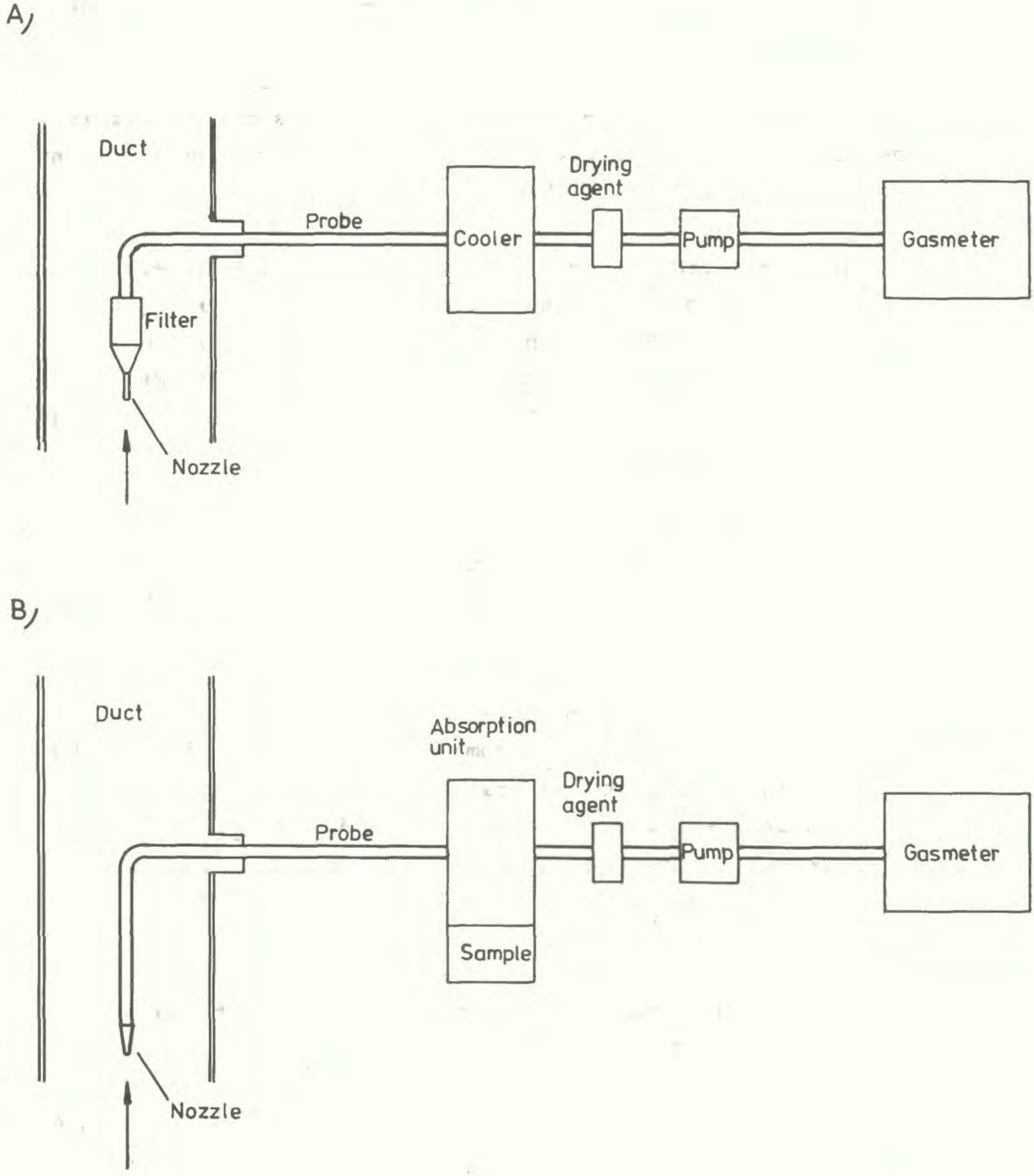


Figure 12.10 Methods for dust sampling
a) Filter method
b) wet chemical method

Ioskinetic sampling procedure is not necessary when collecting gaseous samples unless there is a risk of forming drops (e.g. drops of sulfuric acid) or aerosols or when the gas compound is unevenly distributed over the sampling section.

In order to obtain reliable values of the concentration of the gaseous components, it is essential that losses due to the reactivity of the different components be noticed and allowed for.

Basically, there are three different methods that can be utilized, viz:

1) Absorption method. The gas is bubbled through a liquid solution. After sampling, its content of a given compound is determined by a suitable analysing method. For some compounds, for example H_2S, a solid absorber is used instead of a liquid solution (Figure 12.11 A).

2) Collection method. The gas is collected in a special plastic bag which is transported to the laboratory for analysis (Figure 12.11 B).

3) Continuous method. This method comprises the instant determination of a gaseous component by means of an instrument (Figure 12.11 C).

Of these methods Nos 1) and 2) are preferred for short time sampling while the third method is useful for investigations over both a short and long period.

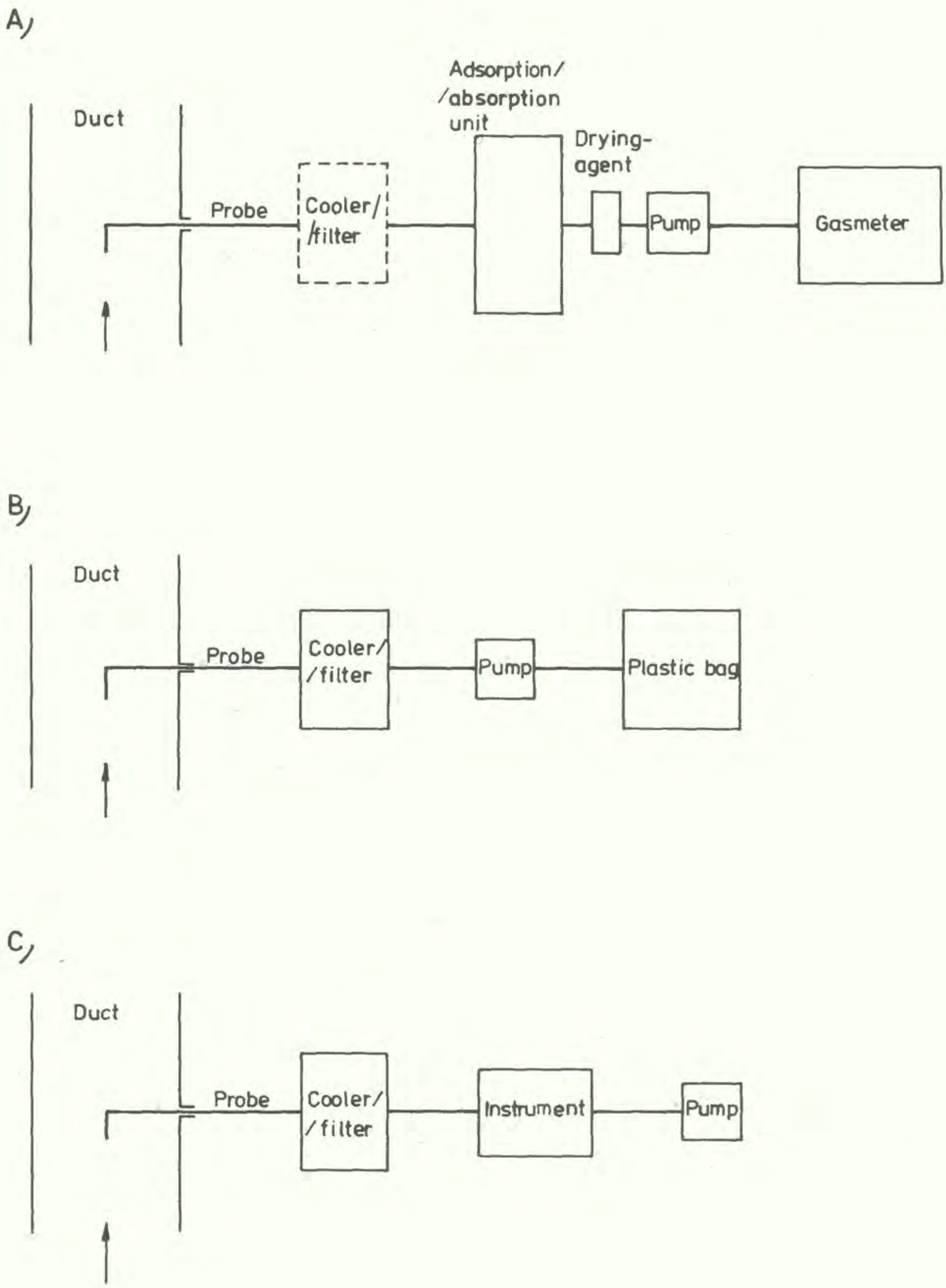


Figure 12.11 Sampling methods for gaseous components
a) Absorption method
b) Gas collection method
c) Instrumental method

As mentioned earlier, the method of sampling chosen depends on the actual gaseous compound to be determined. The sampling method recommended for the most frequent gaseous compounds emitted from pulp and paper mills is given below.

Compound	Method
H_2S	1,2 or 3
SO_2	"
Org. S	2 or 3
Cl_2/ClO_2	1
No_x	(1),2 or 3
CO_2/O_2	2 or 3

Literature reference list Chapter 12

1. Metcalf & Eddy, Inc.
   Waste water engineering, 1973

2. IVL Internal information

3. Bouveng, H.O.
   A guide to flow measurement and sampling with special reference to pulp and paper mill waste water systems
   Pure and Applied Chemistry, vol 19(1969), 271-290

13. ENVIRONMENTAL LAWS AND REGULATIONS RELATING TO THE PULP AND PAPER INDUSTRY

13.1 General

The major forms of environmental regulations are standard setting, incentives, disincentives, permits and enforcement. The major, if not main, purpose of environmental standards and regulations is to protect people, whether in their work places or in the environment at large, from hazards to health or safety that could result from products and substances consumed or released directly or indirectly into the environment. Measures to protect the environment by limiting or preventing the release of pollutants fall into a number of categories. They may be statutory or voluntary, regulations or guidelines, enforced by different agencies, sometimes set up by central governments, sometimes national and sometimes local. Of the different types of standards, three are of particular relevance to industry:

a) Product standards;
b) Emission/effluent standards;
c) Environmental quality standards.

Different countries have used different approaches as well as standards based on the availability and interpretation of scientific area, subjective judgemental value and socio-economic considerations. For ambient quality, some countries set national quality levels, while others do not. For discharge standards, again in some countries, national discharge standards and regulations have been promulgated, while in others the concept of best practical means has been implemented. In the latter approach each hazard is treated separately, pollutant by pollutant, and disposal situation by disposal situation, but using the general knowledge gained through similar cases elsewhere.

(Tables 13.1, 13.2 and 13.3 are examples of standards and regulations adopted by some countries, and serve only as illustrations. They should not be construed as UNEP recommendations.)

TABLE 13.1

SUMMARY OF LEGISLATION RELEVANT TO AIR POLLUTION BY THE PULP AND PAPER INDUSTRY IN SOME COUNTRIES

REGULATIONS APPLYING TO EMISSIONS AND TO AMBIENT AIR CONCENTRATION OF POLLUTANTS.
(m^3 given in emission standards are m^3 dry gas at 0^oC, 1 atm)

COUNTRY	MAIN ASPECTS OF LEGISLATION	PROPOSED STANDARDS		
CANADA	Federal standards for emissions from pulp and paper industry will be stated during 1977.			
	Regional standards exist. Standards given are from Quebec.	Emission from wood - (and woodwaste) fired boilers		
		Particles		
		New Plants: 225 mg/m^3 (corrected to 12% CO_2 concentration)		
		Existing Plants: 450 mg/m^3 (corrected to 12 % CO_2 concentration)		
	Standards to be in practice before 1980 (Quebec).	Emissions from sulphate pulp mills		
		Particles	New Plants	Existing Plants
		Recovery boiler kg/tonne $pulp_{90}$	2	3,5
		mg/m^3	225	450
		Lime kiln g/tonne $pulp_{90}$	500	500
		mg/m^3	380	380
		Smelt dissolver g/tonne $pulp_{90}$	150	250
		Total reduced sulphur		
		Recovery boiler (g/tonne $pulp_{90}$	85	340
		(ppm)	5	20
		Lime kiln (ppm)	20	20
		Stripper evaporation digester (ppm)	5	5
		pulp washing	5	
		black liquor oxidation	5	
		Emissions from sulphite mills		
		SO_2	kg/tonne	
		New plant with recovery of chemicals	10	
		New plant without recovery of chemicals	2.5	
		Existing plant	10	
		Particles		
		All plants with recovery of chemicals	2.5	

<table>
<tr><th>COUNTRY</th><th>MAIN ASPECTS OF LEGISLATION</th><th>PROPOSED STANDARDS</th></tr>
<tr><td>CANADA</td><td>Standards applying to ambient air concentrations.
The standards are divided into desirable acceptable and tolerable levels.
Max. acceptable level is meant to protect humans, nature and climate from negative effects.
Max. desirable level is the long term goal for air quality. At this level no detectable negative biological effects are found.
Max tolerable level indicates danger and requires immediate action.
Standards for H_2S, total reduced sulphur compounds, polyaromatic hydrocarbons etc are being considered.</td><td>Ambient air concentrations (mg/m^3)
<table>
<tr><th></th><th>mean</th><th>max desir.</th><th>max accept.</th><th>proposed max tolerable</th></tr>
<tr><td>SO_2</td><td>1-h</td><td>0.450</td><td>0.900</td><td></td></tr>
<tr><td></td><td>24-h</td><td>0.150</td><td>0.300</td><td></td></tr>
<tr><td></td><td>1 year</td><td>0.030</td><td>0.060</td><td></td></tr>
<tr><td>Particles</td><td>24-h</td><td>-</td><td>0.120</td><td></td></tr>
<tr><td>(geometric mean)</td><td>1 year</td><td>0.060</td><td>0.070</td><td></td></tr>
<tr><td>NO_2</td><td>1-h</td><td>0.06</td><td>0.400</td><td>1.000</td></tr>
<tr><td></td><td>24-h</td><td>-</td><td>0.200</td><td>0.300</td></tr>
<tr><td></td><td>1 year</td><td>-</td><td>0.100</td><td>-</td></tr>
</table></td></tr>
<tr><td>JAPAN</td><td>Standards given are National standards.
Regionally, harder regulations exist.</td><td>Emissions from boilers or waste burning
SO_2
$q = K \cdot 10^{-3} (He)^2$ must not be exceeded
q = emission of SO_2 (m^3/h)
He = effective stack height (m)
K = constant varying between 3.5 - 17.5

For new plants (in central regions) K is 1.17 - 2.34

Emissions from oil-fired boilers
Particles
<table>
<tr><th>max. stack gas flow m^3/h</th><th>standard (mg/m^3) normally</th><th>extreme</th></tr>
<tr><td>40 000</td><td>300</td><td>200</td></tr>
<tr><td>200 000</td><td>200</td><td>50</td></tr>
<tr><td>>200 000</td><td>100</td><td>50</td></tr>
</table>
Emissions from continously operating refuse fired boilers
Particles
<table>
<tr><td>40 000</td><td>700</td><td>200</td></tr>
<tr><td>>40 000</td><td>200</td><td>100</td></tr>
</table>
Emissions from plants producing chemical products
Hazardous substances a.o. Cl_2
30 mg/m^3

Emission from boilers fired with liquid fuels
NO_x
Conc. of NO_x in the stack gas (ppm)
<table>
<tr><th>New plants</th><th>Existing plants</th></tr>
<tr><td>180</td><td>230</td></tr>
</table>
Min. excess of oxygen in stack gas 4%. NO_x conc. is corrected for real excess of O_2.

Emission of odorous compounds
$q = 0.108 (He)^2 \cdot Cm$
q = emission of odorous compound (m^3/h)
He = effective stack height (m)
C_m = ambient air standard (ppm) (see below)</td></tr>
</table>

COUNTRY	MAIN ASPECTS OF LEGISLATION	PROPOSED STANDARDS		
UAPAN	Standards applying to ambient air concentrations.	Ambient air concentrations		
			mean	(ppm)
		SO_2	1-h	≤ 0.1
			24-h	≤ 0.04
		Odorous compounds		
			C_m max conc. at plant area boundary line (ppm)	
		MM	0.002 - 0.01	
		H_2S	0.02 - 0.2	
	When ambient air concentrations reaches high levels (limits are given) extreme actions must be undertaken.	DMS	0.01 - 0.2	
		DMDS	0.009 - 0.1	
SOVIET UNION	The emissions to the atmosphere are regulated through hygienic standards not to be exceeded in residential areas. Around emitting plants there is a restricted area (with a diameter of 1 km) where no residential houses are allowed.	Ambient air concentrations (mg/m^3)		
			max conc.	24-hour mean
		SO_2	0.5	0.05
		NO_2	0.085	0.085
		dust (untoxic)	0.5	0.15
		soot	0.15	0.05
		Cl_2	0.1	0.03
		H_2S	0.008	0.008
		MM	9.10^{-6}	-
		DMS	0.08	-
		DMDS	0.7	-
SWEDEN	If nothing else is stated the emission standards apply to the total emission during one month divided by the amount of product manufactured or by the volume of gas emitted. They also apply to all operating conditions throughout the plant. Emission monitoring is regulated.	Emissions from kraft pulp mills SO_2 Recovery boiler: 5 kg/tonne Particles Recovery boiler New plants: 250 mg/m^{3}N Plants existing before 1969-07-01: 500 mg/m^{3}N Lime kiln New and existing plants: 250 mg/m^{3}N Odorous compounds Cooking, spent liquor evaporation, stripping of condensate Tall oil boiling plant At new plants measures are to be taken such that odour outside the plant area is eliminated H_2S Recovery boiler 10 mg/m^{3}N must not be exceeded more than 5 % of the operation time at new plants and 10 % at existing plants. Lime kiln: 50 mg/m^{3}N Emissions from sulphite mills SO_2 New plants: 10 kg SO_2/tonne pulp produced x) Existing plants: 20 kg SO_2/tonne pulp produced x) x) SO_2 from oil-firing is excluded. Particles Burning of liquor: New plants: 250 mg/m^{3}N Existing plants: 500 mg/m^{3}N		

COUNTRY MAIN ASPECTS OF LEGISLATION PROPOSED STANDARDS

SWEDEN cont.

Emissions from wood and bark burning

Paricles

New and existing plants 500 mg/m^3 (corrected to an excess of air equivalent to 10% CO_2 concentration), but less than 30 kg/h.

Regulations applying to ambient air concentration are based on air quality criteria and are meant to protect human health. Regulations are divided into standards valid under present conditions (max. conc.) and standards acting as a goal for long time planning.

Ambient air concentrations (mg/m^3)

SO_2	max. conc.	planning goal
Wintermean (Oct.-March)	0.100	0.060
24-h mean$^{x)}$	0.300	0.200
1-h mean$^{xx)}$	0.750	-

Soot	max. conc.
Wintermean (Oct.-March)	0.040
24-h mean$^{x)}$	0.120

x) must not be exceeded more than 2% of time October to March.

xx) must not be exceeded more than 1% of the time during a 30-day period

Total suspended particles

No standards exist. The American standard (see below) are recommended.

USA

Regulations of emissions are valid from Sept.-76. They are based on best economically available technique. In specially polluted areas, stricter regulations are valid.

Emissions from sulphate pulp mills

Particles	mg/m^3	kg/tonne
Recovery boiler	100	1.0
Oil-fired lime kiln	300	0.535
Gas-fired lime kiln	150	0.028
Smelt dissolver	120	0.15

Total reduced sulphur	ppm	g/tonne
Recovery boiler	5	75
Oil-fired lime kiln	5	12.5
Gas-fired lime kiln	5	12.5
Smelt dissolver	5	12.5
Pulp washing	5	5
Black liquor oxid.	5	5
Stripper	5	5
Digester	5	5
Evaporation	5	5

Emission from sulphite mills

Federal authorities have recommended that the emission of SO_2 should not exceed 10 kg/ton pulp.

Regulations of emissions of SO_2, NO_x and particles and stackgas opacity exist for fossil-fuelled plants for steam generation with the effect >73MW.

Primary standards are based on air quality criteria and are meant to protect human health.

Secondary standards are based on air quality criteria to protect humans from well-known or expected negative effects associated with the presence of air pollutants.

Ambient air concentrations (mg/m^3)

		prim.	sec.
SO_2	3-h	-	1.300
	24-h	0.365	-
	1 year	0.080	-
Particles	24-h	0.260	0.150
	1-year	0.075	0.060
NO_2	1 year	0.100	

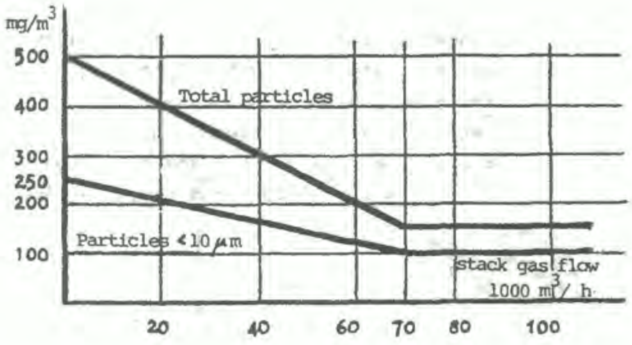
COUNTRY	MAIN ASPECTS OF LEGISLATION	PROPOSED STANDARDS
GERMANY Fed.Rep.	The regulations apply to emissions from new plants or plants which considerably change their site, nature or operation of plant. The standards are valid for normal operation of control equipment.	Particles The particle concentration must not exceed the values given in the figure below. 
	Regulations for emission monitoring exist. Regulations regarding emissions of SO_2 and particles from fossil-fuelled stationary sources exist.	Inorganic gaseous chlorine compounds The concentration of inorganic gaseous chlorine compounds must be ≤30 mg Cl_2/m^3 (0°C, 1 atm, dry gas) when the emitted amount of Cl_2 is >3 kg/h. Reduced sulphur compounds The concentration of dimethyl sulphide and the concentration of mercaptans must not exceed 20 mg/m^3 (0°C, 1 atm, dry gas) when the emitted amount is >0.1 kg/h
	Regulations for ambient air concentrations are divided into long time (IW1) and short time (IW2) mean values.	Ambient air concentrations (mg/m^3) Particles (harmless dust) Particles <10 um IW1 0.10 IW2 0.20 Particles >10 um IW1 0.20 IW2 0.40 Cl_2 IW1 0.10 IW2 0.30 SO_2 IW1 0.140 IW2 0.40 H_2S IW1 0.0050 IW2 0.010 NO_2 IW1 0.10 IW2 0.30 NO IW1 0.20 IW2 0.60 Deposition of particles (harmless dust) IW1 0.35 g/m^2, 24 h IW2 0.60 g/m^2, 24 h

Table I3.2

UNITED STATES

Interim guidelines for effluents. Best Practical Control Technology Currently Available (BPCTCA)

Type of production	BOD$_5$, kg/t a)			SS, kg/t a)		
	24 h	month	year	24 h	month	year
Sulphate, unbleached	5,6	2,8	-	12,0	6,0	-
Sulphate, dissolving	23,6	12,3	6,9	37,3	20,1	11,1
Sulphate, bleached, unintegr	15,5	8,1	4,5	30,4	16,4	9,0
Sulphate, bleached, integr (board,ttissue)	13,7	7,1	4,0	24,0	12,9	7,1
Sulphate, bleached, integr (fine paper)	10,6	5,5	3,1	22,2	11,9	6,6
Sulphite, paper grade (difuser washed)	31,8	16,6	9,3	44,0	23,7	13,0
Sulphite, dissolving	41,4	21,5	12,1	70,7	38,1	20,9
NSSC, Na-base	8,7	4,4	-	11,0	5,5	-
NSSC, NH_3-base	8,0	4,0	-	10,0	5,0	-
Unbl Sulphate - NSSC, cross recovery	8,0	4,0	-	12,5	6,3	-
Chemimechanical	13,5	7,1	4,0	19,8	10,7	5,9
Thermomechanical	10,6	5,6	3,1	15,6	8,4	4,6
Mechanical, integr (newsprint)	7,5	3,9	2,2	12,8	6,9	3,8
Mechanical,iintegr (fine paper)	6,9	3,6	2,0	11,8	6,3	3,5
Soda	13,7	7,1	4,0	24,5	13,2	7,3
Deinking	18,1	9,4	5,3	36,2	18,8	10,6
Waste paper based board	3,0	1,5	-	5,0	2,5	-
Fine paper, unintegr	8,2	4,3	2,4	11,0	5,9	3,3
Tissue unintegr	11,4	6,3	3,5	10,3	5,0	2,9
Tissue, waste paper based (not deink)	13,7	7,1	4,0	17,1	9,2	5,1
Sulphite paper grade (filter washed)	26,7	13,9	7,8	44,0	23,7	13,0
Wet debarking	0,7-3,2	0,4-1,7	0,2-1,0	0,2-7,5	0,1-4,0	0,1-2,2
Log and chip washing	0,1-0,4	0,1-0,2	0,1	0,2-2,6	0,1-1,4	0,1-0,8

a) "t" denotes average yearly production per 24 h
"24 h" denotes maximum per 24 h
"month" denotes maximum monthly average 24 h values
"year" denotes maximum yearly average 24 h values

24 hour and monthly values must be fullfilled by all unites. The average yearly value is applied only to mills with biological cleaning followed by waste water basins with regulated discharges.

TABLE 13.3

Summary of legislation relevant to water pollution by the pulp and paper industry

COUNTRY	MAIN ASPECTS OF LEGISLATION	PROPOSED STANDARDS		
CANADA	Regulations are based on best practicable technology. Federal regulations are minimum standards for national application. Provincial requirements are equivalent or more restrictive. Regulations apply to new mills at startup. Compliance dates for existing mills negotiated individually. Discharge limits are set for SS, BOD_5 and toxic discharges.		Existing mills	New mills
			kg BOD_5/ADMT	
		- BOD requirements:		
		Sulphite 55 % or less yield	116	77
		55-65 % yield	77	52
		more than 65 % yield	68	34
		Sulphite bleaching	16	16
		Kraft pulping	29	16
		Kraft bleaching	12	12
		NSSC	36	27
		- SS allowances calculated using component process categories method.		
		- BOD values for kraft mills are those permitted prior to toxicity reduction systems. Such systems usually result in BOD reduction of 75 to 90 %.		
FINLAND	Discharge of waste submitted to permit only, up-to-now. The administration has set up some general goals for discharges.	Based on water quality, health, etc. Goals for SS and BOD (in kg/tonne):		
			BOD_7	SS
		- Sulphite	57	10
		unbleached	40	10
		bleached	60	10
		dissolving	100	10
		- Sulphate	19	5
		unintegr unbleached	10	5
		unintegr bleached	20	5
		integr unbleached	15	5
		integr bleached	25	5
		- Semichemical	20	5
		- Newsprint, paper and board	9	5
		- Fibre board	20	5
		Eutrophication taken into consideration.		

SS = Suspended solids

BOD = Biological oxygen demand

<table>
<tr><th>COUNTRY</th><th>MAIN ASPECTS OF LEGISLATION</th><th>PROPOSED STANDARDS</th></tr>
<tr>
<td>FRANCE</td>
<td>- By the act of 16th December 1964 polluters may be required to meet a charge for pollution discharged and receive help for financing antipollution investments.
- Minimum discharge standards are fixed in uniform manner. Can be locally stricter.
- An agreement signed with the Minister of the Environment covers a programme of pollution reduction for chemical and semi-chemical pulp mills.</td>
<td>
<table>
<tr><th>Maximum discharge allowed (kg/tonne)</th><th>Primary treatment</th><th colspan="2">Secondary treatment*</th></tr>
<tr><td></td><td>SS</td><td>BOD₅</td><td>SS</td></tr>
<tr><td>Kraft unbleached</td><td>2,5</td><td>5</td><td>10</td></tr>
<tr><td>bleached</td><td>10</td><td>9</td><td>20</td></tr>
<tr><td>Sulphite:</td><td></td><td></td><td></td></tr>
<tr><td>with liquor recovery</td><td>12,5</td><td>45</td><td>50</td></tr>
<tr><td>without liquor recovery</td><td>15</td><td>80</td><td>85</td></tr>
<tr><td>Semi-chemical:</td><td></td><td></td><td></td></tr>
<tr><td>more than 150 tons/day</td><td>5</td><td>8</td><td>5</td></tr>
<tr><td>less than 150 tons/day</td><td>13</td><td>60</td><td>60</td></tr>
</table>
*Biological treatment by aerated lagoon
</td>
</tr>
<tr>
<td>GERMANY Fed.Rep.</td>
<td>A new law has been accepted which means that the discharges will be regulated by charges.
Each mill and community is given a calculated value (so called reference value) for its discharges. The value shall be expressed in "damage units" for different discharges, which are shown in the table.
The cost charged to the polluter is founded on the reference value. Each mill and community is also given a maximum value based on experience for its discharges. This may not be higher than twice the reference value.
The charge will be 12 DM per damage unit in 1981. It will increase each year and reach 40 DM per damage unit in 1986.</td>
<td>
<table>
<tr><th>Substance</th><th colspan="2">Number of damage units/unit of measure</th></tr>
<tr><td></td><td>Damage unit</td><td>Unit of measure</td></tr>
<tr><td>Sedimentable material with an organic content > 10 %</td><td>1</td><td>m³/year or ton/year</td></tr>
<tr><td>Sedimentable material with an organic content < 10 %</td><td>0,1</td><td>m³/year or ton/year</td></tr>
<tr><td>Oxygen demanding material, COD</td><td>2,2</td><td>100 kg/year</td></tr>
<tr><td>Mercury and its compounds</td><td>5</td><td>100 g Hg/year</td></tr>
<tr><td>Cadmium and its compounds</td><td>1</td><td>100 g Cd/year</td></tr>
<tr><td>Toxicity 2) towards fish</td><td>$0,3 \cdot G_F$ 1)</td><td>1000 m³ waste water/year</td></tr>
</table>
1) G_F is the dilution factor at which waste water is no longer lethal to fish. If $G_F \leq 2$, 0 damage units is given.
2) Type of toxicity and test procedure is not specified.
</td>
</tr>
</table>

* SS = Suspended solids

BOD = Biological oxygen demand

<table>
<tr><th>COUNTRY</th><th>MAIN ASPECTS OF LEGISLATION</th><th>PROPOSED STANDARDS</th></tr>
<tr><td>JAPAN</td><td>Under the 1971 act all mills have to observe minimum standards all around the country (applied in successive steps between 1972 and 1976). Can be locally stricter.</td><td>Standards for 1976 deadline (expressed in ppm)
<table>
<tr><th></th><th>BOD</th><th>COD</th><th>SS</th></tr>
<tr><td>Semi-chemical</td><td>300</td><td>600</td><td>150</td></tr>
<tr><td>Sulphite (paper grades)</td><td>300</td><td>600</td><td>150</td></tr>
<tr><td>Sulphite (dissolving grades)</td><td>600</td><td>800</td><td>150</td></tr>
<tr><td>Sulphate (dissolving grades)</td><td>120</td><td>300</td><td>150</td></tr>
<tr><td>Sulphate (paper grades)</td><td>120</td><td>200</td><td>150</td></tr>
<tr><td>Paper and board</td><td>120</td><td>120</td><td>150</td></tr>
<tr><td>Bleached straw</td><td>300</td><td>600</td><td>250</td></tr>
</table></td></tr>
<tr><td>SWEDEN</td><td>Protection of the environment by using the best practicable means.

The regulations are based on the Environment Protection Act of 1969. "Specific values" for pollution load are not discharge standards as they can be lowered when necessary.

The specified values for BOD$_7$ are generally achievable by internal mill measures while those of SS usually require a sedimentation basin.</td><td>No precise standards; each case examined separately on the basis of "specified values" (in kg/tonne) as follows:
<table>
<tr><th>BOD$_7$ from:</th><th>A</th><th>B</th><th>C</th><th>D</th><th>E</th></tr>
<tr><td>- Barking</td><td>1-3</td><td>1-3</td><td>1-3</td><td>1</td><td>1</td></tr>
<tr><td>- Washing</td><td>-</td><td>5</td><td>3-7*</td><td>10-15</td><td>-</td></tr>
<tr><td>- Grinding</td><td>15</td><td>-</td><td>-</td><td>-</td><td>10-20</td></tr>
<tr><td>- Condensate</td><td>-</td><td>2-3</td><td>4-10</td><td>5</td><td>-</td></tr>
<tr><td>- Bleaching</td><td>2-15</td><td>8-9</td><td>10-13</td><td>2-15</td><td>-</td></tr>
<tr><td>- Accidental discharges</td><td>-</td><td>1-3</td><td>-</td><td>-</td><td>-</td></tr>
<tr><td>SS</td><td>2-5</td><td>2-5</td><td>2-5</td><td>2-5</td><td>2-5</td></tr>
</table>
A = Mechanical pulp B = Sulphate
C = Sulphite D = Semi-chemical
E = Fibre building board *Corresponds to 97-98 % recovery</td></tr>
<tr><td>UNITED KINGDOM</td><td>Legislation is based on maintenance of water quality as required by each use.

Amendments to legislation are under consideration.</td><td>Standards related to SS - BOD - toxicity - colour - pH - ammonia, etc.

No national standards. Values generally used are:

BOD$_5$ = 20 mg/l max
SS = 30 mg/l max

Can be more stringent.</td></tr>
<tr><td>UNITED STATES</td><td>The "Federal Water Pollution Control Act Amendments of 1972" declares that it is the national goal that the discharge of pollutants into the receiving water bodies be eliminated by 1985.

In addition to this goal, specific interim requirements are stipulated. They relate to the application of the "Best Practical Control Technology Currently Available" (BPCTCA) (the goal for July 1,1977), the "Best Available Technology Economically Achievable" (BATEA) (the goal for 1983) and "New Source Performance Standards" (NSPS) (present goal for new mills).</td><td>See table 13.1 and 13.2</td></tr>
</table>

Pollution control, especially in the industrialized countries is expected to focus increasingly on the control of hazardous materials such as organochlorines, in pulp and paper mill effluents. There is a trend for more stringent regulations for such pollutants. In Sweden the law requires the industry to use the "best known technology that is economically feasible" to control pollution. In the USA the Environmental Protection Agency has already announced limits for 1983 which mean a 50 to 75% reduction as compared with present regulations. In Finland the government has announced an ambitious plan for 1980 which sets up new goals to reduce discharges.

With regard to air emission, there is a continuing trend towards reduced discharges of SO_2, dust and odorous compounds. A major environmental concern is probably SO_2. This causes acid precipitation resulting in acidified lakes and changed soil conditions with possible adverse effects also on forest and agricultural production.

In a longer term perspective the control of hydrocarbon and nitrogen oxide emissions will probably be emphasized as well.

<u>Literature reference list Chapter 13</u>

1. OECD, 1973, Pollution by the pulp and paper industry, Paris 1973.

2. Strömberg, B.
   SSVL 24, DP 2, of international environmental legislations (in Swedish)

14. ABBREVIATIONS

a Cl = active chlorine
ADMT = air dry metric ton
atm = atmosphere (unit for pressure)

bar = pressure unit (1 bar = 10^5Pa = 1.013 atm)
BDMT = bone dry metric ton
BOD_5 = biochemical oxygen demand during 5 days
BOD_7 = biochemical oxygen demand during 7 days
BOD_{20} = biochemical oxygen demand during 20 days

C = chlorine (Cl_2)
°C = degree Celsius (centrigrade)
cal = calorie
CC = chlorine compounds
CD = cross direction
C/D = chlorine/chlorine dioxide bleaching stage
COD = chemical oxygen demand
CSF = canadian standard freeness

d = day, 1 day = 24 hours
D = chlorine dioxide (ClO_2) or dilution
D_2 = second chlorine dioxide stage
DR = displacement ratio

E = alkali (NaOH) stage
(e) = over-pressure

F = filter
°F = degree Farenheit
FW = fresh water

g = gauge. Sometimes used to indicate pressure relative to atmospheric pressure
Gcal = gigacalorie 1 Gcal = 10^3 Mcal

h = hour
H = hypochlorite (NaClO or CaCl(ClO)) or Hi-Heat
H_{20} = dosification 20 kg hypochlorite/tonne of pulp
h.p. = high pressure

J = joule (unit for energy)

°K = degree Kelvin (unit för temperature)
kcal = kilocalorie/1 kcal = 4.187 x 10^3 J
kg = kilogram
kWh = kilowatthour, 1 kWh = 3.6 x 10^6 J

l = liter
lbs = pounds (=453.6 grams)
l.p. = low pressure

m = meter
M = chlorine monoxide
Mcal = Megacalorie, 1 Mcal = 10^3 kcal
MD = machine direction
MS = mild steel (black iron)
m^3N = cubic meters at standardized conditions

N = Newton (unit for force) 1 N = 0.1020 kp

O = Oxygen (O_2)

P = Press or Peroxide (H_2O_2)
Pa = Pascal (unit for pressure) 1 Pa = 10^{-5} bar
ppb = part per billion
ppm = part per million
Pt = platium. Comparison standard at colour determination
psi = pound-force per square inch, 1 psi = 0.068 atm

R = radial washer (continuous diffuser)

SCAN = scandinavian standard procedure
sec = second
SF = screening plant filter
°SR = degree chopper Riegler (unit för pulp freeness)
SS = suspended solids

t_{90} = tonne 90 % dry pulp
T = wash press
TOC = total organic carbon
TOD = total oxygen demand
ton = short ton (2000 lbs)
tonne = metric ton (1000 kg)
TRS = totally reduced sulphur

US D = United States dollar currency

V = volt (1 V = 1 W/A)

W = watt (unit for heat power) 1 W = 1 J/s

y = year
Yr = year

304 = AISI 304 (lower stainless steel quality)
316 = AISI 316 (higher stainless steel quality)

APPENDIX 1

1977-78 World pulp, paper and board industry at a glance

From the 1979 Annual Review Issue (July 25) of Pulp and Paper International.

	Population (1,000)	Number of mills		Capacity (1,000 m tons)		Paper & Board Consumption Per capita (kg)	Total (1,000 m tons)		Production P&B (1,000 m tons)		Pulp	
Europe		P&B	Pulp	P&B	Pulp		1977	1978	1977	1978	1977	1978
Albania	2,620	5	5	na	na	5.0	13	13	10	10	9	9
Austria	7,502	41	29	1,720	1,311	95	741	736	1,424	1,435	1,080	1,103
Belgium	9,840	25	4	930	420	134	1,203	1,316	743	797	372	335
Bulgaria	8,814	17	na	380	220	53	416	469	340	364	229	255
Czechoslovakia	15,100	49	26	1,200	860	76	1,151	1,142	1,167	1,154	857	859
Denmark	5,075	7	5	152	290	167	772	848	205	239	100	100
Finland	4,753	46	54	6,300	8,125	130	869	898	4,620	5,130	5,247	6,078
France	53,300	188	39	5,400	2,160	111	5,598	5,892	4,722	4,963	1,935	1,920
German Dem. Rep.	16,758	28	21	1,350	700	80	1,323	1,334	1,174	1,206	607	658
Germany, Fed. Rep.	61,310	212	40	8,759	1,991	143	8,435	8,748	6,604	6,850	1,862	1,843
Greece	9,200	16	4	300	65	45	393	415	205	255	27	52
Hungary	10,686	10	6	na	na	60	590	651	424	444	114	127
Iceland	222	—	—	—	—	83	15	18	—	—	—	—
Ireland	3,200	2	1	95	25	81	236	258	74	79	19	20
Italy	56,697	520	77	5,769	1,562	81	4,219	4,590	4,288	4,615	1,190	1,203
Malta	325	—	—	—	—	33	11	11	—	—	—	—
Netherlands	13,936	43	8	2,038	227	148	1,986	2,047	1,637	1,671	177	160
Norway	4,050	32	35	1,740	1,985	136	497	482	1,186	1,240	1,432	1,384
Poland	35,000	54	32	1,453	870	42	1,519	1,479	1,347	1,318	825	821
Portugal	9,774	108	8	550	804	39	393	378	450	456	649	616
Romania	21,650	20	11	750	800	32	680	670	700	700	720	720
Spain	36,300	253	43	2,400	1,500	61	2,304	2,205	2,160	2,175	1,275	1,225
Sweden	8,280	65	79	7,025	11,545	203	1,496	1,522	5,060	5,702	7,656	8,557
Switzerland	6,298	31	7	985	310	151	907	951	777	815	230	241
USSR	260,000	153	60	10,000	10,000	37	8,674	8,900	9,090	9,400	9,100	9,500
United Kingdom	55,822	153	7	4,780	373	130	6,913	7,262	4,083	4,152	306	326
Yugoslavia	21,775	31	24	1,100	750	46	948	993	921	973	652	677
Total Europe	**738,287**	**2,109**	**625**	**65,176**	**46,713**	**73**	**52,302**	**54,224**	**53,411**	**56,139**	**36,620**	**38,733**
North America												
Canada	23,485	145	110	15,096	22,844	221	4,218	4,522	12,441	13,592	18,168	19,646
United States	218,500	690	280	63,507	50,348	274	60,445	63,616	56,267	57,809	45,364	45,791
Total North America	**241,985**	**835**	**390**	**78,603**	**73,192**	**270**	**64,663**	**68,138**	**68,708**	**71,401**	**63,532**	**65,437**
Asia/Australasia												
Afghanistan	20,000	—	—	—	—	0.1	2	2	—	—	—	—
Australia	14,248	17	15	1,450	750	125	1,736	1,791	1,229	1,232	609	635
Bangladesh	85,000	6	7	142	148	0.6	44	50	52	63	52	60
Bhutan	1,200	—	—	—	—	1.5	2	2	—	—	—	—
Burma	30,000	1	1	na	na	1.0	38	38	13	13	13	13
Cambodia (Khmer Rep.)	8,000	na	na	na	na	0.1	0.5	0.5	na	na	na	na
China (People's Rep.)	1,000,000	na	na	na	na	8.1	7,140	8,125	7,140	8,125	4,800	5,200
Cyprus	640	—	—	—	—	59	27	38	—	—	—	—
Fiji	601	—	—	—	—	10	0.6	0.6	—	—	—	—
Hong Kong	4,700	—	—	—	—	119	422	561	—	—	—	—
India	600,000	118	76	1,264	na	2.2	1,217	1,288	1,067	1,108	820	840
Indonesia	135,000	26	8	284	148	3.5	359	476	82	200	16	20
Iran	37,000	17	2	na	na	12	436	395	145	145	69	69
Iraq	12,000	2	2	144	90	8.4	104	103	30	43	11	19
Israel	3,734	5	—	145	—	80	287	297	132	129	—	—
Japan	115,174	649	73	21,164	12,502	142	15,239	16,299	15,702	16,499	9,437	9,391
Jordan	2,217	1	1	10	7	15	32	33	7	7	3	4
Korea, People's Rep.	17,000	5	2	na	na	7.0	120	120	100	100	35	40
Korea, Rep. of	37,019	106	5	1,660	210	37	1,082	1,357	1,170	1,436	130	96
Kuwait	1,100	—	—	—	—	40	44	45	—	—	—	—
Laos	3,500	—	—	—	—	0.5	1	2	—	—	—	—
Lebanon	3,000	3	—	na	—	10	30	30	10	10	—	—
Malaysia	10,300	8	—	na	—	30	213	310	21	38	—	—
Nepal	13,700	na	—	na	—	0.7	9	10	1	1	—	—
New Zealand	3,130	5	6	na	na	123	434	378	650	612	1,095	1,009
Oman	850	—	—	—	—	2.8	2	3	—	—	—	—
Pakistan	75,630	17	17	110	95	1.6	116	124	74	79	47	50
Papua New Guinea	3,000	—	—	—	—	0.1	0.3	0.3	—	—	—	—
Philippines	45,100	22	8	420	241	11	407	421	353	338	159	163
Saudi Arabia	7,200	—	—	—	—	15	100	110	—	—	—	—
Singapore	2,310	2	—	na	—	80	133	184	6	6	—	—
Sri Lanka	15,000	1	1	na	na	1.3	31	34	19	20	5.0	5.0
Syria	8,000	3	—	na	—	3.4	27	27	na	na	—	—
Taiwan	17,136	170	154	1,500	1,000	80	1,033	1,138	966	1,159	167	214
Thailand	45,222	25	4	320	51	8.5	346	384	221	256	33	44
Turkey	43,200	13	15	597	373	13	541	533	459	459	288	302
United Arab Emirates	350	—	—	na	—	13	4	5	60	60	15	15
Vietnam	35,000	30	na	—	na	2.4	80	85	—	—	—	—
Western Samoa	160	—	—	—	—	6.5	1	1	—	—	—	—
Yemen Arab Rep.	7,000	—	—	—	—	0.6	4	4	—	—	—	—
Yemen, Dem. Rep.	1,900	—	—	—	—	2.2	4	4	—	—	—	—
Total Asia/Australasia	**2,465,321**	**1,252**	**397**	**29,210**	**15,615**	**14**	**31,848**	**34,808**	**29,709**	**32,138**	**17,804**	**18,189**

	Population (1,000)	Number of mills		Capacity (1,000 m tons)		Paper & Board Consumption Per capita (kg)	Paper & Board Consumption Total (1,000 m tons)		Production P&B (1,000 m tons)		Production Pulp (1,000 m tons)	
		P&B	Pulp	P&B	Pulp		1977	1978	1977	1978	1977	1978
Latin America												
Argentina	26,000	71	22	950	543	31	904	777	778	653	329	325
Bahamas	205	—	—	—	—	34	6	7	—	—	—	—
Belize	150	—	—	—	—	14	2	2	—	—	—	—
Bolivia	6,000	2	—	na	—	4.0	22	24	1	1	—	—
Brazil	116,000	152	47	3,000	2,500	23	2,472	2,717	2,234	2,534	1,617	2,004
Chile	10,960	18	6	335	733	20	230	224	300	301	604	665
Colombia	24,000	25	7	152	384	14	340	386	281	307	178	192
Costa Rica	2,100	1	—	8	—	57	129	119	8	9	—	—
Cuba	9,500	9	3	100	50	20	187	194	70	74	38	40
Dominican Rep.	5,000	2	—	45	—	8.0	36	40	30	35	—	—
Ecuador	7,300	6	2	30	20	9.2	65	67	25	27	15	16
El Salvador	4,500	2	—	30	—	15	45	52	10	12	—	—
Guatemala	6,500	4	—	35	—	15	94	96	28	33	—	—
Guyana	800	—	—	—	—	12	10	10	—	—	—	—
Haiti	4,800	—	—	—	—	0.8	4	4	—	—	—	—
Honduras	3,400	—	—	—	—	16	55	55	—	—	—	—
Jamaica	2,100	2	—	5	—	26	53	55	4	4	—	—
Mexico	65,800	55	32	1,800	1,000	26	1,751	1,758	1,454	1,597	672	706
Nicaragua	2,500	—	—	—	—	14	36	35	—	—	—	—
Panama	1,850	3	—	15	—	42	70	77	10	12	—	—
Paraguay	2,800	2	—	na	—	3.0	8	8	na	na	—	—
Peru	16,819	13	4	300	250	12	202	187	151	161	108	109
Puerto Rico	3,400	1	1	60	40	65	225	230	50	50	30	30
Surinam	380	—	—	—	—	29	10	11	—	—	—	—
Trinidad & Tobago	1,200	—	—	—	—	29	39	35	—	—	—	—
Uruguay	2,900	12	5	55	15	22	52	63	45	51	16	19
Venezuela	13,122	14	3	683	160	54	662	714	464	493	46	44
Total Latin America	**340,086**	**394**	**132**	**7,603**	**5,695**	**23**	**7,709**	**7,947**	**5,942**	**6,354**	**3,653**	**4,150**
Africa												
Algeria	18,250	5	3	na	na	10	154	158	72	68	21	26
Angola	6,750	3	1	na	na	4.0	25	27	10	12	na	na
Arab Rep. of Egypt	39,630	12	5	160	55	6.9	261	279	118	124	32	46
Benin	3,300	—	—	—	—	1.0	4.0	4.0	—	—	—	—
Botswana	700	—	—	—	—	0.7	0.5	0.5	—	—	—	—
Burundi	3,960	—	—	—	—	0.5	0.2	0.2	—	—	—	—
Cameroon	6,670	—	—	—	—	3.0	20	20	—	—	—	—
Central African Empire	3,400	—	—	—	—	0.1	0.5	0.5	—	—	—	—
Chad	4,200	—	—	—	—	0.4	2.0	2.0	—	—	—	—
Congo Rep.	1,430	—	—	—	—	1.4	2.0	2.0	—	—	—	—
Ethiopia	29,500	2	—	na	—	0.5	14	15	7	8	—	—
Gabon	540	—	—	—	—	3.7	2.0	2.0	—	—	—	—
Gambia	496	—	—	—	—	0.3	0.2	0.2	—	—	—	—
Ghana	10,600	—	—	—	—	3.8	40	40	—	—	—	—
Guinea	4,645	—	—	—	—	0.9	4.0	4.0	—	—	—	—
Ivory Coast	6,500	—	—	—	—	3.4	35	35	—	—	—	—
Kenya	14,000	5	5	55	45	3.2	43	45	56	58	na	na
Lesotho	1,200	—	—	—	—	0.2	0.2	0.2	—	—	—	—
Liberia	1,800	—	—	—	—	1.4	3	3	—	—	—	—
Libya	2,650	2	—	na	—	7.0	18	18	6	6	—	—
Malagasy	9,000	1	2	12	6	1.3	12	13	12	13	5	5
Malawi	5,300	—	—	—	—	2.3	10	12	—	—	—	—
Mali	6,300	—	—	—	—	0.2	1	1	—	—	—	—
Mauritania	1,400	—	—	—	—	0.5	1	1	—	—	—	—
Mauritius	900	—	—	—	—	3.3	3	3	—	—	—	—
Morocco	18,600	5	1	100	100	7.5	144	139	76	84	33	66
Mozambique	9,700	2	—	na	—	3.0	30	27	5	5	—	—
Niger	4,900	—	—	—	—	0.3	1	1	—	—	—	—
Nigeria	80,000	1	—	na	na	1.7	143	154	13	14	—	—
Rwanda	4,400	—	—	—	—	0.2	1	1	—	—	—	—
Senegal	5,200	—	—	—	—	4.2	20	22	—	—	—	—
Sierra Leone	3,300	—	—	—	—	1.5	5	5	—	—	—	—
Somalia	3,400	—	—	—	—	0.6	2	2	—	—	—	—
South Africa	27,394	15	11	1,150	1,000	38	1,025	1,002	991	1,027	882	879
Sudan	11,550	1	—	na	—	1.0	14	14	3	3	—	—
Swaziland	495	—	1	na	na	2.0	1.0	1.0	—	—	152	153
Tanzania	15,950	—	—	—	—	1.3	20	20	—	—	—	—
Togo	2,340	—	—	—	—	0.9	2.0	2.0	—	—	—	—
Tunisia	6,000	1	1	24	24	5.5	22	33	19	22	20	21
Uganda	12,300	1	—	na	—	1.0	11	6.0	1	1	—	—
Upper Volta	6,300	—	—	—	—	0.8	0.5	0.5	—	—	—	—
Zaire	26,500	1	—	na	—	1.0	11	12	2	2	—	—
Zambia	4,800	—	—	—	—	4.2	20	20	—	—	—	—
Zimbabwe Rhodesia	6,750	2	2	na	na	na	na	na	25	25	14	14
Total Africa	**433,000**	**59**	**32**	**1,501**	**1,230**	**5.0**	**2,128**	**2,146**	**1,416**	**1,472**	**1,159**	**1,210**
WORLD TOTAL	**4,218,679**	**4,649**	**1,576**	**182,093**	**142,445**	**40**	**158,650**	**167,267**	**159,186**	**167,508**	**122,818**	**127,774**

Some of the figures included above are estimates,

APPENDIX 2

NON-WOOD FIBRE PULPING CAPACITY 1)

— In 1000 tons —

Country	Straw		Bagasse		Bamboo		Other		Total	
	1978	1982	1978	1982	1978	1982	1978	1982	1978	1982
Algeria	24	27	-	-	-	-	85	85	109	112
Egypt	44	44	20	48	-	-	-	-	64	92
South Africa	-	-	108	108	-	-	-	-	108	108
Tunisia	-	-	-	-	-	-	26	26	26	26
Cuba	-	-	61	69	-	-	-	-	61	69
Mexico	19	19	287	472	-	-	18	18	324	509
Argentina	-	-	-	-	-	-	1	1	1	1
Brazil	-	-	139	149	49	83	36	102	224	334
Colombia	-	-	89	94	-	-	1	1	90	95
Ecuador	-	-	15	15	-	-	-	-	15	15
Peru	-	-	200	235	-	-	-	-	200	235
Uruguay	6	6	-	-	-	-	-	-	6	6
Venezuela	-	-	110	120	-	-	3	3	113	123
Bangladesh	-	-	20	20	30	30	21	27	71	77
Burma	-	-	-	-	12	12	-	-	12	12
China	?	?	415	425	-	-	4675	5305	5090	5730
India	85	85	15	30	685	772	150	150	925	1037
Indonesia	41	45	6	35	14	14	-	-	61	94
Iran	-	-	60	60	-	-	-	-	60	60
Iraq	-	-	5	12	-	-	22	55	27	67
Japan	-	-	-	-	-	-	4	4	4	4
Jordan	4	4	-	-	-	-	8	8	12	12
Kampuchea,Demo.	5	5	-	-	1	1	-	-	6	6
Korea,Rep.of	18	18	-	-	-	-	10	10	28	28
Pakistan	-	-	30	30	-	-	-	-	30	30
Philippines	-	-	27	27	-	-	23	23	50	50
Sri Lanka	17	17	-	-	-	-	1	1	18	18
Syria	-	27	-	-	-	-	-	-	-	76
Thailand	-	-	-	-	6	6	70	70	76	76
Turkey	33	58	-	-	-	-	2	4	35	62
Viet Nam,Soc.Rep	10	10	-	-	-	22	-	-	10	32
Albania	5	5	-	-	-	-	-	-	5	5
Bulgaria	28	28	-	-	-	-	-	-	28	28
Czechoslovakia	-	-	-	-	-	-	25	25	25	25
Denmark	45	45	-	-	-	-	28	28	73	73

1) Source: FAO Pulp and Paper Capacity Survey 1977-1982

—— In 1000 tons ——

Country	Straw		Bagasse		Bamboo		Other		Total	
	1978	1982	1978	1982	1978	1982	1978	1982	1978	1982
German Dem.Rep	-	-	-	-	-	-	53	69	53	69
Greece	32	32	-	-	-	-	-	-	32	32
Hungary	22	22	-	-	-	-	-	-	22	22
Italy	428	444	-	-	-	-	-	-	428	444
Netherlands	45	45	-	-	-	-	2	2	47	47
Poland	21	5	-	-	-	-	2	2	23	7
Portugal	12	12	-	-	-	-	30	30	42	42
Romania	58	58	-	-	-	-	44	44	102	102
Spain	240	240	-	-	-	-	40	40	280	280
United Kingdom	-	-	-	-	-	-	25	25	25	25
Yugoslavia	8	8	-	-	-	-	-	-	8	8
Australia	-	-	-	-	-	-	5	5	5	5
TOTAL	1250	1309	1662	2004	797	940	5410	6163	9119	10422

APPENDIX 3

PARAMETERS TO CHARACTERIZE DISCHARGES AND EMISSIONS

The most common parameters to characterize discharges to water have been assembled in Table 1 which also gives reference to standardized methods for their determination.

Table 1

TESTING PROCEDURES FOR PULP AND PAPER EFFLUENT MONITORING

Parameter	Std.Methods method	page	ASTM method	page	EPA storet No	page	DEV method	Rodier page	SCAN No	INSTA c) No	ISO d) status
pH	424	460	D 1293-78	191				40			
Conductivity	205	71	D 1125-77	116			C8	49			
COD_{Mn}							H4(1)	132	W1:66	SS028111E	WG
COD_{Cr}	508	550	D 1252-78	557	00335 a) 00340 a)	20 21	H4(2)	489		SS028142E	DIS
BOD	507	543			00310 a)	11	H5	479	W5:71	SS028143E	DIS
TOD			D 3250-77	562							DP
TOC	505	532	D 2579-78	541							DP
Colour	204 A	64			00080	36	CI (DIN 38404)				WG
Suspended solids	208 D (0.45 µm)	94	D 1888-67	164	00530 (0.45 µm)	268	H2	31 (glassfiber)	W6:71	SS028112E	
Phosphorus			D 515-72 (surface water only)	455			D11A(1a) b) D11B(2) b)		W8:73		DIS
Nitrogen(Kjeldahl)	421	437	D 3570-78	629	000625	175	H11	123			DIS
Sample preservation					Table 1 & 2						DP
Sampling			D 1192-70(77) D 3370-76	49 68							DIS
Flow measurements			D 1941-67(75) D 2458-69(75) D 2034-68(75)	80 91 97							

a) summary with reference to Std. Methods

b) { 1a: surface water
   2: waste water

c) available in English

d) { WG = Working Group
   DP = Draft Proposal
   DIS = Draft International Standard

Std. Methods	Standard Methods for the Examination of Water Wastewater (APHA-AWWA-WPCF) 14th ed. 1975
ASTM	American Society for Testing Materials: 1978 Annual Book of ASTM Standards, Part 31
EPA	US Environmental Protection Agency: Methods for chemical analysis of water and wastes EPA-625/6-74-003, Washington DC 1974
DEV	Deutsche Einheitsverfahren zur Wasseruntersuchung, Verlag Chemie, GmbH, Weinheim
Rodier	L'analyse de l'eau, 5 ième éd. Dunod 1975
SCAN	Scandinavian Pulp, Paper and Board Testing Committee Secretariat: PB 5604, S-114 86 Stockholm
INSTA	Interscandinavian Standardization, INSTA C 12 Secretariat: Norsk Standardiseringsforbund, Haakon VII's gate 2 N-Oslo 1
ISO	International Organization for Standardisation ISO/TC 147 Secretariat: American National Standards Institute, 1430 Broadway, New York, N Y 10018

APPENDIX 4

FLOW RATE MEASUREMENTS WITH WEIRS

1. General

Flow measurement with weirs is one of the most commonly employed methods of measuring flows in open systems, e.g. channels, flumes or pipe outlets. This is due to the fact that the use of weirs gives a comparatively accurate reading of water flows.

2. Principle

A weir is a dam or constriction placed in the channel etc, over which the water falls freely (Figure 1). The weir causes changed level and velocity of the water and the flow can be calculated from the geometry of the weir and the water upstream of it. In order to obtain an accurate flow measurement it is essential that there is an ambient air pressure under the overfall. See the ventilation hole in Figure 2.

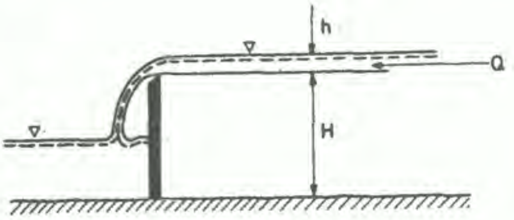


Figure 1. Flow over a weir.

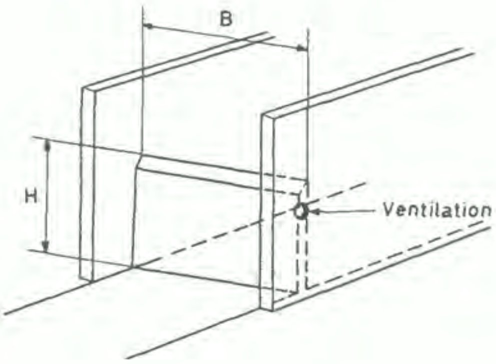


Figure 2. Weir without end-contractions with external ventilation hole.

3. Construction and installation

Weirs are made of steel plate, planed wood or plastic. The edge of the weir plates in contact with the flowing medium should be sharp and cut so as to form an angle of 45° to the direction of flow.

Weirs are mounted accurately at right angles to the direction of flow and with the upper edge horizontal (spirit-level). The mounting can be carried out by one of the following methods, care being taken to ensure tight seals against the walls and the bed of the channel.

1. The weir is mounted between rails or bolts. For temporary installations it will often suffice to bolt strong strips to each channel wall (the water pressure will normally be large enough to keep the weir in position), and to seal with machine felt, foam rubber or foam plastic. The sealing material is chosen with regard to the properties of the flowing medium.

2. The weir, which shall be made slightly wider than the channel, is forced into position, care being taken to avoid damaging the edges.

3. The weir can be secured with wooden wedges, but this method entails problems in sealing.

In general alternative 1 is to be preferred.

4. Types of weir; formulae

The following symbols are used

Q = flow (m^3/s)
g = acceleration due to gravity (m/s^2)
B = width of channel (m)
b = width of weir opening (m)

H = distance from the channel bed to the edge of the weir (m)

h = upstream water level relative to the edge of the weir (m)

μ = coefficient of discharge

4.1 Choice of weir type

The coice of a suitable weir is made on the basis of the channel width, the accessible dam height and the range within which the flow is expected to vary. Insertion of these values into the formulae below will indicate what type is suitable or, alternatively, what changes should be made in the existing system for measurement to be possible.

4.2 Weir without end-contractions

The edge of the weir extends across the entire width of the channel (figure 2). This type is used for heavy flows. The flow is given by

$$Q = \frac{2\mu}{3} \cdot b \cdot h^{1.5} \cdot \sqrt{2g}$$

$$\frac{2\mu}{3} = 0.4224 + 0.00053/h$$

4.3 Weir with end-contractions

The weir is combined with a constriction of the channel (Figure 3). This type is used for moderate flows.

$$Q = \frac{2\mu}{3} \cdot b \cdot h^{1.5} \cdot \sqrt{2g}$$

$$\frac{2\mu}{3} = 0.3838 + 0.0386b/B + 0.00053/h$$

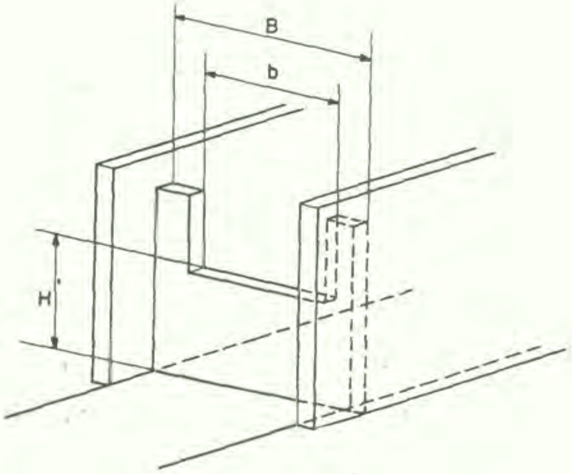


Figure 3. Weir with end-contractions.

4.4 V-notched weir (Thompson weir)

The weir consists of a V-shaped notch (Figure 4) in the dam. This type is used for light flows.

$$Q = \frac{8}{15} \cdot \mu \cdot h^{1.5} \cdot \sqrt{2g} \cdot \tan\frac{\theta}{2}$$

$$\mu = 0.5650 + 0.00868 \cdot \sqrt{\frac{1}{h}}$$

where θ is the angle of the notch. (When, as is usually the case, $\theta = 90°$, $\tan \theta/2 = 1$.)

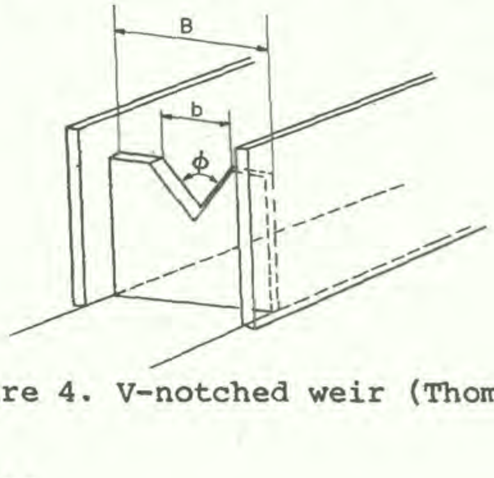


Figure 4. V-notched weir (Thompson weir).

5. Gauges

According to the above the calculation of flow over weirs only requires measurement of the water level relative to the weir edge. For this a gauge is placed upstream of the weir and distant from it (if possible) at least 2.5 times the maximum level (h) above the weir (Figure 5).

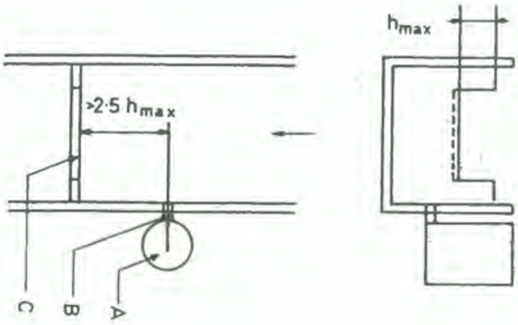


Figure 5. Arrangement of measuring chamber on a weir. A. Measuring chamber (internal diam. 300-400 mm with float; 100-150n mm with bubble tube). B. Connecting tube. C. Weir.

For permanent installations it is preferable to place the gauge in a separate, cylindrical measuring chamber (stilling well) close to the channel and communicating with it. The tendency for microbial growth in the measuring chamber can be counteracted by admitting a tangential stream of fresh water, small in relation to the diameter of the communicating pipe.

5.1 Scale

When the channel is accessible for direct inspection the water level can be observed directly on a scale on the channel wall. This method is suitable for temporary installations where for some reason automatic recording cannot be arranged. The accuracy of measurement is limited to the accuracy with which the scale can be read; the presence of foam in the channel can be a nuisance.

5.2 Bubble tube

This device for measuring the water level consists of a narrow vertical tube (internal diameter c. 10 mm) submerged in the channel with its orifice on a level with the weir edge. (For temporary installations the orifice should be as near this level as possible; the position should be determined with a spirit level.) The tube is fed with compressed air via a reduction valve, so that there is a steady flow from the orifice of 1 or 2 bubbles per second. The pressure in the tube is converted and transmitted to a recording instrument.

5.3 Float

Measurement of level by means of a float should always be carried out in a separate measuring chamber with a diameter of the order of 300 to 400 mm. The level is transmitted by a cable to a meter or, preferably, to a recorder. With a mechanical transmission system a float will be sensitive to corrosion and therefore unsuitable for systems in which the waste water containse sulphide, sulphite and chlorine.

Provided that there is no interference from growth in the measuring chamber or from corrosion, the float yields reliable and accurate measurements.

CONTENTS

1. INTRODUCTION

The pulp and paper industry plays an important part in the economic structure of many countries and paper products are used in all countries.

The paper can be produced from fibrous raw material from both wood and non-wood plants.

Although non-wood plant fibres constitute only about 5 % of the raw material used for pulp and paper on a worldwide basis, they represent today one of the major sources of fibrous raw material for many of the developing countries.

Fibre sources are classified into:

I Wood

- a) softwoods, such as birch, eucalyptus, aspen etc
- b) hardwoods, such as spruce, pine, fir, hemlock etc

II Non-wood

- a) agricultural residues such as wheat straw and other kinds of cereal straw, rice straw, sorghum, and sugar cane bagasse
- b) naturally growing plants such as bamboo, reeds, papyrus, esparto grass, and other grasses
- c) crops which are grown primarily for their fibre content, such as

1) bast or stem fibres of jute, hemp, kenaf, ramie, crotalaria (sun hemp) flax tow
2) leaf fibres of abaca (Manila hemp, musa textilis), sisal (Agave sisalina)
3) Cotton fibres, cotton linters

Bagasse, bamboo, wheat and rice straw are today the most important non-wood raw materials used in papermaking.

This part of the manual deals with the processes by which the raw materials for pulp production are prepared and the best available technology to reduce the discharges from the raw materials preparation.

Since a major of the pulp is produced from wood, the first section is the most detailed. The sections concerning bagasse, bamboo, and straw deal mainly with matters that apply specifically to each of these raw materials and in which they differ from the preparation of wood.

2. PREPARATION OF WOOD

2.1 Wood handling system - Introduction

When the wood or wood chips are received at the mill site the amount of wood is determined, either by measuring the gross volume of the wood or by weighing the wood.

A certain storage capacity of wood is required since the deliveries of wood are not always regular and as a buffer against disturbances. Storage capacity is also required if sulphite pulp is produced to allow oxidation of extractives.

In the storage area a system for turnover of the wood supply is required in order to obtain pulp of a uniform high quality.

The storage area should be well prepared, preferably covered with asphalt or concrete, so that a minimum of sand and stones are mixed with the wood.

Storage of wood results in a degradation of the raw material. This degradation is desired in some cases, as when sulphite pulp is produced.

Efficient washing of the wood before it enters the pulping process is very important to reduce the amount of sand and other impurities. The washing comes after the debarking and precedes the chipping operation.

Excess water from other departments in the mill is used for washing in order to reduce the overall fresh water consumption. After the washing this water is taken to a screen for removal of bark particles and then treated in an external treatment plant eithr alone or together with the water from the debarking operation. The debarking operation is the major source of water pollution from the preparation of wood. Before chipping and debarking, stones and metal pieces must be removed to avoid damaging the equipment.

Most debarking operations are carried out by friction forces between log and log in barking drums or between log/debarking equipment.

Barking drums are the most widely used equipment and the debarking can be carried out wet or dry.

The debarking method is determined by the amount of wood to be debarked and by the type of pulp to be produced.

The bark may be burnt in a bark boiler after being pressed to high dryness.

After debarking the wood is chipped and stored in chip piles before it is transported to the pulping process.

The consumption of wood in the process depends on the density of the wood, on the yield in the cooking and bleaching processes and on the losses of fibres.

2.2 Debarking

The logs must be debarked for many reasons before the wood is used in the process.

- Bark particles decrease the brightness of the pulp and in many paper products, as for example printing papers, specks are not accepted.
- The dissolution of organic substances from the bark is high as the bark fibres do not contain high amounts of cellulose.
- After cooking, undissolved bark particles such as bark specks and bark knots can be the starting points for web breaks in the paper machine.
- A high amount of suspended solids and fibres from the bark may cause dewatering problems in the paper machine.
- The demand for chemicals in the cooking process is higher for bark than for wood.

- Bleached pulp requires a lower degree of debarking since a high amount of the bark particles is dissolved in the alkaline medium, but a larger quantity of bleaching chemicals is required to reach a certain brightness level.

- The debarking operation, especially wet debarking, is the main source of discharges of organic substances to water. The choice of debarking method is determined by pulping process and the quantity of wood to be debarked.

In pulping of wood it is an avantage if the pulp can be produced from unbarked wood. The production of sulphate pulps from not too old eucalyptus requires not debarking. Eucalyptus bark is 10-17 % by weight of the tree and contains a high amount of fibres. The yield is about 80% of that of the wood. The advantages are a more utilized forest area and no costs for debarking or bark handling.

2.2.1 Composition of bark

Bark consists of fibres as does wood but the cellulose content is lower. The amount of fines, the content of lignin and the content of extractives and of water soluble substances are higher in the bark than in the stem of the wood.

TABLE 1. Chemical composition of the bark from some Scandinavian species

Bark	Cellulose %	Hemi-cellulose %	Lignin %	Soluble exractives %	
				Water	Ether
Spruce	36-37	18-20	36	20	5
Pine outer	25	18-20	48	20	5
inner	36-45	15-24	18-29		
Birch outer	3-4	1	1-2	20	38
inner	18-20	20	20	15	2
(Softwood, average	43	28	29)		
(Hardwood, average	45	34	21)		

TABLE 2. Analysis of bark from some Canadian wood species (unextracted, dry basis)

		Extractives					Sum of
Species	Ash cont. %	Ethyl ether %	Hot water %	Successive extractions % *	Successive extractions % **	Lignin %	last columns %
Balsam fir	2.0	23.6	26.7	36.2	58.7	20.6	79.3
Black spruce	2.4	25,5	32,3	38,7	58.8	16.7	75.5
White spruce	3.1	22.9	41.8	47.7	70.7	14.3	85.0
Douglas fir	0.9	34.4	29.2	42.9	68.3	26.1	94.4
Eastern hemlock	1.0	23.9	30.0	40.2	59.7	31.5	91.2
Western red cedar	0.9	6.3	6.4	11.5	51.3	36.7	88.0

* Ethanol: benzene, ethanol, hot water

** Ethanol: benzene, ethanol, hot water, 1 % NaOH

Table 1 shows the chemical composition of bark from Scandinavian species (1) and Table 2 that from Canadian species (2).

Table 3 shows the chemical composition of bark and different parts of the stem for black spruce (2).

TABLE 3. Analysis of bark spruce fractions unextracted (dry basis)

Species	Ash %	Protein %	Pentosans %	Uronic acid anhydride %	Methoxyl %	Lignin %	Tannin %
Outer bark	1.2	2.1	11.8	8.6	4.0	33.9	1.9
Inner bark	3.2	3.8	12.0	10.0	2.2	6.6	7.6
Cambium	3.6	7.1	6.3	4.6	0.7	1.8	0
Young sapwood	0.4	12.7	8.1	3.8	4.7	24.9	0
Sapwood	0.3	0.3	12.0	3.7	4.9	26.3	0
Heartwood	0.3	0.4	12.5	3.9	4.8	26.1	0

2.2.2 Debarking methods

The result of the debarking depends mainly on the debarking resistance of the wood and on the intensity of the mechanical treatment in the debarking process.

Freshly cut wood is easily debarked as the bark is still not dried, but after storage for a short period the bark is more difficult to remove.

Debarking can be carried out in the forest before transportation to the mill but it is mostly carried out in the mill.

The choice of debarking method is determined by the pulp process and amount of wood to be debarked.

Debarking in the forest is carried out manually or mechanically in a single log equipment. This method is hardly applied at all in the industrial countries as a high number of man hours is required and the bark is not available for energy production in the mill.

Debarking in the mill is carried out by friction debarking or by hydraulic debarking.

Debarking log against log in rotating drums, wet or dry, is the most frequent method. The drums can be designed for short logs or for logs more than 3 m in length. Long-wood drums are mostly used, since the debarking capacity is higher than for short-wood drums. A discontinuous debarking equipment of the pocket type can be used for wood of small dimensions. In the hydraulic debarking operation the logs are debarked with a high-pressure jet of water.

Wet debarking drums are more efficient and they are therefore used when mechanical and sulphite pulps are produced. Debarking is carried out in two stages in some mills. The logs are first dry debarked and then wet debarked.

The degree of debarking is dependent not only on the debarking method but also on the time the logs stay in the drum and on the rotation speed of the drum.

Figure 1 shows the influence of wood species and method of storage on the required debark also shows that pine is easier to debark than spruce and birch.

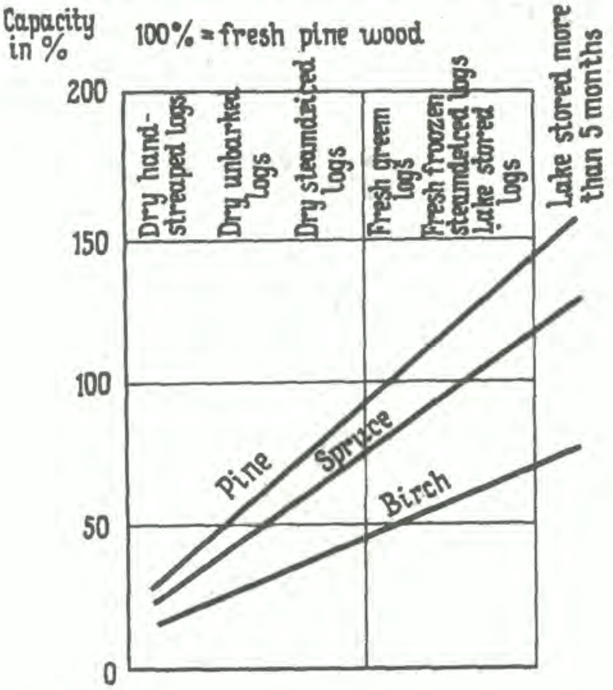


FIGURE 1. The reuired debarking capacity depends on the raw material and on the method of storage.

According to Figure 1 homogeneous wood is required in the debarking drum, since for instance a mixture of pine and birch results in a well debarked pine while the bark remains on the birch.

2.2.3 Dissolution of organic substances

Wet debarking is the debarking method which is responsible for most of the discharges from the wood handling system. The degree of debarking is higher in wet debarking than in dry debarking why wet debarking is carried out in spite of the higher discharges. Mechanical pulps and sulphite pulps require a very high degee of debarking.

The fresh water consumption in the wet debarking operation can be as high as 10 m^3/m^3 s wood if water is not recycled from other departments in the mill. In a highly closed system an addition of 1 m^3/m^3 debarked solid wood is required.

The amount of water required depends on the following factors:

- to obtain a high degree of debarking more water is required

- warm water is required in cold a climate to heat the wood before entering the process

- measures to avoid discharges of suspended and dissolved solids require water

Figure 2 shows a schematic flow sheet of a wet debarking system.

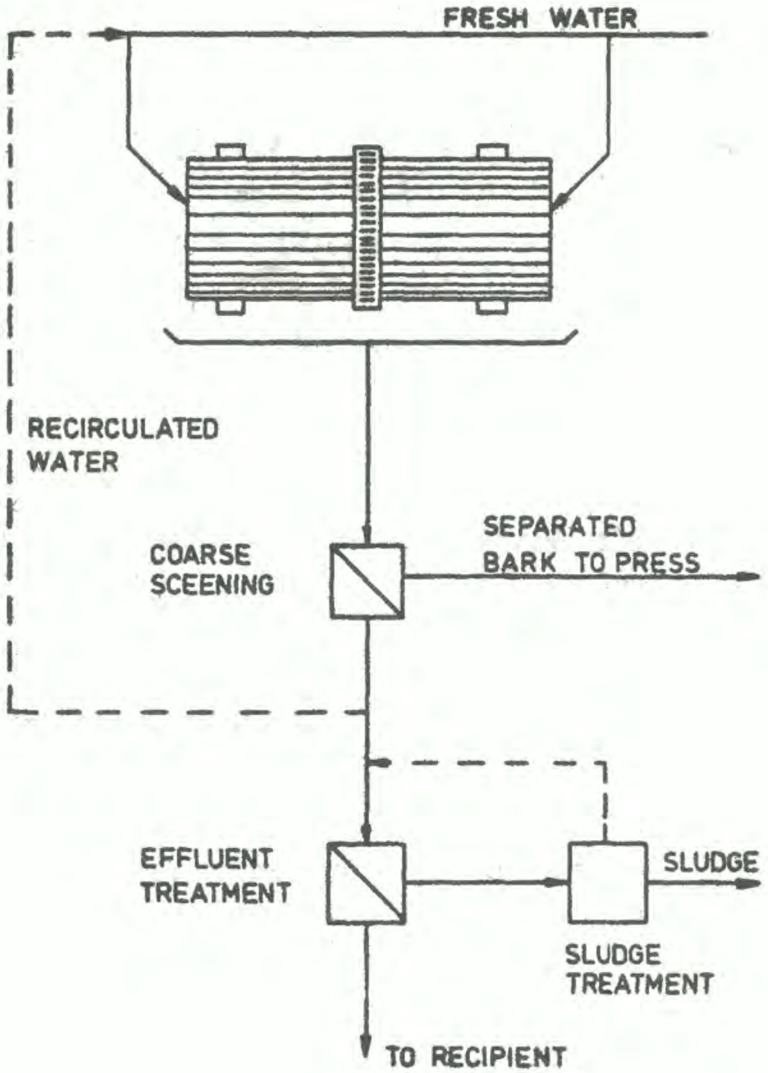


FIGURE 2. A schematic flow sheet of a wet debarking system

The removed bark leaves the drum together with the spent shower water which passes a coarse screening equipment. As much as possible of the screening water is recirculated and the excess water is sent directly to the recipient either directly or via an external treatment plant.

In the barking drum, the bark is ground to fine particles which it is not possible to remove in the coarse screening equipment and these particles result in a discharge of suspended solids (SS) from the wood handling system unless it is treated in an external treatment plant. The amount of suspended solids depends on the debarked wood species, on the retention time, on the storage time, on the intensity in the debarking equipment and the efficiency of the coarse screening equipment.

Hardwoods result in higher amounts of suspended solids than softwoods. The chemical composition of the bark from hardwood differs from that of softwood, which is probably the reason for the higher discharge of suspended solids.

The difference between hardwood and softwood in the amount of suspended solids passing the coarse screen is shown in the following example

hardwood:	12 kg SS/m^3 s wood
softwood:	3-5 kg SS/m^3 s wood

There are also differences between different wood species and this comparison is between Scandinavian wood species.

In order to minimize the amount of supended solids in the effluent it is important to remove the bark from the drum as soon as possible.

The coarse screening usually separates 85-95 % of the bark if the diameter of the holes in the screening plates is 2-8 mm.

The amount of dissolved substances (DS) is determined by the wood species, the size of the bark particles and the time that the bark particles are in contact with water.

The size of the bark particles is the most important factor.

Table 4 shows the results of a laboratory investigation of bark particles of different sizes. The amount of dissolved substance was analysed after extraction for 2-94 h (3).

TABLE 4. Extraction of bark of different dimensions. Dissolved COD, g/kg bark, as function of extraction time

Size	Extraction time, h 2	5	22	29	94
Pieces 20 x 20 mm	36	45	78	79	149
Pieces 10 x 10 mm	59	75	123	116	211
Pieces 5 x 5 mm	104	138	190	208	318
Turmix suspended 3 min	595	595	634	557	595

This means that a wet debarking system with a high discharge of suspended solids also has a high discharge of dissolved substances.

Figure 3 shows the relation between the discharge of suspended solids after coarse screening of the effluent from the wet debarking operation and the discharge of BOD_7 in Scandinavian mills.

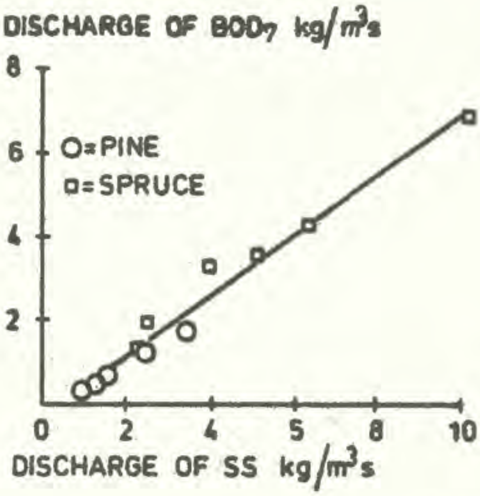


FIGURE 3. The relation between the discharge of BOD_7 and solids after coarse screening of the effluent from the wet debarking operation in Scandinavian mills.

This relation is valid for softwood but for hardwood the slope of the curve is lower as the amount of suspended solids is higher in the effluent from hardwood.

General figures for the discharge of dissolved substances from wet debarking plants after coarse screening cannot be given, so the figures in table 5 only can be regarded as approximate.

TABLE 5. Discharge of dissolved substances from wet barking plants.

Discharge		Wet debarking softwood	Wet debarking hardwood
BOD_7	kg/m^3s	2-5	3-7
COD	"	5-10	10-20
Colour, Pt	"	1-5	2-8
Phosphorus	g/m^3s	5-10	8-10

The acute toxicity of the effluents from two softwood wet debarking plants has been investigated. LC_{50}-values of 2-3 % after 96 h were obtained. The high acute toxicity depends mainly on the high amount of resin acid in the effluents.

2.2.4 Bark handling system

For each solid m^3 of softwood about 40 kg bark are removed from the debarking drum and the corresponding figures for hardwood is about 70 kg. Bark waste from receiving tables, conveyors, log washing should also be included when the required bark handling capacity is calculated.

In dry debarking systems the bark usually has a dryness of about 40 % and is dry enough to be burnt directly.

In wet debarking systems, the bark is pressed to a high dryness before burning. The water removed from the bark is externally treated together with the water from the debarking after the coarse screening.

The bark is homogenized by mechanical disintegration to avoid problems in conveyors and bark bins and to obtain a favourable air distribution in the boiler. A certain storage capacity of bark is required to provide a continuous operation of the boiler.

The amount of bark waste is usually 10-20 % (or 5-10 kg/m^3 s wood of the total amount of bark. This bark waste is contaminated by stones and soil and also by tops, branches and wood pieces of different sizes.

In wet debarking plants there are established methods of handling the bark waste. The most convenient method is to integrate the handling of the bark waste into the ordinary bark handling system. Stones and sand are separated in a wet stone trap and the bark waste is then treated in the ordinary bark handling system.

The bark waste can also be handled separately and it is then mixed with the rest of the bark before pressing and burning. A wind separator is installed in some mills in order to remove stones from the bark but sand is not removed. Sand may be removed in a disc-screen.

In dry debarking systems the bark waste from log feeder and classifier may be fed to a channel designed as a sand trap. The bark is removed from the top of the trap by a scraper in combination with a strainer while stones and sand are removed from the bottom by a specially designed conveyor. The bark is burnt in the bark boiler together with bark from the debarking drum.

It is important to minimize the sand content in the bark to be burnt otherwise it increases the amount of ash which can be sintered to slag.

2.3 Chip handling system

In all pulping processes other than stone groundwood pulping, the debarked logs are chipped. After debarking and immediatly before chipping the logs are washed.

The most common chippers are of the disc type, but chippers of the drum type are also used especially for rechipping of oversize chips.

A main factor in the production of high quality chips is sharp and properly adjusted knives. A maximum distance of 1 mm is tolerated as a shorter distance substantially increases the amount of fines and increases the compression damage of the chips.

The wood handling operation including the chipping operation is noisy so that the wood handling system ought to be closed.

In order to obtain a uniform raw material in the pulping process the chips are classified by screening.

The chips are transported to the pile by belt conveyors or pneumatic systems.

A certain storage capacity is required so that a system for chip storage usually exists.

In sulphite pulping, the chips must be stored to obtain the desired oxidation of extractives.

In Scandinavia spruce chips are stored for ten weeks but more recently other methods have been introduced.

In chip pile oxidation, the chips are piled to a height of about four metres or more and the pile is then compacted. If the chips are not frozen the reaction starts and in a few days the temperature reaches 60-70°C and sufficient oxidation takes place within 4-6 weeks.

If the chips are stored in a silo and heated with steam oxidizes the extractives are oxidized in 4-6 days.

2.4 Treatment of effluents from the wood handling system

Most of the discharges of organic substances to water are effluents from the wet debarking operation. In the dry debarking system only a small amount of organic substances is discharged.

A change from wet debarking to dry debarking or a combination of dry debarking followed by wet debarking reduces the discharges of organic substances to water to a great extent but the degree of debarking is lower.

This section deals only treatment of the effluents from the wet debarking system.

The main part of the water in the wet debarking plant is recirculated after coarse screening. The excess water is then treated for removal of both suspended solids and dissolved substances.

Suspended solids and sand are removed in a filter or a fractionator and the water is then usually treated in a sedimentation or a flotation plant.

Figure 4 shows the design of the external treatment system for removal of suspended solids.

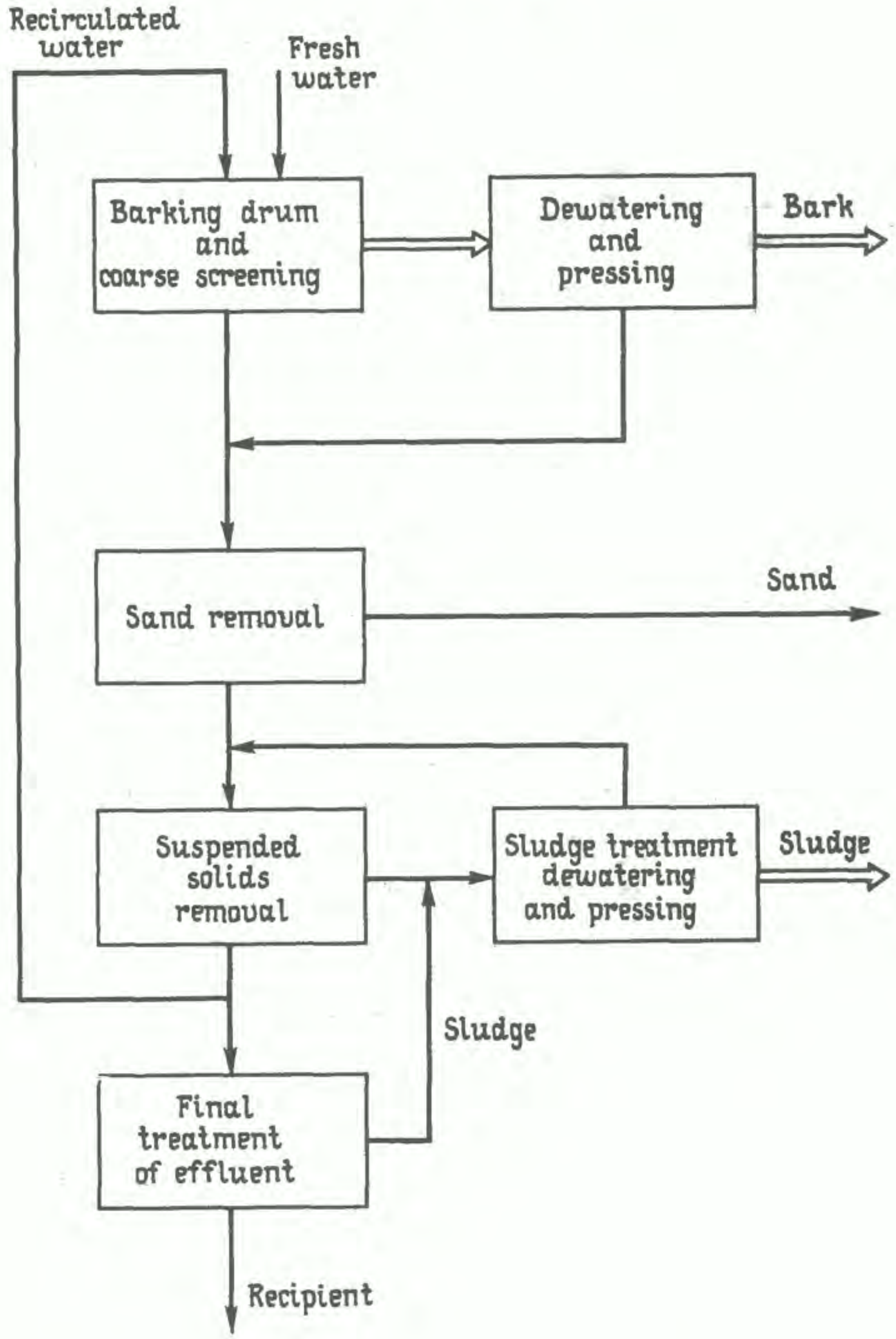


FIGURE 4. External treatment system for removal of suspended solids from the effluent from a wet debarking plant.

2.4.1 Suspended solids

Table 6 shows the discharges from the wet debarking operation after different external treatment methods.

TABLE 6. Discharge of suspended solids from barking plant effluents treated by different methods

	kg/m^{3}s wood
Coarse screening	4
Coarse screening and suspended solids removal	2
Coarse screening and suspended solids removal followed by	
- sedimentation	1
- flotation	0.6
Coarse screening and final treatment together with other effluents	1

The efficiency of the sand separation varies depending on the equipment and design of the system for the removal of suspended solids and sand.

Table 7 shows the sand content in the sludge from debarking plants in four Scandinavian mills with different equipment for the removal of sand

TABLE 5. Analyses of sludge from sand removal equipment in four Scandinavian mills

	Mill No			
	1	2	3	4
Sludge dryness, %	24	25	23	33
Inorganic material, % of dry sludge	15	8	6	61

In mill No 1 the sand is removed by a scraper at the bottom of the sump to the water circulation pump. Mill No 2 and 3 have specially designed sand traps. Mill No 4 has no separate equipment for the removal of sand as water-stored wood is used and an old settling thickener is used intermittently.

In mills 1-3 the discharge of suspended solids from sand separation is high, but most of the sludge consists of settled bark particles and the content of sand (inorganic particles) is low, only 5-15 %.

The thickener used in mill No 4 is more selective in the separation of sand. The inorganic content in the sludge is about 60 %, which depends on a high flow of water and a low removal of sludge from the thickener (about 1 m^3/d).

Removal of suspended solids in a filter results in a sludge of 10-15 % dryness while the reject water from a fractionator has a dry solids content of 0.5-2 %. The sludge from a fractionator is dewatered to 10 % dryness. Both methods reduce the amount of suspended solids by about 50 %.

The bark particles in the effluent from the fine fraction separation are finally removed in a sedimentation or a flotation plant.

In a sedimentation plant, 60 % of the suspended solids in the water from a softwood plant are separated. The corresponding figure from a hardwood plant is as high as 90 %.

The inlet amount is higher in a hardwood plant so that the amount of suspended solids in the effluent is 1-2 kg/m^3,s wood from both softwood and hardwood plants. Sedimentation does not reduce the amount of BOD$_7$ in the effluent.

The flotation plant requires that sand and dense particles are removed from the effluent to avoid sedimentation at the bottom of the flotation plant. Polyelectrolytes are added to the water and the suspended solids are flocculated. The amount of suspended solids in the effluent from the flotation plant is 0.5-1 kg/m^3,s wood, which means a suspended solids separation of 80-90 % in a softwood debarking plant. A reduction in BOD$_7$ of 30-50 % is also obtained.

2.4.2 Dissolved substances

The amount of dissolved substances is not greatly reduced in a sedimentation or a flotation plant so the effluent is also treated by chemical flocculation or in a biological treatment plant. Chemical flocculation by addition of alum results in a COD-reduction of 60 % and a BOD$_7$ reduction of 40 %.

Table 8 shows the effect of effluent treatment in an aerated lagoon. The BOD$_7$ reduction is more than 70 % and the COD reduction is more than 50 %.

TABLE 8. BOD_7- and COD-reductions in an aerated lagoon.

Retention time days	Temp. °C	BOD_7-value untreated water g/m^3	BOD-reduction %	COD-reduction %
5	21	750	84	54
5	10	1100	71	50

The acute toxicity is also reduced by 80 %.

2.4.3 Examples of effluent treatment

The design and the effects of external treatment plants are demonstrated in a few cases below

Debarking plant 1:

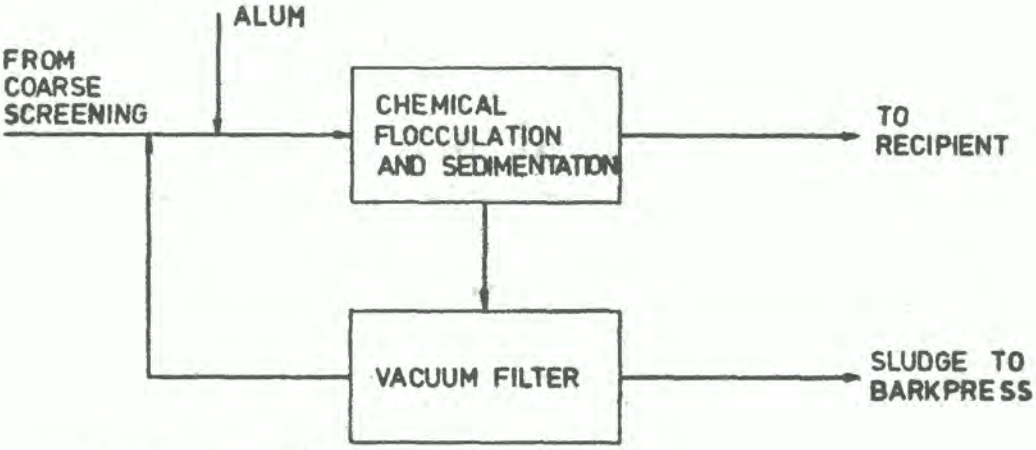


FIGURE 5. Debarking plant 1

Raw material: softwood (pine, spuce)

Effluent treatment methods: Chemical flocculation (alum), sedimentation

Debarking plant 2:

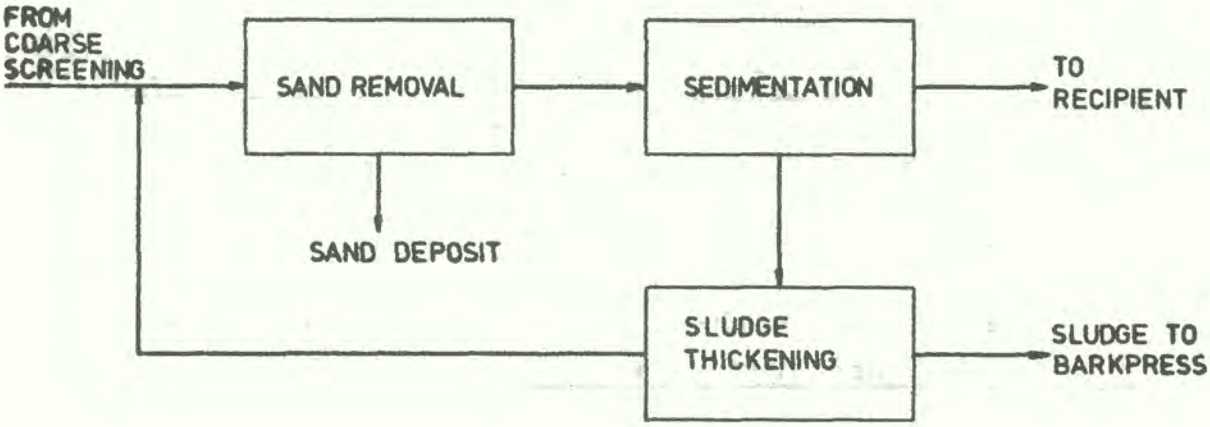


FIGURE 6. Debarking plant 2

Raw material: hardwood (birch)
Effluent treatment methods: sand trap, sedimentation

Table 9 shows the results of the effluent treatment in debarking plants 1 and 2.

TABLE 9. Effects of sedimentation treatment (mill investigations)

		Debarking plant 1	Debarking plant 2
Wood type		softwood (pine, spruce)	hardwood (birch)
Effluent water flow	m^3/h	110	175
	m^3/m^3s	1.0	4.0
Pond load	$m^3/m^2,h$	0.55	0.95
Suspended solids			
- to pond	kg/m^3s	3.4	16
- from pond	kg/m^3s	1.5	1.7
BOD_7			
- to pond	kg/m^3s	1.73	3.14
- from pond	kg/m^3s	1.65	2.64
Separation degree			
- suspended solids	%	56	89
- BOD_7	%	6	15
Sludge consistency			
- from pond	%	8.5	6.8
- from thickener	%	-	10

Debarking plant 3:

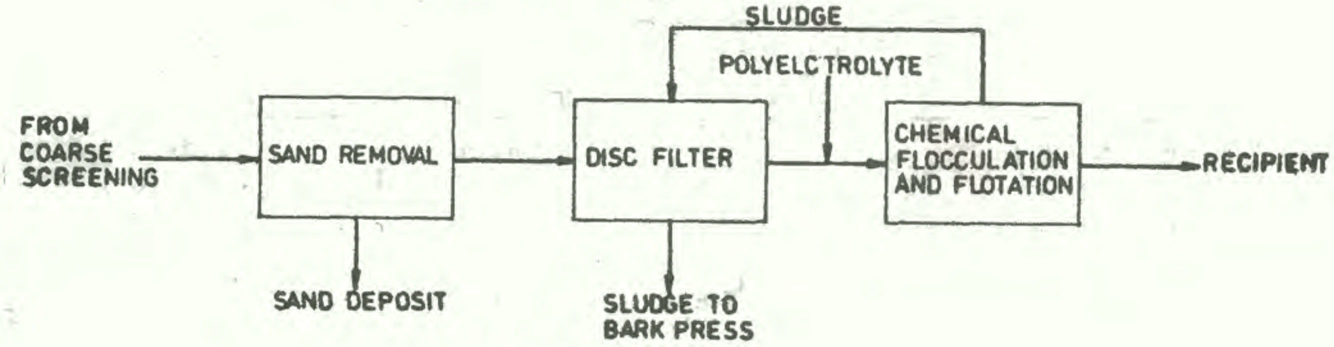


FIGURE 7. Debarking plant 3

Raw material: spruce, pine
Effluent treatment methods: sand trap, discfilter,
chemical flocculation,
flotation

Debarking plant 4:

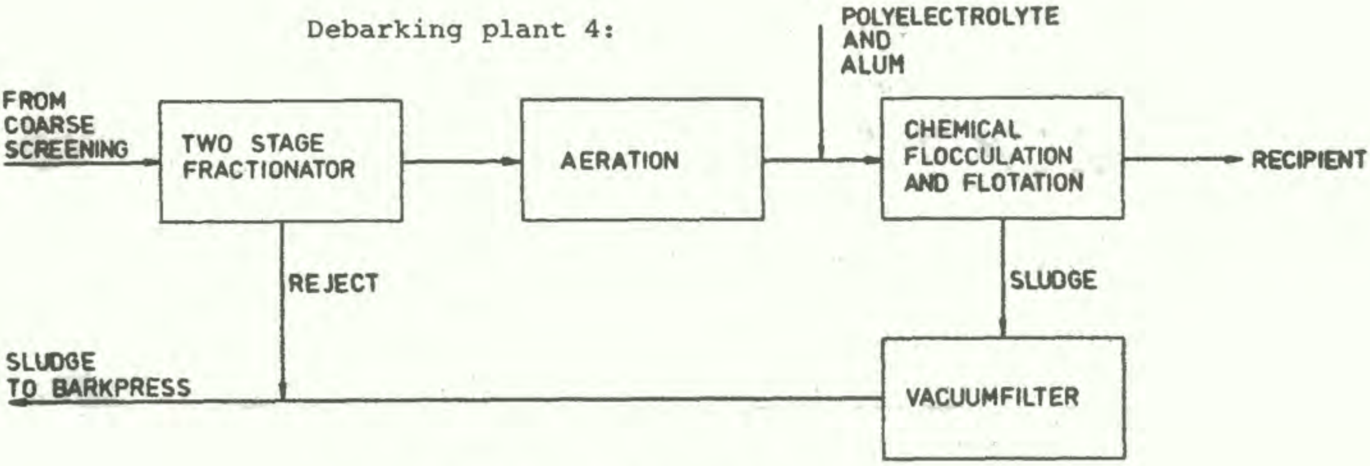


FIGURE 8. Debarking plant 4

Raw material: spruce
Effluent treatment methods: fractionator, aerated tank
chemical flocculation,
flotation

Table 10 shows the results of the effluent treatment in debarking plants 3 and 4.

TABLE 10. Effects of flotation treatment of debarking waste water.

		Barking plant 3	Barking plant 4
Wood type		spruce + pine	spruce
Effluent water flow	m^3/h	125	135
	m^3/m^3f	1.7	1.6
Load of the basin	$m^3/m^2,h$	3.6	4.5
Suspended solids			
- to basin	kg/m^3s	3.0	5.8
- from basin	kg/m^3s	0.6	1.9
BOD_7			
- to basin	kg/m^3s	3.2	1.2
- from basin	kg/m^3s	2.0	0.5
Separation degree			
- suspended solids	%	80	70
- BOD_7 .	%	40	60
Sludge consistency	%	9.3	2.1

Debarking plant 5:

Table 11 shows the effects of effluent treatment by chemical flocculation compared with biological treatment followed by chemical flocculation. Biological treatment followed by chemical flocculation results in a BOD_7-reduction of 95 % and a COD-reduction of 90 %.

TABLE 11. Efficiency of flocculation-sedimentation compared with the same treatment combined with biological treatment

		Flocculation-sedimentation	Biological treatment
Suspended solids	g/m^3	15	30
COD-reduction	%	62	90
BOD_7-reduction	%	38	95
Phosphorus reduction	%	89	99
Colour reduction	%	61	91

The effluent treatment in debarking plants 1-5 relate to the separate treatment of waste water from the debarking plant. This is, however, unusual. The effluents from the debarking plants are usually mixed with effluents from other departments in the mill which are then treated together in the external treatment equipment.

Different types of bark sludge are produced in the pretreatment, the fines fraction separation and the final treatment.

The sludge from the coarse screening contains bark and wood pieces. The bark is homogenized and dewatered in a bark press. The dryness is increased from 15-18 % to 40 % and the sludge is then disposed or burnt.

The fines fraction contains bark particles 0.2-2 mm in size. This sludge is easily dewatered and is mixed with the bark and pressed.

The sludge produced is different in a sedimentation plant differs from that from a flotation plant. All sludge fractions are rather similar in a sedimentation plant.

Chemical flocculation increases the amount of sludge and the sludge is voluminous, which lowers the drainage rate and the dryness.

3. PREPARATION OF BAGASSE

3.1 Introduction

Bagasse is the fibrous residue after removal of the sugar-containing liquor from sugar cane.

In 1980 the production of pulp from bagasse is estimated to be about one Mton/year which should be compared with a pulp production from softwood and hardwood of around 115 Mton/year. The total production of pulp from non-wood raw materials is about 7 Mton/year.

3.2 Sugar cane

Sugar cane is a tropical grass from Asia and a number of different species of sugar cane are used. The chemical composition and the morphological properties vary considerably.

Sugar cane is grown within the tropical and sub-tropical regions of the world. The canes, which reach a height of 3-6 m and have a diameter of 5-6 cm, take from 8-18 months to grow. The crop is ready to harvest just before flowering during a period of 4-10 months. In some countries the canes are harvested all round the year.

The growth per hectare results in about 100 tons of bagasse and 15 tons of sugar.

The leaves do not contain significant amounts of sugar but they do contain high amounts of silica, which cause problems both in the sugar mill and in the pulp and paper mill. As much as possible of the leaves and the tops are therefore removed before treatment in the sugar mill. This is usually done just before harvesting by burning the plants, or manually at the time of harvesting.

The best raw material for sugar production is achieved if the canes are cut and cleaned by hand and delivered fresh to the mill. Mechanical harvesting methods produce a less clean sugar cane.

In the sugar mill the canes are cut into pieces and crushed, which produces a juice for further treatment to yield different sugar products. The process is shown in Figure 9.

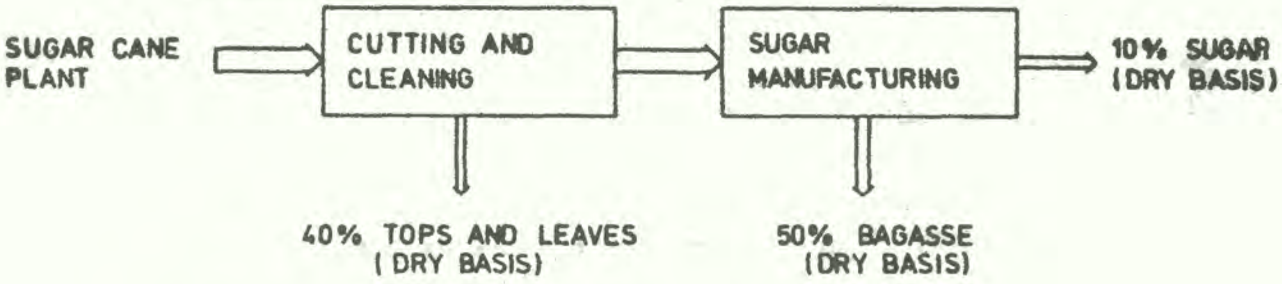


FIGURE 9. Sugar cane handling

The sugar cane consists of 10 % fibres which can be used for paper production.

3.3 Bagasse

The main part of the bagasse is used as fuel for the generation of steam. The heat value of bagasse is about 2.0-2.3 kWh/kg bagasse (50 % dryness and 15 % ash content on dry bagasse).

Bagasse is easily transported from the sugar mill to the pulp mill but there are also problems in the pulping of bagasse since bagasse

- is a bulky material
- is seasonally delivered
- requires proper storage
- contains a high amount of silica

Figure 10 shows a schematic flow sheet of the pulping of bagasse.

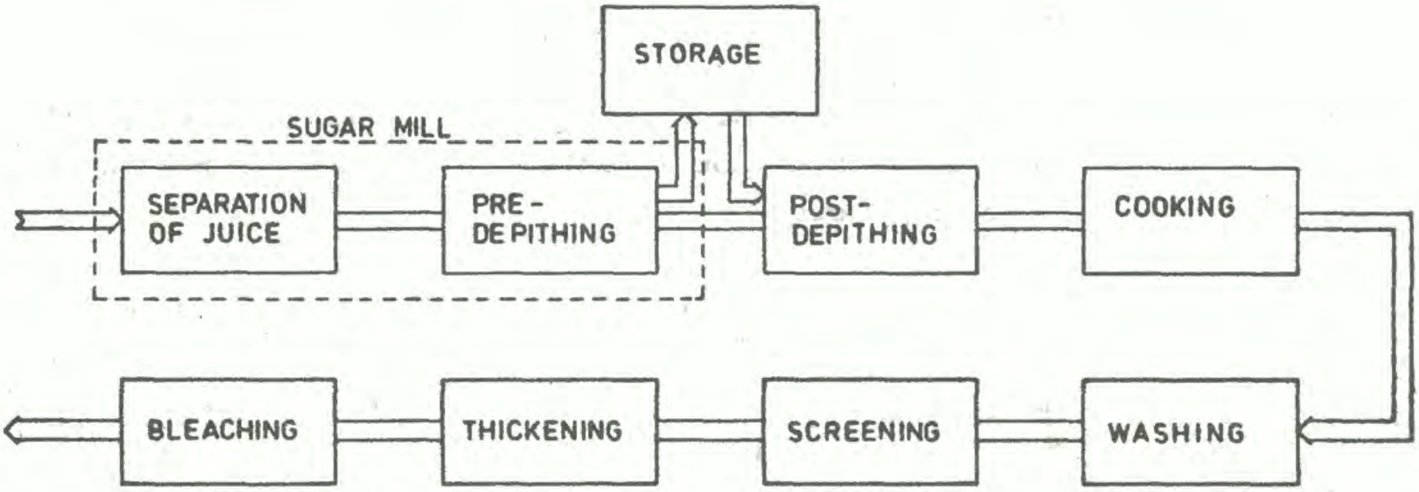


FIGURE 10. Pulp production from bagasse

3.4 Storage of bagasse

In pulp and paper mills located in the same area as a sugar mill, the bagasse is transported by belt conveyors etc. but many bagasse mills also require additional bagasse from other sugar mills.

The sugar cane is usually not harvested all the year around so that bagasse must be stored to permit continuous operation at a pulp and paper mill.

A large storage area is required as the density of bagasse is low, approximately 100 kg/m^3.

3.4.1 Dry storage

Dry storage is usually adopted at mills not integrated with a sugar mill. The bagasse is baled in the sugar mill, which considerably reduces the volume, and is then transported to the pulp and paper mill. The storage time varies from months to several years and the yield loss can be as high as 10-20 %.

The chemical demand in the pulping process is increased as a consequence of dry storage. During harvesting only bagasse which cannot immediately be used for pulping is baled and stored.

The bales are piled to a height of 6-10 m and should be covered to avoid fibre losses. No chemicals are added. Among dry storage methods the Celatex, Thobidaux and Taiwan systems can be mentioned.

3.4.2 Wet storage

A number of alternative wet storage methods exist. The most widespread is the Ritter method, which was developed in South Africa and was first used in the Ngoye Paper Mills, Felixtown.

After the first pith separation (moist depithing) the bagasse is stored at a consistency of 2-4 %. Excess liquid is drained off and is recirculated after the addition of Ritter liquid, which consists of a lactic acid culture with the addition of molasses. The liquor is added to the bagasse during piling in order to control the pH, which should be just below 5.

The Ritter method claims the following advantages compared with dry storage

- costly handling of bales is avoided
- bulk storage is done at 10-40 % dryness so that the risk of spontaneous ignition is low
- no dust problem and bagassassis is avoided
- the wet fibre is soft and impregnation with cooking liquor is facilitated and improved, which improves the pulp quality
- increased pulp yield
- lower chemical consumption in cooking and bleaching due to reduced lignin content during storage

- the fibre losses can be kept as low as 5-6 % compared with 10-20 % in dry storage

- during storage the sugar content is reduced considerably, which reduces the foaming problems in the washing

- fibre bundles are opened and pith released

Investigations during recent years have shown that these advantages can also be achieved without the addition of a lactic acid culture addition patented by Ritter. The pH can be both low (pH 4.5-5.0) or high (pH 9-10) under anaerobic conditions and a high relative humidity in the pile.

3.5 Depithing

The pith should be removed before pulping as the cells are not suitable for papermaking and they increase the chemical demand in the cooking. The pith is concentrated to the nodes and to the middle of the stalk.

Depithing is carried out in two stages with or without intermediate storage. Pre-depithing is carried out in the sugar mill and storage and post-depithing are normally carried out in the pulp mill. As the pre-depithing is done in the sugar mill, the rejected pith can be used as fuel. The heat value of pith is just about the same as for bagasse itself, but many sugar mills lack depithing equipment.

Even though undepithed bagasse can be used for paper making it is an advantage to remove as possible of the pith before the pulping. The main reasons are the following:

- Pith gives a lower pulp and paper quality
- Reduced pulp yield
- The chemical demand is higher for pith mainly because of its high sugar content.
- Pulp drainage is reduced by pith.
- Pith in the paper impairs the printing properties.
- A lower pith content makes it possible to keep a higher wood to liquor ratio in the cooking process which reduces the steam consumption.
- The silica and ash content in the pith is high.

The influence of pith on some pulp properties is shown in Figure 11.

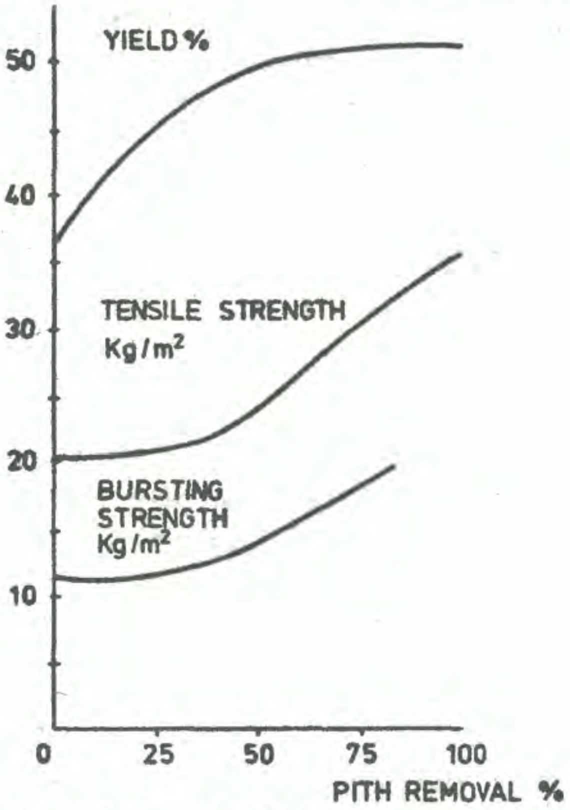


FIGURE 11. The effect of pith removal on some pulp properties

The ideal depithing operation would result in the complete remove of pith, fines and dirt, but such a system does not exist. Many methods of removing the pith from the fibres have been developed but it is only recently that efforts have been made to optimize the depithing operation.

3.5.1 Mechanical depithing

The mechanical methods can be divided into:

- dry separation
- moist separation
- wet separation

In the dry separation method the bagasse dryness is 80-85 % and the operation is carried out in some type of disintegrator. Pith, fines and dirt are usually removed by screening plates, but equipment also exists to fractionate the pith-fibre mixture by air. Around 50 % of the pith cab be renivedl by dry separation. The method has some disadvantages

- High losses of fibres.

- Generation of bagasse dust which may cause bagassasis.

Due to the low degree of pith separation it is not possible to produce high quality pulp by dry separation. The method is therefore not widespread.

3.5.2 Moist depithing

Moist depithing is carried out at about 50 % relative humidity. The equipment may consist of hammer mills or disintegrators, equipped with special screens. Up to 60-70 % pith separation can be achieved. Relatively fresh bagasse contains about 50 % water so this method is very suitable for depithing in the sugar mill.

3.5.3 Wet depithing

Wet depithing is carried out after storage if fresh bagasse is not available. The bagasse is refined in a pulper at a consistency of 2-10 % followed by dewatering to 15-50 % depending on the next stage in the treatment, which may be some kind of screening.

If dry stored bagasse is to be wet depithed, it may be necessary to use some steam to softening the fibre bundles. Wet depithing is the superior mechanical method of pith separation. Further, a good separation of impurities such as sand, colloidal particles and water-soluble material is achieved. A very clean bagasse fibre is thus obtained. A disadvantage is that the dryness of separated pith must be increased from about 2 % to 40-50 % in order to be able to use the pith before it can be used as fuel.

For optimal pith separation wet depithing is required as a final stage. Several mills have the sequence moist depithing, storage and wet depithing.

3.5.4 Chemical depithing

Chemical depithing is only used for the production of dissolving pulp. A separation of at least 50-60 % of the pith is required as the pith disturbs the viscose process to a great extent. For a high quality of dissolving pulp, a depithing degree of 70-80 % is needed.

The method is based on hydrolysis with sulphuric acid or warm water which degrades the hemicellulose. After the hydrolysis the pith can be separated from the fibre by some wet method.

3.6 Enviromental problems and effluent treatment cost

The bagasse always contains some amounts of residual juice which consists of sugar, salts and organic acids and the organic material will rapidly start to ferment.

Treating the bagasse with water during storage and particularly during the depithing always results in an effluent containing organic substances and suspended solids.

The liquid used when the bagasse is stored is recirculated, thus there is generally no effluent from this stage. However, treating the bagasse with water during the post-depithing stage results in considerable quantities of suspended solids in the effluent.

The discharges vary in the range of:
10-60 m^3 water/t pulp
30-150 kg suspended solids/t pulp
10-60 kg BOD_5 /t pulp

The suspended solids in the effluent from the post-depithing are removed by means of mechanical treatment e g a sedimentation basin and a dewatering filter for the sludge removal from the basin. For further treatment of the effluent this could be sent to a biological treatment plant installed for treatment of the combined effluent from the mill.

4. PREPARATION OF BAMBOO

4.1 Introduction

Bamboo has become an interesting raw material for paper production because of its rapid growth and it is used in many countries as a major source of pulping raw material.

The production of bamboo pulp is about 1.5 million tons and that of non-wood pulp is about 7 million tons.

When bamboo is treated as a raw material for the manufacture of pulp and paper, one has to consider that bamboo is not the only pulping raw material in most mills but is often blended with other grasses and/or hardwoods in the digestion operation.

4.2 Bamboo

Bamboo belongs to the grass family and consists of several different species. The physical characteristics and chemical composition vary to a great extent.

Bamboo is annually grown, but the roots are perennial. As soon as the root system is established, the culms grow rapidly and attain their full growth within the season. The hardening of the culm occures within a period of 6 to 10 years and the harvesting should be done during this period. In India, however, the cutting cycle is 2 to 5 years.

Bamboos flower at regular intervals. Depending on the species the interval varies from 15 to 50 years. After flowering, the bamboo perishes and the seeds, which fall to the ground, start a new growth. In this cycle there is pause in the supply of natural bamboo over a period of about 8 to 20 years. Gregarious flowering spreads like a wave and covers hundreds of kilometres in a year. It is, therefore, advisable to have a bamboo crop of different species flowering at different periods to avoid shortage of raw material.

Bamboos vary in size according to the species. Some of them are giants growing to a height of 30-50 metres and with a diameter of 20 cm. Others are only reaching a height of 3-7 metres and a diameter of 1-5 centimetres.

The bamboo stem consists of:

- a woody portion of hollow tube (culm)
- ground tissue of parenchyma with fibrovascular bundles.

The culm is jointed at nodes at regular intervals along the length of the stem. These nodes constitute a problem in pulping since they are denser than the rest of the stalk and, are therefore, penetrated with great difficulty.

Bamboo may be divided into three types:

1) Green bamboo = fresh bamboo
2) Yellow bamboo = bamboo stored for a short time
3) Dried bamboo (black bamboo) = bamboo stored for a long time

Measurement of moisture, volume and weight is quite a difficult problem as the moisture content of bamboo is different for green bamboo, yellow bamboo, dried bamboo and decayed bamboo, which normally results in a false weight and moisture content.

4.3 Preparation of bamboo for pulping

4.3.1 Collection and handling

Bamboo is cut into lengths of about 3 metres and bundles of bamboo stems are prepared. Tops, branches etc, which represent 6-10 % of the total amount of bamboo are left unutilized. Compared with the felling of wood, bamboo is usually more difficult to cut because of the fact that it grows clusters, its height, branches with thorns etc. Bamboo is usually transported to the factories by trucks or wagons, but even quite primitive means of transport are in use. Bamboo is hollow and, relatively voluminous, so that transportation costs are high.

4.3.2 Storage and preservation

Bamboo is usually not harvested all the year around so that bamboo has to be stored during a period. The period when no bamboo is cut is usually in the rainy season, due to impassable roads.

Storage of fibrous raw materials is accompanied by degradation of the raw material. The manner of storage of the bamboo is important.

The bamboo bundles to be stored are stacked to a height of 6-8 metres, and one stack could contain 1000-2000 tons of bamboo. The distance between the stacks should be more than 30 metres, for fire protection.

4.3.3 Chipping

Chipping is a primary and vital operation in the manufacture of pulp. The quality of the final product, i.e., pulp or paper, and the cost of production are significantly dependent on chip quality.

Originally, chipping of bamboo was always carried out at the pulp mill, but there is now a tendency to install mobile chipping equipment in the forest and thus transport chips instead of bundles. Though the volume of bamboo chips often exceeds that of bamboo bundles, chipping in the forests would eliminate several problems since mechanization of bamboo handling is very difficult due to the nature of bamboo.

Chipping of green (fresh) bamboo is generally avoided due to the high fraction (about 10 %) of long slivers, resulting in relatively large amounts of oversize chips. Dried bamboo contains only about 3 % of slivers. However, the content of fines in green bamboo is only about 3 % (about 10 % on dried bamboo) due to the higher moisture content. Fines are usually not used so that the chipping of green bamboo may increased in interest. By the use of appropriate chipping equipment the content of long slivers may be reduced, and a more uniform size of the chips obtained.

However, while wood has a solid mass, bamboo is hard only on the outer crust and solid at the nodes. In order to break up the internodes and separate the fibre bundles and make them more accessible to chemicals during digestion, the bamboo stems are often crushed between heavy iron rolls prior to chipping. Between the nodes, bamboo is hollow with a soft material on the innerside of the crust. Bamboo, specially green bamboo, is rather elastic. For these reasons slightly modified wood chippers are not suitable for chipping of bamboo and create problems, e.g. blunted knives and chipping disturbances leading to varying quality and size of the chips. Variations in the diameter of the bamboo stems are also a problem.

The ideal chipper for bamboo, minimizing most of the problems, should be equipped with a suitable crusher ahead of the chipper to reduce the load on the knives. Variations in the diameter of the bamboo will cause little or no problem. With a variable speed feeding device after the crusher, it will also be easier to hold the bamboo stems in position and the chipper will be fed uniformly. Water conveyors and/or pressure jet nozzles may be used. An increase in moisture content leads to a considerable reduction in considerably the dust nuisance in the chipper house.

The advantage of chip washing is thus:

- removal of soil, sand and silica
- removal of fines.

The silica removal in chip washing is more efficient for dry bamboo than for fresh (green) bamboo. Soaking and agitation of chips result in a silica removal of 20-25 %.

Recycled white water may be used for washing the chips.

Screening leads to an efficient control of the chip quality.

The reject of nodes varies from 0.5 to 5 % of the bamboo stem.

4.4 Environmental problems

The handling of bamboo during transport, storage and preparation cause hardly any environmental problems.

The bamboo should be washed in order to remove sand and soil etc. This water will not cause high BOD discharges It should if possible be recirculated passing a sand trap.

A second washing of bamboo chips results in a dissolution of higher amounts of extractives due to greater exposed area. No information is available about BOD-discharges but they should cause no environmental problems. The consumption of washing water is about 10 m^3 /ton, which can be reduced by recirculation to different degees depending on the amount of sand and soil that accompanies the bamboo.

A problem connected with bamboo preparation is the dust coming from soil accompanying the bamboo or produced in the crushing and chipping, screening and conveying of the bamboo. This dust contains a rather high amount of silica. The amount of dust is reduced if the bamboo is kept wet and if this problem is considered in the design of the equipment.

5. PREPARATION OF STRAW, REEDS ETC

Straw, reeds etc are suitable raw materials for pulp production and give a short fibre pulp. The costs for collection and transport of these raw materials are considerable. The harvesting period is often very short, only a few weeks, which means that a large storage capacity is required.

During storage the raw material is degraded but this is avoided by wet storage. Straw is quite dry when harvested Reed can be harvested and dried in small bales before pulping and storage.

The raw material preparation in this case is limited to chopping and screening afterwards. If possible removal of lighter leafy material and nodes is desired.

Dust and sand should also be separated. A dry dusting and cleaning system is quite satisfactory for straw harvested by mechanical means. Straw manually harvested and cut ground level requires a wet cleaning system in case the straw contains a high percentage of sand and soil.

There are no water pollution discharges from the raw material preparation of straw, reed etc. The silica containing dust is a problem which appears in the handling of dry material and can be avoided in the design of the system.

6. REFERENCES

1. The Swedish Association of Pulp and Paper Engineers. "The use of bark" Report 18 (in Swedish). Stockholm 1972.

2. Rydholm S., Pulping process, Interscience Publishers, New York 1965.

3. The SSVL Environmental Care Project. Subproject 9. "Bark". "Closing of Wet Barking Plants" (in Swedish). Stockholm 1978.

4. B.C. Research. "Identification and Treatment of the Toxic Materials in Pulp and Paper Woodroom Effluents". CPAR Report 148-1 and 148-5. Vancouver 1973.

PART III - IN-PLANT MEASURES FOR SULPHITE PULPING AND RECOVERY

CONTENTS

1. INTRODUCTION

1.1 Scope and restrictions

Calcium base sulphite pulping was the dominant method of producing chemical pulps until the early 1960's. Because of the cheap raw materials used for preparation of cooking liquor, lime stone and sulphur, there was no incentive to recover these chemicals from the spent liquor. The spent liquor was normally sewered to the nearest river or lake and sulphur dioxide gas expelled from various points in the process was freely discharged to the atmosphere. In this way the sulphite pulp industry became a heavy polluter to both air and water.

The only purpose for recovery of spent liquor was to utilize the dissolved organics for the manufacturing of various chemical products (alcohol, Torula yeast, vanillin, glue products etc). To some extent it was also used for stabilization of road surfaces. In countries with high energy prices it could be economical to burn it for heat recovery.

The introduction of the more expensive soluble bases has necessitated the development of systems for a more complete recovery of both heat and chemicals. This development has been strongly promoted during the last twentyyears by a widespread recognition of the need for protection of the environment. Thus many sulphite mills have been virtually forced by legislation towards pollution, either to install means for an effective disposal or recovery of the spent liquor, or to close down.

Though the spent liquor is carrying an overwheling part of the polluting substances produced in sulphite pulp mills, there are a few other very important sources of pollution, e.g. condensates, bleach plant effluents and accidental spills. During the last two decades an enormous amount of development work has been carried out in efforts to reduce their impact on the environment.

The scope of this volume is to discuss and exemplify the pollution abatement technology for sulphite pulp mills. As a basis for this discussion, brief surveys of the processes and equipment applied must be made.

There are a great number of different sulphite pulping processes in operation. In this context, however, the emphasis has been judged to be the most important. In most cases the same methods for pollution abatement can be applied also in other sulphite processes, with minor changes. The different technology used in NSSC pulping is also reviewed.

1.2 Terms, units and abbreviations

Polluting discharges, chemical consumption etc, are often referred to in terms of a quantity of pulp produced, e.g. per ton of pulp. In this volume the expression "per ton of pulp" stands for "per metric ton of air-dry pulp", i.e. per 1000 kg of 90 % dry pulp.

The metric system is used throughout this volume. SIS units are applied, in some cases with conversion to other units within brackets.

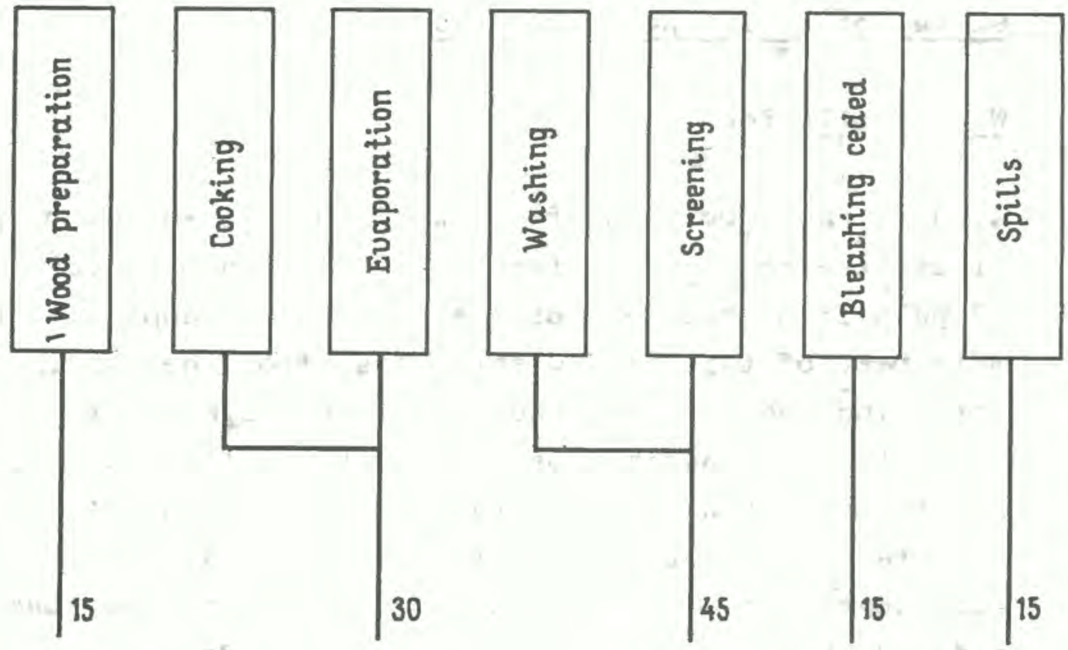
The abbreviation "ptp" is used for "per ton of pulp".

1.3 Survey of polluting discharges

1.3.1 Water pollution

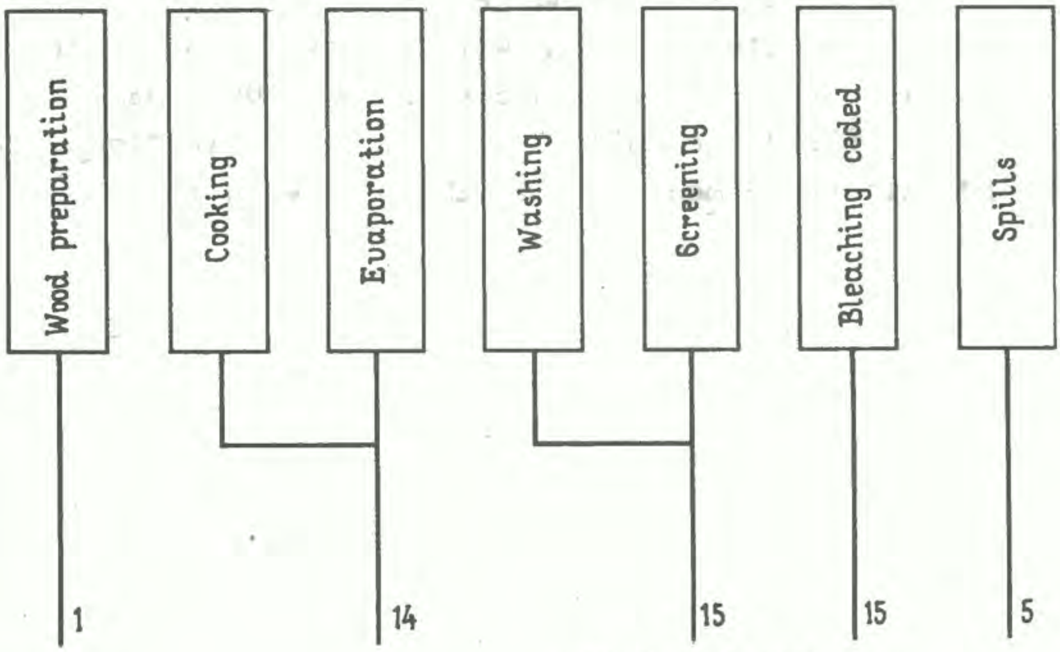
Acid sulphite pulping of softwood to paper-grade pulps gives rise to a total discharge of 300 kg BOD_7 per ton of pulp if no recovery of spent liquor is applied. The main part of this is a washing loss from the washing and screening departments. When a recovery system is installed the washing loss is substantially reduced, but on the other hand some of the polluting substances are transferred to the evaporation condensates. The pollution abatement effect of the recovery system is also reduced by accidental spills in various departments.

Figures 1.1 to 1.3 show typical BOD discharges from acid sulphite pulping of softwood to paper-grade pulps with three different levels of pollution abatement measures. In this comparison discharges from the wood preparation plant are included, which will otherwise not be discussed in this context as they are treated in UNEP Manual Part 2 (Volume 3). The comparison is summarized in Figure 1.4 and will be commented on in the following text.



Total: 120 kg BOD_7 ptp

FIGURE 1.1 Typical BOD discharges from a sulphite pulp mill of type no 1



Total: 50 kg BOD_7 ptp

FIGURE 1.2 Typical BOD discharges from a sulphite pulp mill of type no 2

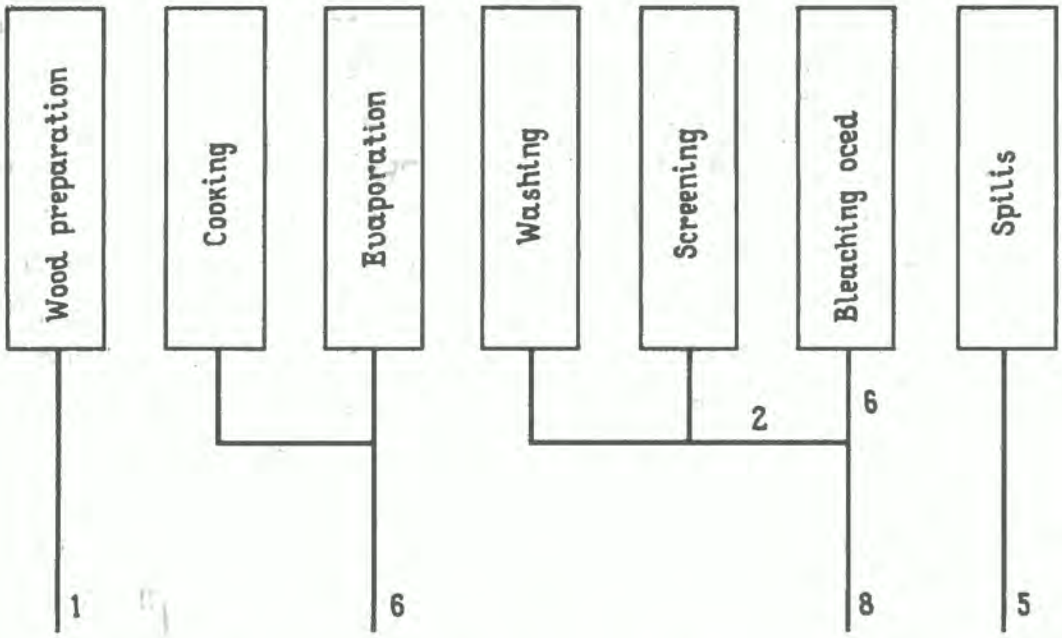


FIGURE 1.3 Typical BOD discharges from a sulphite pulp mill of type no 3

Position	Mill type		
	1	2	3
Wood preparation	15	1	1
Washing loss	45	15	2
Condensates	30	14	6
Bleaching	15	15	6
Spills	15	5	5
Total discharge	120	50	20

FIGURE 1.4 Comparison of BOD_7 discharges in kg ptp from sulphite pulp mills with different levels of pollution abatement

The case of mill type no 1 is to be regarded as an average situation for calcium base sulphite mills having a liquor recovery efficiency of 85 %, which means a washing loss of 45 kg BOD_7 ptp. This mill has a wood preparation plant with wet barking drums, and the bleaching is performed according to the conventional sequence CEDED. The evaporation and cooking condensates are discharged without any treatment and no special measures have been taken to prevent accidental spills. The total discharge of BOD_7 is about 120 kg ptp.

The mill of type no 2 has a pollution situation which is typical for soluble base sulphite pulp mills. The wood preparation plant is equipped with dry debarking machines, but the bark presses give rise to a small discharge. The spent liquor recovery efficiency has been increased to 95 % by installation of e.g. filter washers. The BOD content of evaporation condensates is reduced by neutralization of thin liquor prior to evaporation and a spills collection system has been installed. In this way the total discharge from a mill of this type has been reduced to 50 kg BOD_7 ptp.

Mill type no 3 represents the best available technology of today. In addition to neutralization of thin liquor the evaporation condensates are treated with stripping in order to further reduce their BOD content. Prebleaching with oxygen has been introduced and this stage has been included in the closed washing-screening system. A small remaining washing loss of about 2 kg BOD_7 ptp leaves the system via the open stages in the final bleaching. The final bleaching in itself gives rise to a discharge of 6 kg BOD_7 ptp. The total BOD_7 discharge from this mill is approximately 20 kg ptp.

1.3.2 Air pollution

Soluble based sulphite mills normally are more closed and the air pollution is much lower than in calcium based mills. The sulphur dioxide emitted from the liquor combustion can be as low as 1 - 2 kg SO_2 ptp under favourable conditions and quite normally it is between 5 and 8 kg SO_2 ptp. The dust emission with the flue gas is normally less than 1 kg ptp.

The best results reported so far have been obtained in a Swedish magnefite mill equipped with a combination of electro precipitator and venturi scrubber for dust separation followed by ball scrubber with four stages, where the majority of sulphur dioxide is adsorbed. In this way the sulphur dioxide emission from the combustion has been reduced to about 1 kg SO_2 ptp and the dust quantity is just around 10 g ptp.

Normal quantities of air pollutions from some types of sulphite pulp mills are reviewed in Figure 1.5.

MILL TYPE AND SOURCE OF EMISSION	Emission in kg ptp	
	SO_2	Dust
A. Calcium sulphite without liquor combustion		
Acid preparation	7 - 15	-
Pulp washing	2 - 6	-
Other sources	1 - 4	-
Total	10 - 25	-
B. Calcium sulphite with liquor combustion		
B1 Without flue gas scrubber		
Acid preparation	7 - 15	-
Pulp washing	2 - 6	-
Liquor combustion	60 - 120	70 - 100
Other sources	1 - 4	-
Total	70 - 145	70 - 100
B2 With flue gas scrubber		
Acid preparation	7 - 15	-
Pulp washing	2 - 6	-
Liquor combustion	15 - 30	1
Other sources	1 - 4	-
Total	25 - 55	1
C. Soluble based sulphite		
Liquor combustion	1 - 8	0.1- 1
Other sources	2 - 4	-
Total	3 - 12	0.1- 1

FIGURE 1.5 Air pollution from different sulphite pulp mills

2. COOKING

2.1 Sulphite cooking processes

Introduction

Sulphite cooking includes a great number of different processes. There are the acid sulphite processes in one stage with different bases (calcium, magnesium, ammonium or sodium) as well as the bisulphite and the neutral sulphite processes with magnesium or sodium as base. Furthermore there are two-stage and multistage cooking processes with combinations of acid, bisulphite or neutral stages. In two-stage and multistage cooking the base normally is sodium, but in some cases it is magnesium.

In this context, however, a survey will be given only of the one-stage processes with acid sulphite and the neutral sulphite process for semi-chemical pulping (NSSC).

Acid sulphite cooking

The one-stage acid sulphite cooking is usually carried out in stationary, batch (discontinuous) digesters with a volume normally varying from 50-60 m^3 up to 300 m^3 or more. The cooking procedure is a little different depending on the type of pulp to be manufactured and the kind of raw material used. The following description refers to a standard type of paper pulp from softwood.

The cooking starts with the filling of the digester with wood chips (or other fibrous raw material) from chip bins above the digester room. The filling is normally performed with the help of steam, which facilitates the charging and enables a more complete filling of the digester by packing the chips. The steam also expels air that is entrapped between and in the chips, so that the cooking liquor can penetrate into the chips more easily, which is essential for a uniform digesting.

Cooking liquor, with a composition of 1.0-1.2 % combined SO_2 and approximately 6 % total SO_2, is charged from the bottom of the digester (in order to remove still remaining air) up to a level that covers the chips. The temperature is then raised according to a specified schedule by means of direct or indirect heating with steam. To ensure a uniform temperature throughout the digester, the cooking liquor is extracted from the digester and pumped through an external heat exchanger (indirect heating). Figure 2.1 and 2.2 show two different ways of circulating the liquor through an external heat exchanger. When using direct heating, the steam is introduced directly into the digester or in the forced circulation pipe line outside the digester.

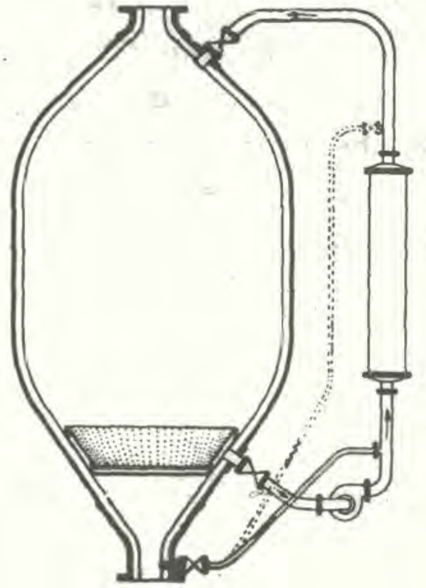


FIGURE 2.1 Sulphite digester with liquor circulation system according to Brobeck

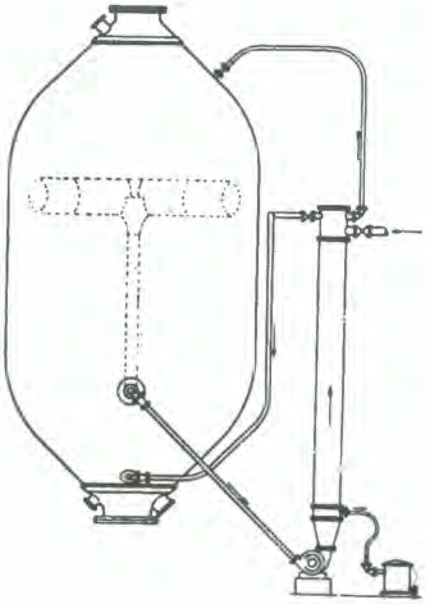


FIGURE 2.2 Sulphite digester with liquor circulation system according to NAF-Schauffelberger

During the heating period the digester pressure rises rapidly until the maximum allowed level, 0.5-0.7 MPa (5-7 kp/cm^2), is reached and the top relief valve is opened. The top relief gas goes to a pressure acid tank for preparation of new cooking liquor. At a temperature of about 105°C, when the chip level in the digester has decreased a little, the surplus of cooking liquor is drawn off and returned to the cooking liquor preparation.

When the maximum temperature (125-145°C) is reached, the steam is shut off. The cook procedes with the liquor circulation in operation until it is time for blow down. The digester pressure is then released by gassing down to that of the atmosphere. The relief gas from the blow down is cooled, and the condensate that contains various organic substances is taken care of. The non-condensed gas goes to the acid preparation.

At the end of the blow down, the spent liquor is drained from the digester. A preliminary washing of the pulp has already been carried out in the digester by displacement with weak spent liquor and hot water. After that the pulp is dumped to a pulp chest or blow pit with perforated bottom for further washing.

In the cooking of viscose (rayon) pulp, the main differences from paper pulp cooking is a lower content of combined SO_2, approximately 0.9 %, and a higher top temperature, around 148°C. The total cooking cycle is usually shorter for viscose pulps and takes 9-12 hours "from cover to cover", while it takes up to 20 hours in extreme cases for hemicellulose rich paper pulps, as for instance glassine paper pulp.

NSSC cooking

Neutral sulphite pulping is today the dominating process in semichemical pulping. Applied on hardwood the pulp yield is in the range of 65-85 %. The cooking conditions give the pulp a pronounced stiffness, which is of great importance in making corrugated board, for which purpose it is predominantly used.

The normal NSSC (Neutral Sulphite SemiChemical) pulping process consists of three steps

- a pressure impregnation of the chips with a cooking liquor of sodium sulphite and carbonate or bicarbonate
- a short digestion at rather high temperature (160-200 °C)
- a mechanical defibration (refining) to give pulp of the softened chips.

Many old sulphite mills with batch digesters have been converted to NSSC pulping. In these cases the cooked but undefibred chips are drained in pulp chests with perforated bottom and then transported to refiners by screw or chain conveyors.

A flow sheet of continuous NSSC pulping is shown in Figure 2.3.

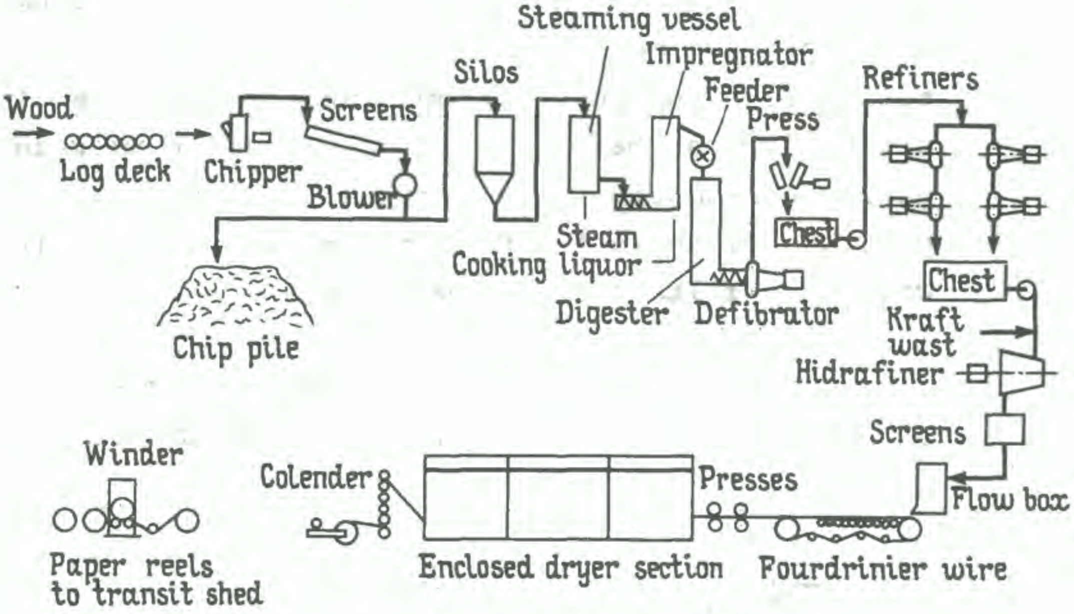


FIGURE 2.3 NSSC pulping principle flow sheet

Wood chips or other raw material enter a screw feeder, where they are impregnated with cooking liquor. In the case of screw digesters the concentration of the cooking liquor is fairly high so that the chips can be cooked in the vapour phase. In the Kamyr and Impco systems, however, the digesting is performed mainly in the liquid phase and consequently the cooking liquor can be weaker. Maximum temperature is adjusted according to the retention time in the digester and the pulp quality desired. In screw digesters the retention time is short (10-20 minutes) and the maximum temperature around 200°C. In vertical digesters the cooking time may be 1-3 hours at 160-175°C.

After cooking the chips are broken up by an impeller or a defibrator under full digester pressure. The pulp is then discharged into a blow tank and dewatered in a disc or screw press before refining. In order to reduce the energy consumption, the refining is performed at a temperature close to 100°C. After refining the pulp is washed on filters or screw presses.

The system shown in Figure 2.4 has been designed by Kamyr for higher production capacities of NSSC pulps.

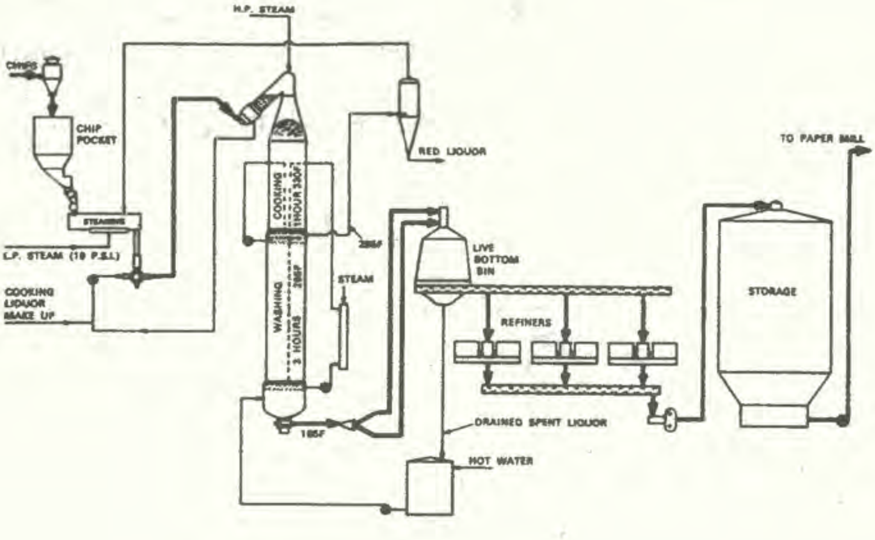


FIGURE 2.4 NSSC pulping system with Kamyr vapour/liquor phase digester

The digester is of the vapour/liquor phase type developed mainly for cooking of various sulphite pulps. Mechanically this digester is very similar to the Kamyr hydraulic digester normally used for sulphate cooking. The main difference is the design of the digester top, where a top separator is located outside the digester at an inverted and inclined position.

This makes it possible to drain off the excess liquor and feed only the impregnated chips into the digester, which thus operates with vapour phase further down. The digester is heated with steam added directly to the digester top. The first commercial full size NSSC digester of this type has been in operation at a Swedish mill since 1969 and has a nominal capacity of 450 tons per day.

A system for production of NSSC pulps for corrugating medium in a smaller scale developed by Kamyr is shown in Figure 2.5.

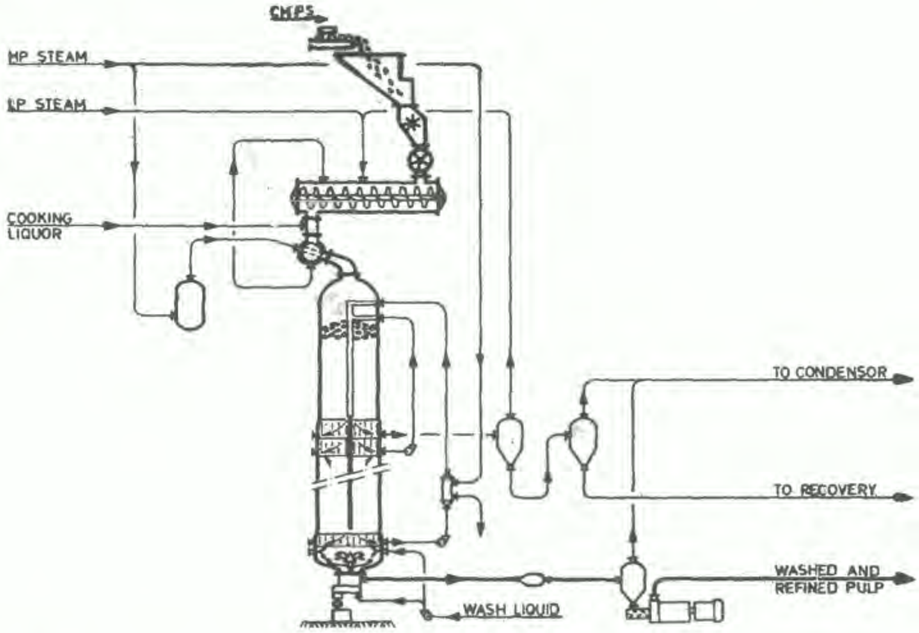


FIGURE 2.5 Kamyr system for smaller productions of NSSC corrugating medium

The chip feeding system and the steaming vessel are the same as in the standard sulphate digester. The cooking takes place partly in the vapour phase and partly in the liquid phase. The digester is equipped with a standard Hi-Heat washing, which means that the washing is performed in the digester. The chips are blown via a blow cyclone directly to the refiner at about 10 % consistency. It is interesting to note that in spite of the high yields for NSSC cooking, the Hi-Heat washing can still be very efficient.

The Kamyr continuous cooking unit for annual plants (straw) shown in <u>Figure 2.6</u> is a combined vapour and liquid phase digester very similar to the one described above. In this application, however, it is preceded by a preimpregnator. This is a double deck vessel equipped with two mixing and conveying screws on each deck. After cooking the stock is cooled by weak liquor injection prior to discharging, but no washing is done in the digester.

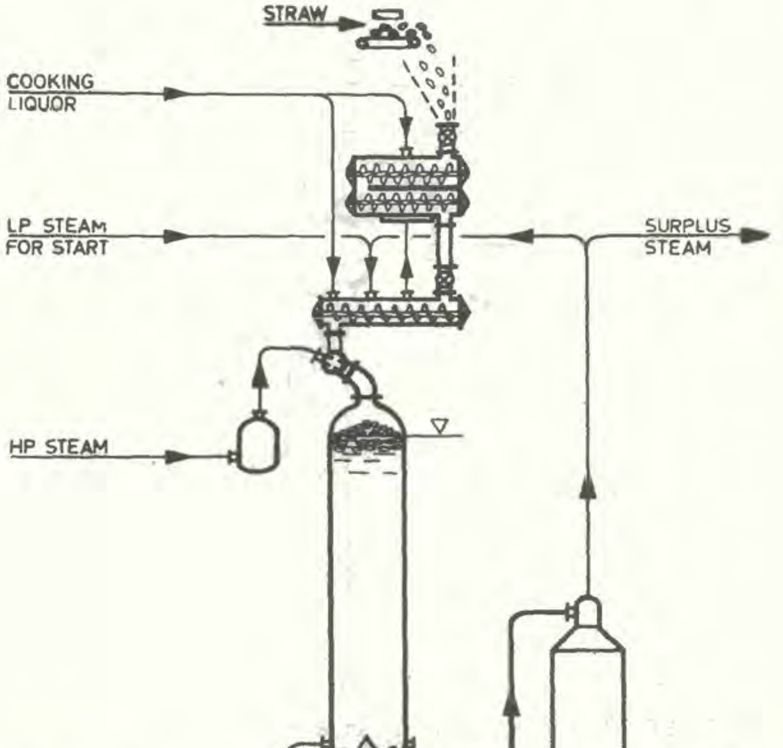


FIGURE 2.6 Kamyr continuous cooking unit for annual plants

Figure 2.7 shows a horizontal tube digester used for cooking annual plants or bagasse according to the Sunds-Defibrator system.

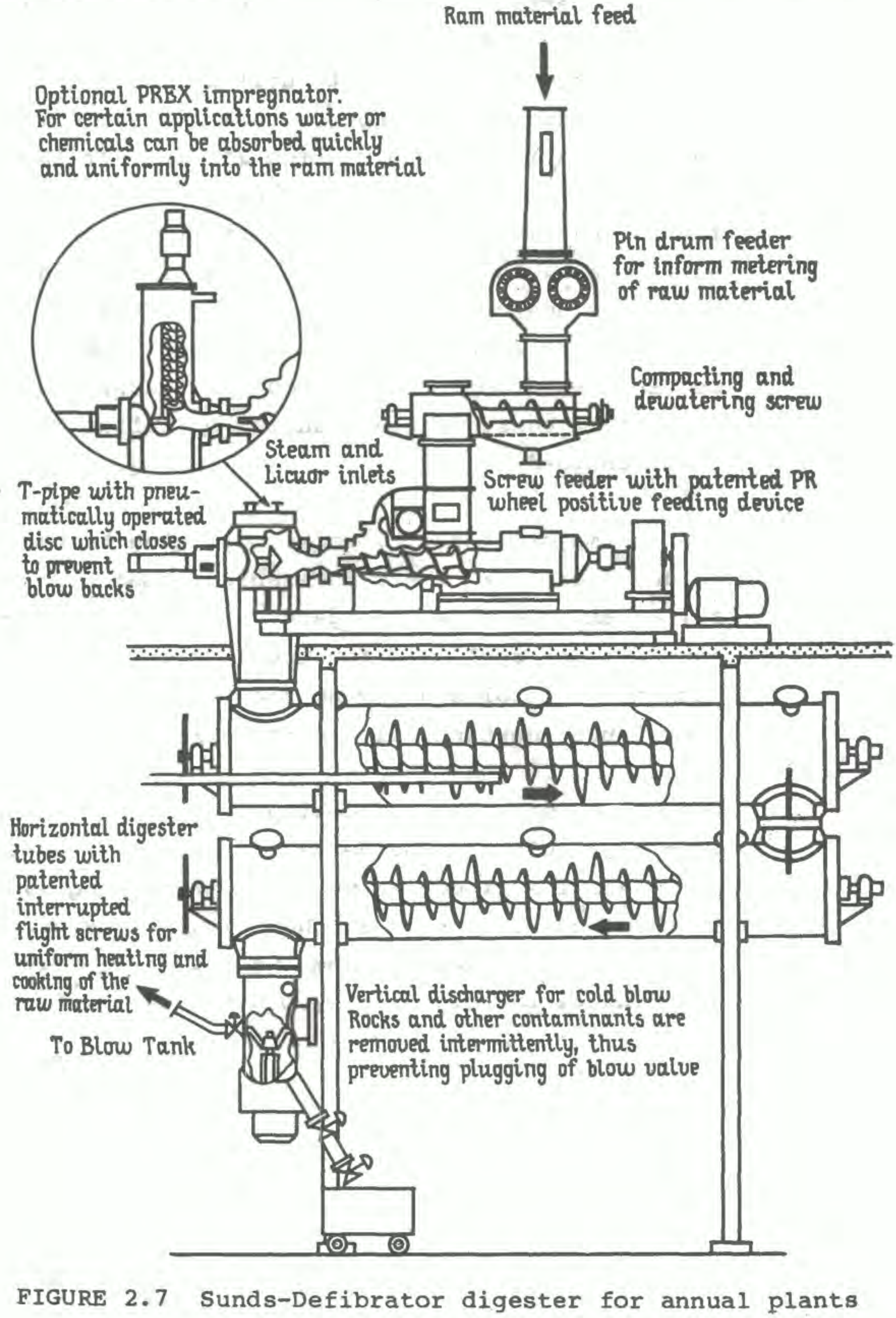


FIGURE 2.7 Sunds-Defibrator digester for annual plants

2.2 Polluting discharges from cooking

In the sulphite process with calcium base it is difficult to arrange an effective recovery of the spent cooking liquor due to problems with scaling. Furthermore, it may be possible to utilize the fuel value of the spent liquor, but not to regenerate the chemicals for preparation of new cooking liquor. For obvious reasons, it is therefore not usually economically justifiable to aim at a very efficient liquor recovery in such a case. As a rule the washing is carried out in the digesters and/or in pulp bins. In the worst cases the whole lot of spent liquor is let out to the recipient, but even when most of the liquor is recovered for burning, a considerable quantity of polluting material is discharged.

Another major source of water pollution is the cooking condensates, i.e. the condensable components of the top relief and the blow down gases. Part of these condensates may be reclaimed for the extraction of by-products such as methanol and cymene etc, but the remaining part contribute substantially to pollution.

Air pollution from the cooking department consists mainly of sulphur dioxide gas leaking from various points in the liquor as well as the gassing systems. Enormous quantities of sulphur dioxide gas are usually lost to the atmosphere from the blow pit during the emptying of the digester by blowing or dumping.

2.3 Antipollution measures

Polluting discharges of spent cooking liquor due to insufficient washing capacity can be reduced, either by increasing the quantity of washing liquor (water), i.e. increased dilution, or by installation of additional washing equipment. These two methods are further discussed in Chapter 3, "Washing and recovery of spent liquor". In many cases, however, the necessary prerequisite for the required improvement of the washing efficiency can be achieved only by switching from calcium to a soluble base.

Pollution from cooking condensates can be elimintated or reduced by treatment with ion exchangers. This method is further discussed for evaporation condensates in paragraph 6.4, "Treatment of contaminated condensates".

A still better way of taking care of the cooking condensates, which is applied in modern sulphite mills, is to recycle them to the preparation plant for cooking liquor. In this way the volatile polluting components are transferred to the evaporation condensats via the spent cooking liquor, and can be treated together. By using a pressure acid preparation station in three stages and applying a countercurrent system, the relief and blow down gases can be absorbed in fresh cooking liquor without cooling and separation of condensates.

2.4 Cooking liquor preparation

The preparation of raw acid for use in sulphite cooking with magnesium and sodium base will be dealt with in

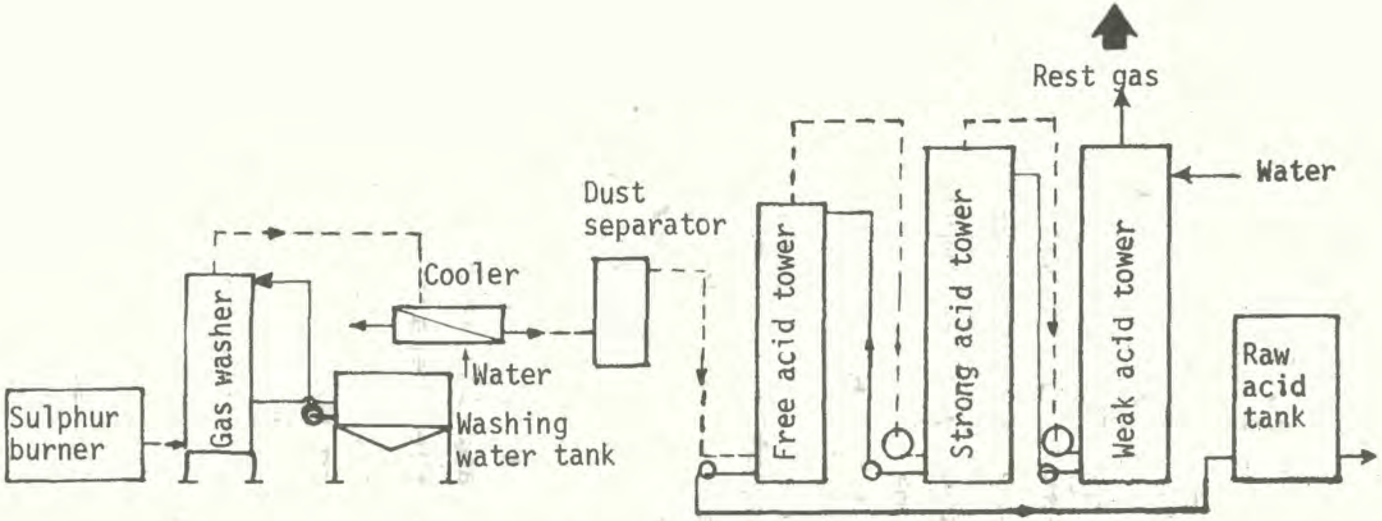


FIGURE 2.8 Raw acid preparation, calcium base

paragraph 7.4 and 7.5 where regeneration of chemicals in combination with combustion of spent liquor is discussed. The fortification of raw acid to acid sulphite pulping liquor follows the process normally used for preparation of calcium sulphite liquor, which will be briefly described in this paragraph.

Raw acid for calcium sulphite cooking is made from sulphur dioxide and lime stone. The sulphur dioxide gas is usually produced by roasting pyrite or by burning sulphur. Sometimes liquid sulphur dioxide can be used. After cooling and washing of the roast gas it is reacted with lime stone in towers where water is sprayed from the top, Figure 2.8.

Typical analyses of tower acids are 4.0-4.2 % total and 1.5-1.6 % combined SO_2. The high content of combined SO_2 is later reduced when the acid is diluted with side reliefs from the digesters, before being charged to a new cook.

Fortification of the total SO_2 content up to the 6-7 % normally required is carried out in a pressure acid system, where top relief gas and blow down gas are absorbed in the raw acid. This system operates with a series of acid tanks, where the gases are absorbed in counter current to the flow of acid. A system with two pressure tanks is shown in Figure 2.9. With the installation of a third pressure tank in a Swedish mill the need for cooling the gases has been eliminated and consequently the pollution problem with cooking condensates has disappeared.

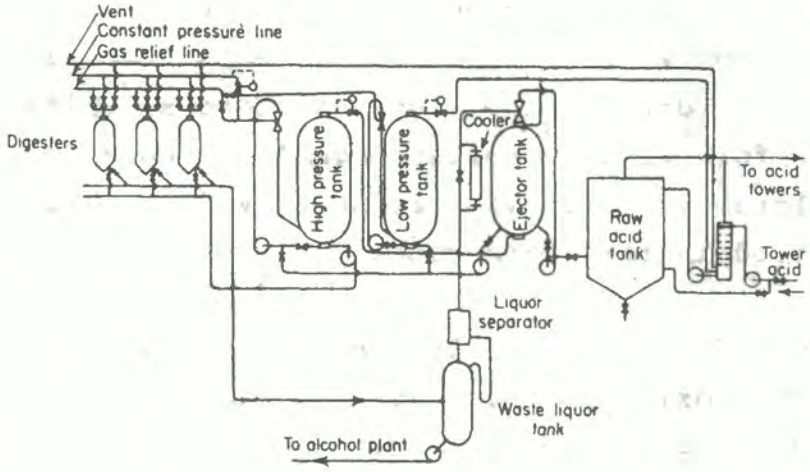


FIGURE 2.9 Pressure acid system

Literature, reference list, Chapter 2

(1) Rydholm, S.
Pulping processes
Interscience Publishers, New York 1965

(2) SSVL
The Environmental Care Project, Technical Summary, Stockholm 1974

(3) SSVL
Skogsindustrins miljövårdsprojekt. Systemslutning i kokeri-tvätteri-sileri (in Swedish), Stockholm 1973

(4) Haas, H.
Continuous acid sulphite pulping
TAPPI October 1970, Vol 53, No 10, 1857

(5) van Eyken, H.
Continuous magnefite for newsprint
Pulp and Paper Magazine of Canada, September 1964

3. WASHING AND RECOVERY OF SPENT LIQUOR

3.1 Background

After cooking of semichemical and chemical pulps, the spent cooking liquor contains dissolved organic and inorganic substances, the quantity of which can be quite considerable. For sulphite paper-grade pulps of softwood with a pulp yield of 52 % on wood, the total quantity of dry solids in the original spent liquor is about 850 kg per air dry ton of pulp. These dissolved substances may cause serious water pollution if they are not taken care of and destroyed. Furthermore, they are of considerable value if recovered and burnt for steam production. The inorganic chemicals may also be of great value as raw material for the preparation of new cooking liquor. This however, depends on the base used in cooking.

Thus the washing process serves several purposes. Firstly, the dissolved substances present in the pulp suspension after the cooking must be separated from the pulp before any further treatment like screening, bleaching or paper making can be performed. Secondly, chemicals and organic matter should be taken care of and destroyed in order to avoid pollution of the effluent from the mill. In most countries this is a necessity according to environmental protection legislation before permission is given to run the mill. Thirdly, the spent liquor may be recovered for evaporation and incineration in order to produce heat from the organic matter and to re-use the chemicals in the preparation of new cooking liquor.

The primary reason for washing, to obtain a pulp free of soluble impurities, is of course most essential, but it has made less impression on the washing methods used because the subsequent operations, especially the screening, involve repeated dilution and concentration of the pulp which has the same effect as a continued washing. Leaving out the ordinary washing process, however, would affect the efficiency of both screening and bleaching, and would not be acceptable from the viewpoints of stream pollution or chemicals and heat recovery.

Ever since the sulphite process was introduced, calcium has been the dominating base. This is explained by the fact that limestone has been cheap and easily available as well as sulphur. Because of that sulphite mills have, as a rule, been much worse with regard to water pollution than sulphate mills. This is mainly caused by difficulties in arranging an effective recovery of spent liquor in the sulphite process with calcium base, due to problems with scaling.

Furthermore, no practicable method for regeneration of the chemicals has been available, and the fuel value of the liquor dry substance has not bu itself been a sufficient economical inducement for advanced liquor recovery.

Originally the liquor from the digester was just sewered except when it was used for fermentation and ethanol production. With the increasing cost of external fuels, attempts have been made to make use of the fuel value of the organic part of the liquor. In a number of calcium based mills equipment has been installed for collection of the liquor from the digesters or the blow pit and subsequent evaporation of the recovered liquor and burning of the organic dry substance.

In this way about 85 % of the liquor dry substance is withdrawn from the effluent, but still the remaining part causes serious pollution - in addition to BOD containing condensates from the evaporation and sulphur dioxide from the burning. Attempts have been made to increase the efficiency of the liquor recovery systems but they have often failed because of the high deposits of calcium sulphate in the liquor systems and evaporation plant.

The introduction of soluble base has greatly changed the conditions for the recovery of spent cooking liquor in sulphite mills. Owing to a reduced scaling tendency, it has become possible to apply the same technology as in sulphate mills, and in addition, the higher value of the chemicals has provided an economic incentive for the installation of more efficient washing equipment. Thus filter washers have become common, and in some mills Hi-Heat washing and continuous diffusers are used. In certain applications, as in combination with oxygen bleaching, it has been found advantageous (or necessary) to install presses of various types for washing. These presses can be of the screw, roll, cylinder or disc type.

3.2 General principles

If the aim of the washing operation only is to remove dissolved substances and the washing liquor not have to be taken care of for economical or other reasons the washing procedure can be made very simple. This is, however, usually not the case. On the contrary, there are many restrictions tied to the washing process:

- The pulp should be as free as possible from dissolved impurities of any kind, as they will negatively affect the following processing of the pulp.
- As much as possible of the removed impurities, including ray cells and lost prime fibres, should be reclaimed in order not to pollute the effluent.
- The use of washing liquor should be minimized for economical reasons.
- The reclaimed dissolved substances should be as concentrated as possible in order to facilitate the destruction of polluting material and to minimize the cost of evaporation for subsequent burning and recovery of chemicals.
- The loss of prime fibres should be minimized.

It is well known that in order to gain one thing another thing will have to be sacrificed. Likewise it is quite obvious that in washing the recovered amount of dry substance is in opposition to the concentration of the recovered liquor.

Thus, when the spent cooking liquor is to be recovered for evaporation and burning, the aim must be to have as much as possible of the dry substance at the lowest possible dilution. Every volume of washing water accompanying the original spent liquor to the evaporation will of course cost steam.

From the mill's point of view, the efficiency of the liquor recovery is primarily a question of economics. The greater the value of the dry substance, the higher the dilution (the quantity of water to be evaporated) that can be afforded, and the more advanced the equipment that can be installed.

The process of washing can be of two fundamentally different types, either a displacement, or a washing with successive dilution and thickening. A practical washing is likely to consist of both types.

An ideal displacement washing implies that the washing liquor successively replaces the original liquor in the pulp bed by pushing it ahead of itself without any mixing of the two liquors. The ideal displacement is, of course, never achieved, but for a good displacement efficiency it is essential to avoid channelling in the pulp layer, and also to avoid excessive mixing of original liquor and washing liquor.

The former aim is fulfilled by uniform packing in the blow pit or diffuser. To avoid mixing liquors it is important to maintain as great a difference as possible in the density of original liquor and washing liquor. If the liquor to be recovered is heavier than the washing liquor, as in most cases of sulphite spent liquors, displacement with washing liquor should be carried out from above, whereas with very cold washing liquor and hot sulphite spent liquor the reverse is true and the best displacement is carried out from below.

Another factor to prevent excessive mixing between the original liquor and washing liquor is the rate of flow, which is as important as the density difference. Besides the risk of channelling at high flow rates it is found that a uniform flow also results in less washing efficiency at a higher rate, probably because of turbulence around individual fibres. Slow diffusion from the interior of the fibres into the surrounding liquor may also be a limiting factor for higher flow rates. Obviously these circumstances limit the displacement efficiency of the filter washer, and affect the capacity of digester, blow pit and diffuser washing as well.

The extent of displacement in filter washing is likely to be less than in diffuser washing, because flow rates 10 to 100-fold that of a diffuser are applied. Therefore multistage washing on filters is necessary to achieve the same result as in a diffuser. It has also been suggested that a retention volume for diffusion should be placed between the filters.

Presses of the screw, roll or disc type are normally not equipped for displacement operations. The effect here is entirely limited to dilution and compression of the pulp. However, they have the advantage of guaranteeing a forced flow from the luminae of the fibres, the content of which in the other types of washing processes is left mainly to diffusion and capillary flow.

Even with presses the entire liquor volume of the pulp does not mix with the dilution liquor. Practical experience indicates that up to about 0.3 m^3 per ton of pulp does not take part in the mixing before and under a press stage, although there is evidence of almost complete mixing in other cases. The difference probably depends on the mixing device prior to the press, and on the manner of liquor addition, which ought to follow directly upon the previous pressing stage.

3.3 Definitions of terms used

The schematic flow sheet shown in Figure 3.1 is an illustration of the washing process with the main flows of liquor, pulp and solids content into and out from a washing plant. Designations used in the Figure will be used throughout the following discussion. Other terms and definitions that will be used in the following, are listed in Figure 3.2.

In the sulphite industry the recovery traditionally is expressed as substance yield, designated U (4), which is in the ratio of solids content in the recovered liquor, S_3, to the original spent liquor from the digester, S_o. Usually U values about 0.75-0.98 are obtained, complete recovery corresponds to U=1.0.

The dilution of the recovered liquor is characterized by the concentration quotient, f, which is the concentration ratio of the recovered liquor, C_3, to the original spent liquor from the digester, C_o.

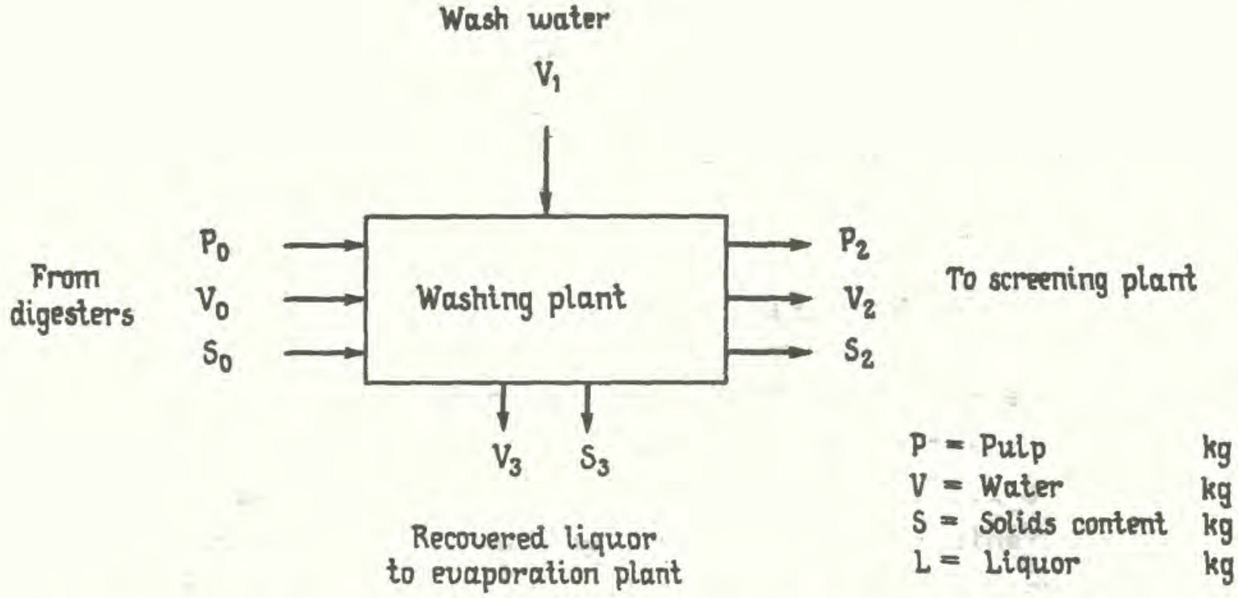
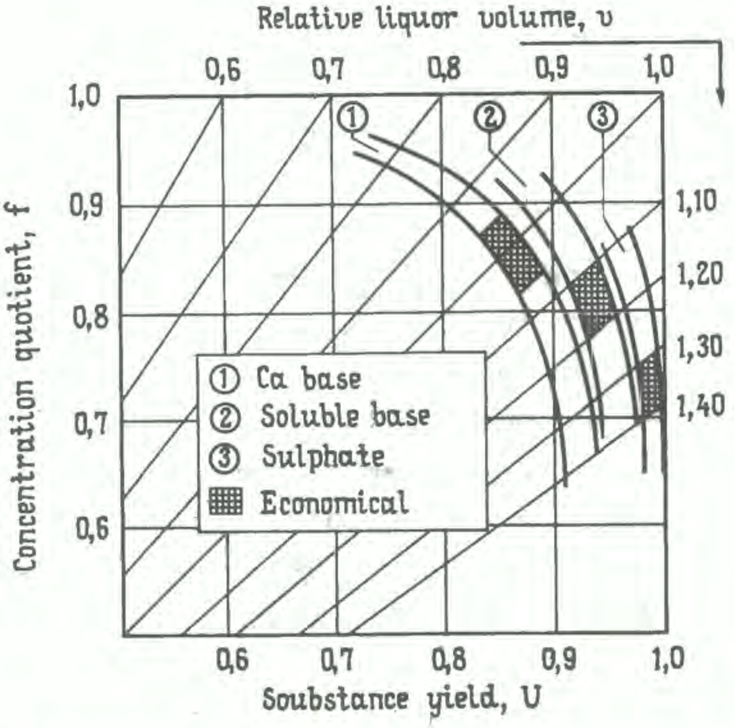


FIGURE 3.1 Principle flow sheet for a washing plant

Term	Definition	Remark
Original liquor	$L_0 = V_0 + S_0$	
Liquor lost	$L_2 = V_2 + S_2$	with outgoing pulp
Recovered liquor	$L_3 = V_3 + S_3$	to the evaporation
Substance yield	$U = S_3/S_0$	
Dry content	$DS = S_3/L_3$	of recovered liquor
Displacement ratio	$DR = \frac{C_0 - C_2}{C_0 - C_1}$	
Concentration quotient	$f = \frac{S_3 \times (V_0 + S_0)}{(V_3 + S_3) \times S_0}$	

FIGURE 3.2 Terms and definitions in washing

The result of the washing can be illustrated by a diagram of the type shown in Figure 3.3, where a certain recovery system is represented by a curve of corresponding values for U and f. It is obvious that the more liquor extracted from a system, the higher the substance yield (U) and the lower the concentration quotient (f) obtained. An f value below 0.8 is seldom economically motivated in efficient sulphite liquor recovery (4).



FIGUR 3.3 Liquor recovery diagram

Another term that is often used to characterize sulphite pulp washing, is the relative liquor volume, v, which is the volume of liquor recovered in relation to the volume of original liquor in the digester.

The point on the washing curve, where U=f (and v=1.0) is said to represent the efficiency of the system. The closer to the upper right corner of the diagram the curve, the more efficient the washing.

In Figure 3.3 curves are shown, which represent normal washing systems of calcium based and soluble based sulphite mills as well as sulphate mills. The diagram also shows the economical limit for the recovery, i.e. the highest U values, which are justified by the value of liquor dry substance in relation to the marginal cost for evaporation of an extra quantity of water. It is obvious that calcium based mills have an economical limit at a relative liquor volume, v, around 1.0, while it may be 1.1-1.2 for soluble based mills. In sulphate mills it could be economically justified to go as far as to v=1.3 or even 1.4.

There are several reasons for the difference between sulphate and soluble based sulphite mills regarding the washing efficiency that it is possible to reach with a reasonable economic effort. As a rule the sulphate process gives a higher quantity of dry substance in the spent liquor per ton of pulp. This will induce a higher capital cost and a higher U-value at the same quantity of dry substance lost. Furthermore the sulphite pulp can be more difficult to wash and may, because of that, give a higher loss in the same type of equipment.

In addition to that, sulphite recovery equipment requires more expensive construction materials, because of the more corrosive liquors and gases.

The economical limits of recovery systems will be further discussed in paragraph 3.6.

Another way to illustrate the recovery result is demonstrated in Figure 3.4. There the washing loss is given as a function of the dilution factor (DF). These terms are normally used in sulphate mill practice. The washing loss is the total loss of dry substance after washing, most of which is left in the pulp. In other terms it equals (1-U) times the original quantity of dry substance in the digester. It is usually expressed in kg DS per air-dry ton of pulp. The dilution factor is the amount of washing water (counted in tons per ton of air-dry pulp), which accompanies the recovered liquor to the evaporation.

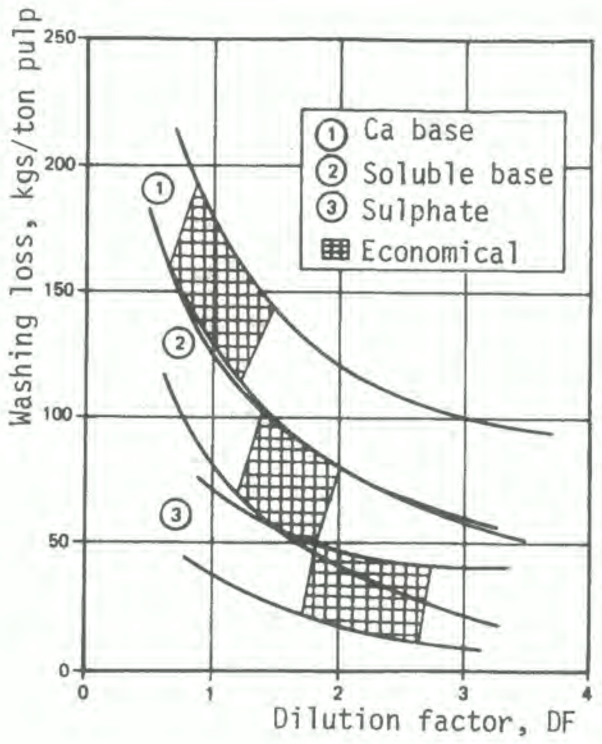


FIGURE 3.4 Washing loss diagram

The curves shown in Figure 3.4 correspond to those in Figure 3.3, i.e. they represent the same washing systems described in different ways.

The term displacement ratio, DR, has been introduced to characterize the displacement effect of a single washing apparatus. If the liquor concentration of the in-going pulp (C_o % solids content) is reduced to that of the washing liquor (C_1 % solids), the difference (C_o-C_1) is the maximum reduction possible. However, this is never achieved, and the concentration of the liquor in outgoing pulp (C_2 % solids) is always higher. The resulting reduction is C_o-C_2 and the displacement ratio, DR, is calculated according to the formula:

$$DR = \frac{C_o - C_2}{C_o - C_1}$$

Normal DR values for filter washers are 0.6-0.8 at a dilution factor of 2.0-2.5. The displacement ratio is increased by higher dilution factor and is reduced by air mixed into the pulp, e.g. by foaming. It is also influenced by pulp characteristics and specific filter loading.

3.4 Washing practice

Introduction

The problems involved in washing and spent liquor recovery are essentially the same as those of separation of dissolved substances from suspended particles, which are faced in most processing industries. For instance the sulphate industry in the beginning borrowed washing equipment, diffusers, from the sugar industry. In the sulphite industry, however, the liquor has been drawn from the digester and replaced with hot water, or drained from the blow pit, where the pulp is washed with water. This technique of washing in the digester or in the blow pit has been predominantly used until recently, when antipollution legislation has enforced improvements of the washing efficiency beyond the limits of this system.

Besides the digester and blow pit washing, filter washing and pressing are in common use for sulphite pulp washing. During the last decade also the same type of equipment as is used in the sulphate industry has been introduced, i.e. Hi-Heat washing in continuous digesters and continuous diffuser washing. A special type of continuous belt washer has been developed.

The technique for sulphite washing on filters and in continuous diffusers is very much the same as for sulphate pulp washing and will not be discussed here. Nor will the equipment be described. For details of construction and function of these machines the reader is referred to appropriate textbooks and to volume 3 of this series of handbooks. Only processes and equipment typical for the sulphite pulp industry will be treated in this chapter.

Digester and blow pit washing

The digester washing decreases cooking capacity and is used in mills where the digesters are not the bottle neck of the production, and where the digesters are comparatively small and numerous. Usually one intermediate washing with weak liquor should be applied before hot water is introduced. A high temperature in the washing liquors is beneficial, especially when displacement from the top is practised.

Blow pit washing has the advantage of working on defibrated pulp, which is easier to wash. Under optimal conditions, however, practically the same results have been achieved with digester and blow pit washing. The best results reported on blow pit washing is a substance yield factor of U=0.93 with a concentration quotient of f=0.86 as a long-term average.

To achieve recovery results corresponding to U=0.97-0.99, which are necessary in the recovery of cooking chemicals, in a reasonable time, diffusers or filters have to be used. A moderate improvement over a simple digester washing can be achieved by serial displacement.

Serial displacement in digesters

The efficiency of the recovery system, and hence the cost, is decided by the substance yield (U-value) required from an environmental point of view. If U=0.8 is sufficient, a simple digester washing like the one in

Figure 3.5 will do, but if U=0.9 is required, a better system is needed, as for instance serial displacement in digesters, seen in Figure 3.6. After blow down of digester no 1, it is washed with weak liquor from digester no 2, which has previously been prewashed. Strong liquor is extracted from digester 1 to the evaporation. When a suitable quantity of liquor has been taken from digester 1 to the evaporation, digester 2 is disconnected and its content of ready washed pulp is dumped the blow pit or pulp chest.

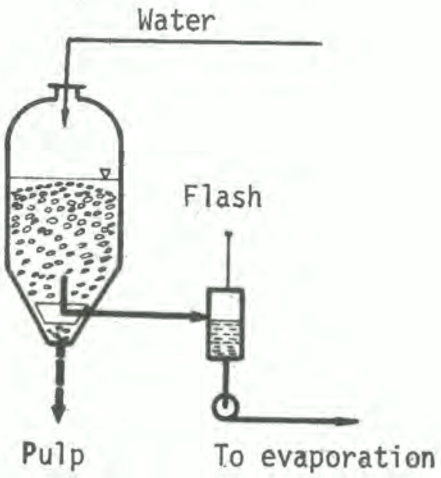


FIGURE 3.5 Digester washing

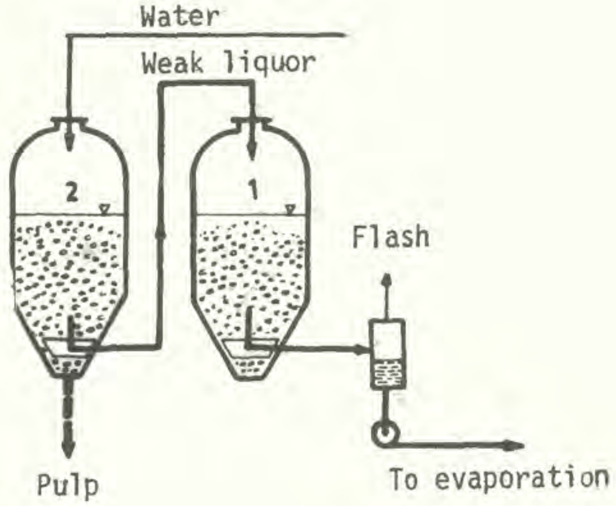


FIGURE 3.6 Serial displacement in digesters

As the next digester has been blown down, it is placed in the position no 1 in the displacement process. The former digester 1 will become no 2 and the displacement is continued (5).

A waiting time is inevitable in this process as two digesters must always be connected to each other during the washing. Thus, serial displacement is best suited for mills with many digesters. If there are a few digesters only, the waiting times will be too long. In such cases the weak liquor can be extracted from digester 2 and stored in a layered tank until the next digester is ready for washing. The result is reported to be just slightly deteriorated (5).

The serial displacement technique can be applied in calcium as well as in soluble base mills.

Examples of digester and blow pit washing as well as serial displacement in digesters will be given in paragraph 3.5.

Horizontal belt washer

The development of this new pulp washing and liquor collection technology was carried out in Canada and the first full scale installation was completed in 1974 in the sulphite mill of the Ontario Paper Co Ltd., Thorold, Ont. It has been reported to be a very successful installation with an advantageous system of liquor recovery (3).

The two horizontal belt washers in use at Ontario Paper were designed for a maximum total production rate of 350 oven-dry tons per day (odtpd) but normally operate at 220-270 odtpd. Each washer handles one half of this production. The washers have a 1.2 meters wide drainage area and are 14.0 meters long. Each washer has two 0.6 meter wide continuous rubber drainage belts. The surface of the belts consists of evenly spaced canals to carry the spent liquor. A row of evenly spaced holes in the centre of each belt line up with the slot in the two vacuum boxes under the washer table. Vacuum is applied to the vacuum boxes from a common vacuum system.

The drainage belts are driven by a variable speed hydraulic drive at a normal operating speed of 10-15 meters per minute. The speed is varied to maintain a 5-8 cm thick pulp pad and to control the vacuum level. An open mesh polyester drainage fabric is located on top of the two drainage belts. This fabric is the filtering medium which prevents fibres from entering the spent liquor system.

With the installation of horizontal belt washers, it was necessary to change the method of blowing the digesters as well as handling the hot stock. Prior to and during blowing, about 45 m^3 of spent liquor is pumped into the top and bottom of the digester as a blowing aid. During blowing, an additional 115 m^3 of spent liquor is pumped into the blow line to reduce the consistency in the blow tanks to 4-5 %.

The pulp and spent liquor slurry is pumped to the washer head boxes via an intermediate storage tank using a fibrilizer. This unit operates as a pump and is also breaking down some of the chips present in the hot stock. Under normal operating conditions, each washer is supplied with 1700-1900 litres per minute of pulp and spent liquor slurry at 3.5-4 % consistency. The slurry is distributed over the width of the headbox and then flows onto the moving drainage fabric-belt combination.

The table of the belt washer and the vacuum boxes are divided into six sections down the length of the washer. The first is the formation section where the strongest spent liquor is removed without the use of any washing liquor. This liquor is recycled back to the digesters after cooling in a plate type heat exchanger. After the formation section five washing stages follow. The pulp pad entering each stage is flooded with a curtain of washing liquor from the wash box located at the beginning of the section. The liquor removed from any stage is used as washing liquor in the previous stage. On the final (fifth) wash box hot water (70°C) is used. In this way countercurrent washing is achieved.

Washed pulp is discharged from the end of the washer at 14-16 % consistency.

Spent liquor from the first washing stage is used for production of chemical byproducts (alcohol and vanillin) and is finally evaporated in the chemical recovery plant.

The dissolved solid in the washed pulp is in the range of 30-35 kg DS per oven-dry ton of pulp. This corresponds to 2.5-3.0 % of the spent liquor solids available in the digester. Losses of spent liquor due to packing gland leaks, etc., are estimated at less than 1 % of spent liquor. During two years of operation the dilution factor has averaged 0.75 (10.6 % dilution). Average reported liquor recovery is 93 % but because of seasonal variation in spent liquor concentration in the digester, this recovery has varied from 95-96 % during the warm months of the year to 86-87 % during the coldest three months of the year.

The replacement of blow pit washing with the belt washers has resulted in a decrease in the BOD loading of the sulphite mill sewers from 15-20 tons per day to 5-6 tons per day.

The sulphite mill at Ontario Paper is capable of producing 250 oven-dry tons per day (odtpd) of pulp using four 155 m^3 digesters. Of the production, 180 odtpd are used for newsprint manufacture and the remainder is processed for outside sales.

The belt washing technology related above is marketed on a world-wide basis by Powlesland Engineering Ltd, 23 Westmore Drive, Rexdale, Ont., M9V 3X7.

NSSC pulp washing

In washing semichemical pulp consideration must be given to the combination with refining. As long as stream pollution presents no objection, the soft chips in the blow tank are passed over a drainer conveyor to the refiner and the spent liquor is allowed to drain to the sewer. However, where stream pollution is a problem, or when spent liquor recovery is profitable, the soft chips are refined in the hot spent liquor, sometimes after passing through a breaker trap for coarse fiberizing, and the spent liquor is recovered from the refined pulp by conventional methods. As continuous cooking is general for semichemical pulps, the continuous washing systems on filters or presses, or combinations thereof, are natural.

3.5 How to improve the washing efficiency - case studies

Introduction

When a sulphite mill is enforced by law to reduce its water pollution, an improvement of the washing and liquor recovery system usually is a key problem. The choice of way to solve this problem mainly depends on the base, whether it is calcium or soluble. In some cases the best way may be to switch from calcium to a soluble base. Such a change will fundamentally simplify the washing problem but involves heavy investment in a chemical recovery system. The choice of way also depends on the status of the existing washing system, whether it can be improved sufficiently by installation of additional equipment or has to be replaced by a complete new system.

Calcium based system

In the early history of the sulphite process the spent cooking liquor was just allowed to drain from the digester. In that way as much as 40 % of the dry substance could be recovered. Later it was found that the recovery could be approximately doubled by a technique using weak liquor for displacement. First the concentrated liquor is drained and taken care of for evaporation. Then weak liquor from a previous cook is added to the digester while the recovered liquor is still taken to the evaporation plant. When the concentration of the draining liquor has decreased to a certain level the washing is continued with water and the draining liquor is collected in a weak liquor tank to be used for washing of the next cook. Using this technique as shown in Figure 3.5, a recovery (U-value) of 0.83 often can be reached.

This washing technique can be further improved with the use of more weak liquors with different concentrations. It has a drawback, however, in that the digester can not be used for cooking during the washing. The time "cover to cover" is prolonged and extra digester volume is required. To overcome this, pulp bins with perforated bottoms and equipment for distribution of washing liquor have been used. The digester is emptied into the bin when the cook is ready, and the pulp is washed while the digester is being filled with chips for a new cook. Displacement with one weak liquor can give an efficiency of 0.84-0.86 and U-values around 0.90 are possible if the relative liquor volume is increased to v more than 1.

Another technique that may be a solution to the washing problem in some old calcium based mills is serial displacement in the digesters, as is shown in Figure 3.6. Two digesters at a time are used for washing. After having delivered its liquor to the evaporation plant digester 1 is placed in position 2 and the next digester ready for washing takes position 1. The efficiency of this system is 0.86-0.88. Almost the same result can be reached by displacement with layered weak liquor. The concentration gradient then is maintained by using a tank with intermediate bottoms for collection of the liquor.

Serial displacement in the digesters requires plenty of digester volume as two digesters at a time are out of production all the time of the liquor recovery. To reach high U-values channelling must not occur in the pulp bed and the pulp should be easily drained and homogenous. If these pre-requisites are not met the result will not reach the level mentioned above.

By increasing the recovered liquor from volume to v = 1.25-1.30 it has under favourable circumstances been possible to reach substance yields close to 0.96. The evaporation of the huge quantities of liquor when v =

1.25 requires an evaporation capacity that is much higher than is normal in relation to the pulp production. Usually on can not expect better results than substance yields around 0.90-0.92 in serial displacement with reasonably high liquor volumes (v= 1.10-1.15).

If even better washing results should be required more efficient and advanced equipment must be installed as for instance filter washing. This can not, however, be recommended for calcium based mills because of the serious scaling troubles that have been met where this technique has been tried.

Soluble based systems

When a calcium sulphite mill is changed to soluble base it can for economic reasons be advantageous to keep the washing system in digesters and bins but increase the number of weak liquors to get a better substance yield without the use of too much water. In this way it is quite possible to reach U-values of 0.90-0.92 at a relative liquor volume of v=1.15 (Figure 3.7).

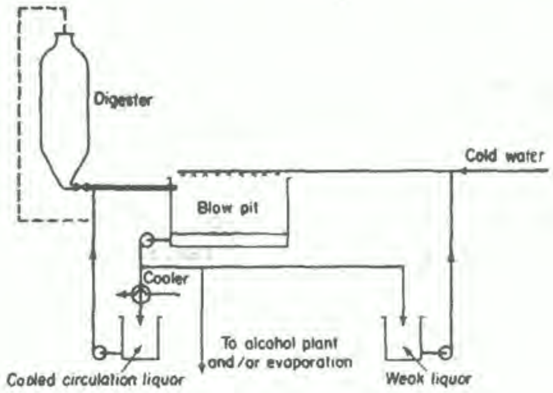


FIGURE 3.7 Blow pit washing

If this result is not sufficient the solution can be to install a filter washer (drum washer) after the digester and blow pit washing system. After completed displacement in the blow pit or pulp bin the pulp is diluted with filtrate from the filter washer and is then pumped to the filter. There it is dewatered in the usual way and washed with water that is fed through spray nozzles. For dilution the filtrate is also used as the last washing liguor in the bin system. Some buffer volumes are needed for pulp as well as for liquor to compensate for variations in the flow caused by the periodically operating bin system being connected to a continuously working filter washer.

The efficiency of the system can be improved by using a filter washer with two or three washing zones where the filtrate from one zone is fed as washing liquor to the previous zone in countercurrent to the pulp flow, Figure 3.8.

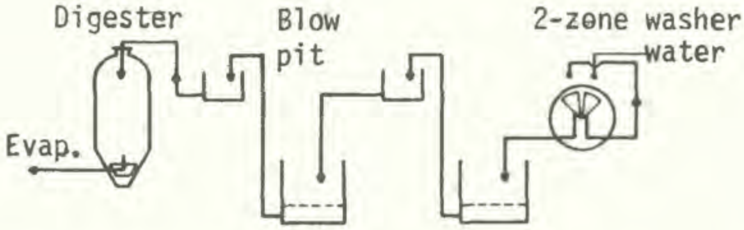


FIGURE 3.8 Digester and blow pit washing with additional 2-zone filter washer

In some cases even more filters are used in series following the bin washing system, Figure 3.9.

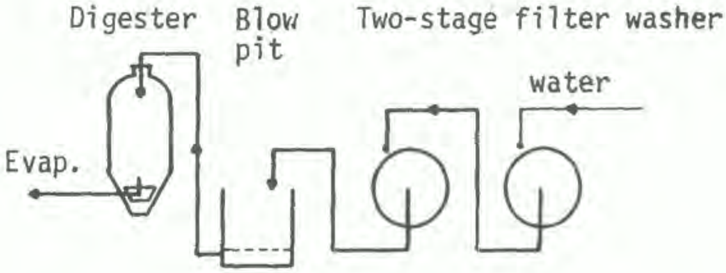


FIGURE 3.9 Digester and blow pit washing followed by filter washers in two stages

This is, however, a rather expensive solution considering the oveall efficiency of the system compared to a pure filter washing system.

In the following some examples (case studies) will be given of experience obtained in sulphite mills where various solutions to the washing problem have been tried.

In a magnesium base mill a 2-zone filter was put in after an existing washing system with three weak liquors, one in the digester and two in the bin. The existing system had a washing loss of 120 kg per ton of pulp (U=0.90), and was modernized in various respects in connection with the filter installation. It was shown that the loss could be reduced down to 21 kg per ton at a dilution of 1.8 tons per ton of pulp (v=1.2 U=0.98). Normally a washing loss of 30 kg per ton could be expectea with a system of this type (U=0.97). In spite of the number of weak liquor used in this case, the system proved to be reliable and easy to operate.

In other mills with more normal bin washing systems and one weak liquor only, an additional filter washer can reduce the washing loss to 65-105 kg per ton of pulp. If the loss from the existing system is higher than 180-240 kg per ton of pulp more than one filter will probably be needed to reach the same level.

In mills where the old digester and bin washing system has been abandoned usually the same technique with filter washing as in the sulphate industry has been adopted. In some cases, however, bins are still in use to collect the pulp from batch digesters prior to the filter washing.

A magnesium based mill producing high yield pulp with a Roe-number of 21 has installed a filter washing system. At this high yield the pulp is not quite defibrated and is consequently very difficult to wash. The liquor recovery is performed in the digester, bin refiner and on three filter washers. The refiners for defibration of the pulp are placed between the bin and the filters. For this mill a loss of 55 kg per ton of pulp (U=0.93) has been achieved at the very low dilution of 0.5 tons per ton of pulp. This result corresponds probably to a loss below 40 kg pei ton (U=0.95-0.96) as a mean value with a dilution of 1.5 tons per ton of pulp.

Another mill has installed a system consisting of a blow tank and three filters. The raw material is spruce and the pulp is cooked with sodium base to a Roe number of

10-11. With a dilution of 3.6 tons per ton of pulp (V=1.6) a loss of 23 kg per ton of pulp was obtained (U=0.98). It has been possible to keep the quantity of recovered liquor so high because of overcapacity in the evaporation plant and extremely low evaporation costs. Under normal conditions the result should correspond to a loss of approximately 50 kg per ton of pulp (U=0.95).

In a magnesium based mill the pulp is cooked to a Roe number of 7 and is blown to a tank before the washing filters. The three filters are of the 2-zone type and consequently each filter has two filtrates. Under normal conditions the washing loss is 35 kg per ton (U=0.97).

In the final example the mill has completely renewed its fibre line and throughout applied the sulphate technique. A continuous digester with countercurrent Hi-Heat washing zone has been installed. From there the pulp is blown directly to a continuous diffuser washer operating in two stages. The Hi-Heat washer has a retention time of three hours at nominal production. As the digester has an overcapacity with the present production the retention time is four hours, which should have a favourable effect on the washing result. At a dilution of 1.5-2.0 tons per ton of pulp the washing loss is as low as 45 kg per ton of pulp (U=0.96). As the circumstances are far from normal it is difficult to say what the result would be at nominal conditions.

3.6 Increased dilution or additional equipment - an economical comparison

In the following a comparison from economical points of view will be given of two possible ways to improve the liquor recovery efficiency, viz.

- increasing the washing liquor volume, i.e. increasing the dilution
- installation of additional washing equipment.

The decision of how to increase the recovery capacity is closely related to the local conditions of the mill, with regard to process and space available as well as economical view points. The cost may differ so much from one case to another that it is impossible to make a general statement on the economy. Thus it should be borne in mind that cost estimations given in this paragraph are indicative only. In actual cases, the cost of complete filter washing stage has been in the range of USD 1-2 million for a capacity of 200-300 tons of pulp per day.

From the investment cost point of view, the cheapest way to reduce the washing loss is to increase the volume of washing water thereby increasing the dilution of the recovered liquor. A prerequisite for the use of this principle is that the evaporation capacity is sufficient or can be increased in a reasonable way. In a batchwise operation there must as well be sufficient time for extraction of an increased amount of liquor.

Increased dilution

In general, the most economical dilution is achieved when the value of the last quantity of dry substance recovered, equals the extra cost of evaporation for its recovery. In sulphite mills with soluble base this balance is usually reached at a dilution factor of 0.5-1.5 tons per ton of pulp (v=1.05-1.20). As soon as an evaporation plant is in operation, its capital costs are invariable and are not influenced by a variation in the dilution. Thus the marginal evaporation cost does not include any capital cost, and so it is economically advantageous to wash the pulp to a dilution factor which is somewhat higher than the plant was calculated for, as long as the evaporation capacity is sufficient.

In the following example a magnesium based mill has a washing system that gives a washing loss of 140 kg per ton of pulp (U=0.88) at a dilution factor of 1.0 ton per ton of pulp (v=1.05 approx.). If the washing loss should be reduced to 105 kg per ton of pulp (U=0.91), an increase in the dilution factor of 1.5 tons per ton of pulp is required for most normal washing curves. The marginal extra cost of investment for the corresponding extension of the evaporation capacity would have been about USD 0.4 million for the 19 tons per hour extra quantity of water to be evaporated in a 300 tons per day mill. It is difficult to say what the cost would be of an extension made later on, but it is always more expensive. Including consequential investments in the boiler house, the total investment cost has been estimated at USD 0.8 million.

From the cost/income calculation shown in Table 3.1, it is evident that the increased evaporation cost caused by the higher dilution is USD 485 000 per year, which corresponds to USD 3.2 per ton of water evaporated. The total cost increase (capital + costs of operation and maintenance) is USD 640 000 per year, while the value of the increased chemical recovery is USD 395 000 per year (USD 113 per ton of dry solids). Thus the net cost increase is USD 245 000 per year or USD 2.45 per ton of pulp. The increased chemical recovery of 3 500 tons per year corresponds to a BOD reduction of about 880 tons per year. The cost of this pollution abatement is consequently USD 280 per ton of BOD.

If the dilution is further increased, the cost rises very rapidly in relation to the improvement achieved. The possibility of reducing the pollution by this technique is consequently rather limited.

TABLE 3.1 Cost/income calculation for an increased dilution in order to reduce the washing loss from 140 to 105 kgs per ton of pulp. Pulp production: 100 000 tons per year (300 tpd)

Investment cost	USD	800 000
Capital cost	USD/year	130 000
Evaporation cost	USD/year	485 000
Maintenance	USD/year	25 000
Value of chemicals recovered	USD/year	395 000
Net cost	USD/year	245 000
Net cost per ton of pulp	USD	2.45
Net cost per ton of BOD reduction	USD	280

Installation of extra equipment

In the same mill as in the example above, one could instead choose to install an extra filter washing stage. In such a case it should be possible to reduce the washing loss down to 85 kg per ton of pulp (U=0.93) without any increased load on the evaporation plant. The investment cost is estimated at USD 1.7 million.

As is shown in the cost/income calculation in Table 3.2, there is just a little increase in maintenance in addition to the capital cost, adding up to USD 330 000 per year. The value of chemicals recovered, however, is USD 620 000 per year, which leads to a calculated net profit of USD 290 000 per year for the installation.

TABLE 3.2 Cost/income calculation for the installation of an extra filter washer in order to reduce the washing loss from 140 to 85 kg per ton of pulp. Pulp production: 100 000 tons per year.

Investment cost	USD	1 700 000
Capital cost	USD/year	280 000
Evaporation cost	USD/year	0
Maintenance	USD/year	50 000
Value of chemicals recovered	USD/year	620 000
Net cost reduction	USD/year	290 000

3.7 Possible pollution reductions

The total amount of polluting substances in the pulp after cooking that should be removed and reclaimed in the washing process has a BOD_7 of 250-550 kg ptp depending on the type of pulp produced, the lower the pulp yield, the higher the BOD value. Simple washing systems like digester and blow pit washing and serial displacement washing in digesters can give a substance yield of 0.90 or even more under favourable circumstances. This means that the remaining impurities in the pulp can be reduced down to a level of 25-50 kg BOD_7 ptp.

To achieve a substance yield of 0.95+ it is necessary to apply more advanced washing equipment like filters, presses and diffusers. In new installations of belt washers a substance yield of 0.98 is guaranteed, which means that the remaining of impurities can be reduced to around 5-10 kg BOD_7 per ton of pulp.

3.8 Washing plant calculations

In this paragraph some calculations regarding washing practice, that may be useful in environmental as well as economic considerations, are exampled. For definitions of terms used, see paragraph 2.3 and Figure 2.2.

A. Fuel value of dry solids (DS) in spent liquor from acid sulphite cooking of paper pulp

Heat value: 4 300 Mcal per ton of DS (4)
Fuel value of dry solids in concentrated liquor with 55 % DS at 90°C:

$$\frac{4\ 300 \times 0.55 - 550 \times 0.45}{0.55} = 3\ 850 \text{ Mcal per ton of DS}$$

Steam generation in a recovery boiler with 85 % efficiency:

$$\frac{3\ 850 \times 0.85}{580} = 5.6 \text{ tons of low pressure (LP) steam per ton of DS (1 ton of steam = 580 Mcal)}$$

Evaporation capacity of generated steam in a quintuple effect evaporation plant with a specific steam consumption of 135 Mcal per ton of water:

$$\frac{3\,850 \times 0.85}{135} = 24 \text{ tons of water per ton of DS}$$

Fuel value compared to oil. 1 ton of heavy fuel oil has a heat value of 40.8 GJ (9750 Mcal) and costs USD 200. In a normal oil fired boiler with 90 % efficiency its steam generation capacity is:

$$\frac{9\,750 \times 0.90}{580} \text{ tons of LP steam per ton of oil, and}$$

consequently the fuel value of dry solids in spent liquor compared to oil is:

$$\frac{200 \times 580 \times 3\,850 \times 0.85}{9\,750 \times 0.90 \times 580} = \text{USD } 74.58 \text{ per ton of DS, or generally } 37.3\ \% \text{ of the oil price.}$$

B. Value of chemicals in spent liquor from magnesium based acid sulphite cooking of paper pulp

Inorganic content (ashes) of dry solids: 12-14 % (1), in these calculations assumed to correspond to 130 kgs of MgO per ton of DS.

Price of MgO: USD 260 per 1 000 kgs.

Value of MgO in spent liquor (MgO recovery efficiency in the recovery system is 99 %):

$$0.13 \times 260 \times 0.99 = \text{USD } 33.46 \text{ per ton of DS}$$

Sulphur content of dry solids: 8 % (1)

Sulphur price: USD 70.0 per 1 000 kgs

Value of sulphur in spent liquor (sulphur recovery efficiency in the recovery system is 95 %):

0.08 x 70.0 x 0.95 = USD 5.32 per ton of DS

Total value of chemicals in spent liquor:

33.46 + 5.32 = USD 38.78 per ton of DS

C. Value of chemicals and fuel in spent liquor from magnesium based sulphite cooking of paper pulp

Fuel (A):	USD 74.58 per ton of DS
Chemicals (B):	USD 38.78 per ton of DS
Total:	USD 113 per ton of dry solids

D. Value of chemicals and fuel in spent liquor from other cooking processes

In the same way as demonstrated above, corresponding values of dry solids in spent liquor from some other cooking processes have been calculated. The results are summarized below.

Calcium based acid sulphite paper pulp:

Fuel	USD 75 per ton of dry solids
Chemicals	not recovered

Magnefite paper pulp:

Fuel	USD 59 per ton of dry solids
Chemicals	USD 56 per ton of dry solids
Total	USD 115 per ton of dry solids

NSSC paper pulp:

Fuel	USD 49 per ton of dry solids
Chemicals	USD 32 per ton of dry solids
Total	USD 81 per ton of dry solids

Sulphate paper pulp:

Fuel	USD 67 per ton of dry solids
Chemicals	USD 27 per ton of dry solids
Total	USD 94 per ton of dry solids

E. Evaporation cost for extra water in spent liquor recovered

The marginal investment cost of an evaporation plant, including consequential investments in steam generation capacity, is estimated at USD 40 000 for 1 ton/h of water evaporated, if the extra capacity is planned from the beginning.

The capital cost of this investment at a 10 years depreciation period and 10 % interest, i.e. 16.3 % annuity, is USD 0.163 x 40 000 per year, or:

$$\frac{0.163 \times 40\,000}{8\,400} = \text{USD } 0.78 \text{ per ton of water evaporated}$$

The maintenance cost is estimated at 3 % of the investment cost, i.e. USD 0.03 x 40 000 per year, or

$$\frac{0.03 \times 40\ 000}{8\ 400} = \text{USD } 0.14 \text{ per ton of water evaporated}$$

The extra electricity required is 4 kWh per ton of water evaporated and the corresponding cost is (1 kWh = USD 0.03):

4 x 0.03 = USD 0.12 per ton of water evaporated

At an oil price of USD 200 per ton, and a specific steam consumption of 135 Mcal (565 MJ) per ton of water evaporated, the evaporation cost is (cf. section A):

$$\frac{200 \times 135}{9\ 750 \times 0.90} = \text{USD } 3.08 \text{ per ton water evaporated}$$

Summarizing:

Capital cost	USD 0.78 per ton of water
Maintenance cost	USD 0.14 per ton of water
Extra electricity cost	USD 0.12 per ton of water
Evaporation (oil) cost	USD 3.08 per ton of water
Total cost	USD 4.12 per ton of water

F. Lowest concentration of liquor recovered

From an economical point of view the lowest concentration of spent liquor to be recovered is the point at which the content of dry solids has sufficient value to pay for the water evaporation cost.

With a dry solids concentration of C % in the last volume of liquor recovered and 55 % DS in the concentrated liquor, the amount of water to be evaporated is:

$$\frac{100 - C}{C} - \frac{100 - 55}{55} \text{ tons of water per ton of DS.}$$

If the evaporation plant is already installed, the capital cost is invariable and should not be included in the marginal evaporation cost, which is USD 3.34 per ton of water with the assumptions made in section E.

For a spent liquor from sulphite cooking of paper pulp with magensium base the dry solids value is USD 113 per ton according to section C. Thus the lowest concentration of liquor to be recovered is calculated as follows:

$$\frac{100 - C}{C} - \frac{100 - 55}{55} \times 3.34 = 113;$$

$$\text{and } C = \frac{55 \times 3.34 \times 100}{113 \times 55 + 100 \times 3.34} = 2.81 \%$$

In the same way the corresponding lowest concentration of spent liquor from other processes have been calculated with the following results:

Calcium base acid sulphite	4.1 %
Magnefite	2.8
NSSC	3.8
Sulphate	3.3

Literature reference list, Chapter 3

(1) Sveriges Skogsindustriförbund
Yrkesbok Y-206 Tvättning av massa (in Swedish)
Markaryd, Sweden, 1979

(2) SSVL
The environmental care project, Technical Summary
Stockholm 1974

(3) Sexton, E.A. and Wilkinson, E.G.
Spent liquor recovery at Ontario Paper
Pulp and Paper Canada January 1980, Vol. 81, No. 1, 86

(4) Rydholm, S.
Pulping processes
Intescience Publishers, New York 1965

(5) Jönsson, S-E
Pollution problems in small sulphite mills (in Swedish)
Norsk Skogsindustri No. 11 1971, 336

4. SCREENING

4.1 Introduction

The main purpose of the screening process is to remove impurities from the pulp. These impurities are of various types. Some of them have their origin in the wood, as for instance knots, undercooked chips, shives, bark fragments and "dirt" particles from resin deposits. Others are of mineral (sand and stones) or metallic nature.

In addition to the removal of impurities, it is quite common, especially in the manufacture of sulphite pulp from resinous softwood, to remove ray cells in connection with the screening. These cells cannot be considered as impurities in a proper sense but, if they are left in the pulp, they will give rise to serious impurities by causing resin deposits and dirt specks.

For these purposes a great variety of machinery has been developed, such as knotters, fine screens of various kinds, centricleaners and ray cell filters. Refiners, frotapulpers and other machines are also used for treatment of rejected knots and wood particles. Dewatering filters or deckers, as well as presses are exploited for the final separation of the screened pulp from the "white water". However, this machinery will not be further discussed in this context. For details on construction and function the reader is directed to appropriate textbooks and manufacturers' bulletins.

The screening operations are usually carried out in very dilute suspensions at pulp consistencies varying from

0.2 to 2 or 3 %. Therefore huge quantities of water are involved and the consumption of electric energy for pumping is considerable. The water demand, however, can be substantially reduced by system closure, i.e. recycling of the white water. At the same time, water pollution can be considerably decreased, which will be further discussed later on.

4.2 Screening principles

Usually one single screen is not sufficient to obtain the result desired. Depending on the fibre raw material, the cooking process, the pulp quality and the cleanliness required among other factors, a more or less complex combination of different screens and other machines is necessary.

Besides the demand for cleanliness of the pulp, the loss of acceptable fibres with the discharged reject should be minimized for economical reasons. In other words, the separation of impurities from the prime pulp should be as selective as possible. These demands are usually fulfilled by using a multistage screening system. Principally this involves a primary screening to remove the impurities as completely as possible, followed by a secondary screening of the rejected material, where accompanying prime fibres are separated from the impurities and returned to the main pulp stream. Sometimes it has even been found necessary to rescreen the reject from the secondary screens on tertiary screens for further reduction of the fibre losses. These concepts are illustrated in Figure 4.1.

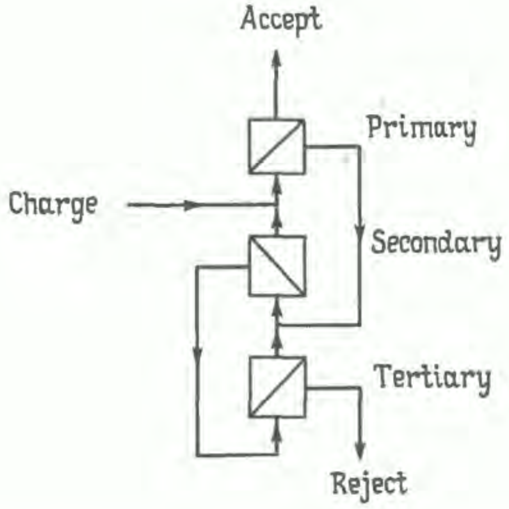


FIGURE 4.1 Coupling principle of primary, secondary and tertiary screening stages

However, the accepted pulp from the primary screening may not have sufficient purity to meet the requirements. In such cases, rescreening of this accept will be necessary. This double screening is usually practised in the manufacture of high quality unbleached or semibleached pulps, when the bleaching effect is not sufficient to remove small shives. A simplified system of double screening in combination with secondary screening is shown in Figure 4.2.

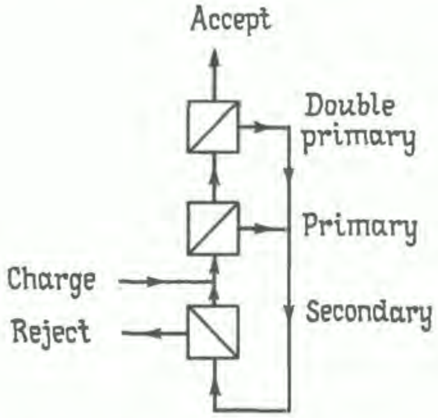


FIGURE 4.2 Principle of double screening and secondary screening.

4.3 Screening practice

Strong sulphite pulps of paper-grade type have a great deal of fibre bundles left after the cooking and should be pretreated with some kind of defibration prior to screening. In this kind of pulp the knots are still comparatively hard, and the risk of their being crushed during defibration, is not great, and there is little risk of creating an increased number of impurities.

Dissolving pulps on the other hand, have a lower Kappa number, and the fibres are almost free from each other. Besides the knots are softer and more sensitive to crushing. Consequently this kind of pulp is usually knotted, i.e. knots are separated on knotter screens, without any pretreatment.

As a rule, the only pretreatment of sulphite pulp before the screening is a cautious kneading in a separator (opener) or a double mixer. High yield sulphite and NSSC pulps, however, need some refining for fibre separation prior to the screening. This can be performed in an in-line disintegrator between the blow tank and the washing. The energy consumption is low, about 20 kWh per ton of pulp and the treatment does not have any beating effect on the pulp.

In mill practice a screening system of the type described above, normally is preceded by a coarse screening on some kind of knotters in order to remove knots, undercooked chips and any other coarse impurities prior to the fine screening system. After rescreening of the reject to recover accompanying prime fibres, the coarse reject is usually treated separately in some way that will be discussed below.

Figure 4.3 illustrates the principles of a modernized sulphite mill screening system, which is rather well closed. This is achieved by the use of modern pressure type screens in the primary as well as in the secondary stages. The accepted pulp from the primary screens is deresinated on ray cell filters and then goes to bleaching via a decker (dewatering filter) and a storage tower.

An open knotter screen is used for the reject from the secondary screens. The knotter accept is cleaned in a two-stage centricleaner installation of the big cleaner type. After dewatering and refining the accept is returned to the main pulp stream.

The knotter reject and possibly the final reject from the second centricleaner stage can be utilized for production of knotter pulp. In other cases it is burnt in bark burning boilers. The coarse reject from sulphite pulp screening is normally not sent back to the digesters for recooking, as is quite often the case with sulphate pulp coarse reject.

White water from the dewatering filters is collected in a white water tank (not shown in the figure). It is used for internal dilutions in the screen room as well as for transportation of pulp from the washing department to the screen room. The surplus of white water obtained is freed from its fibre content on a special type of fibre filter and is then sewered.

4.4 Deresination

Pitch trouble is a very common problem in sulphite pulp manufacture. It is mainly caused by resinous deposits in

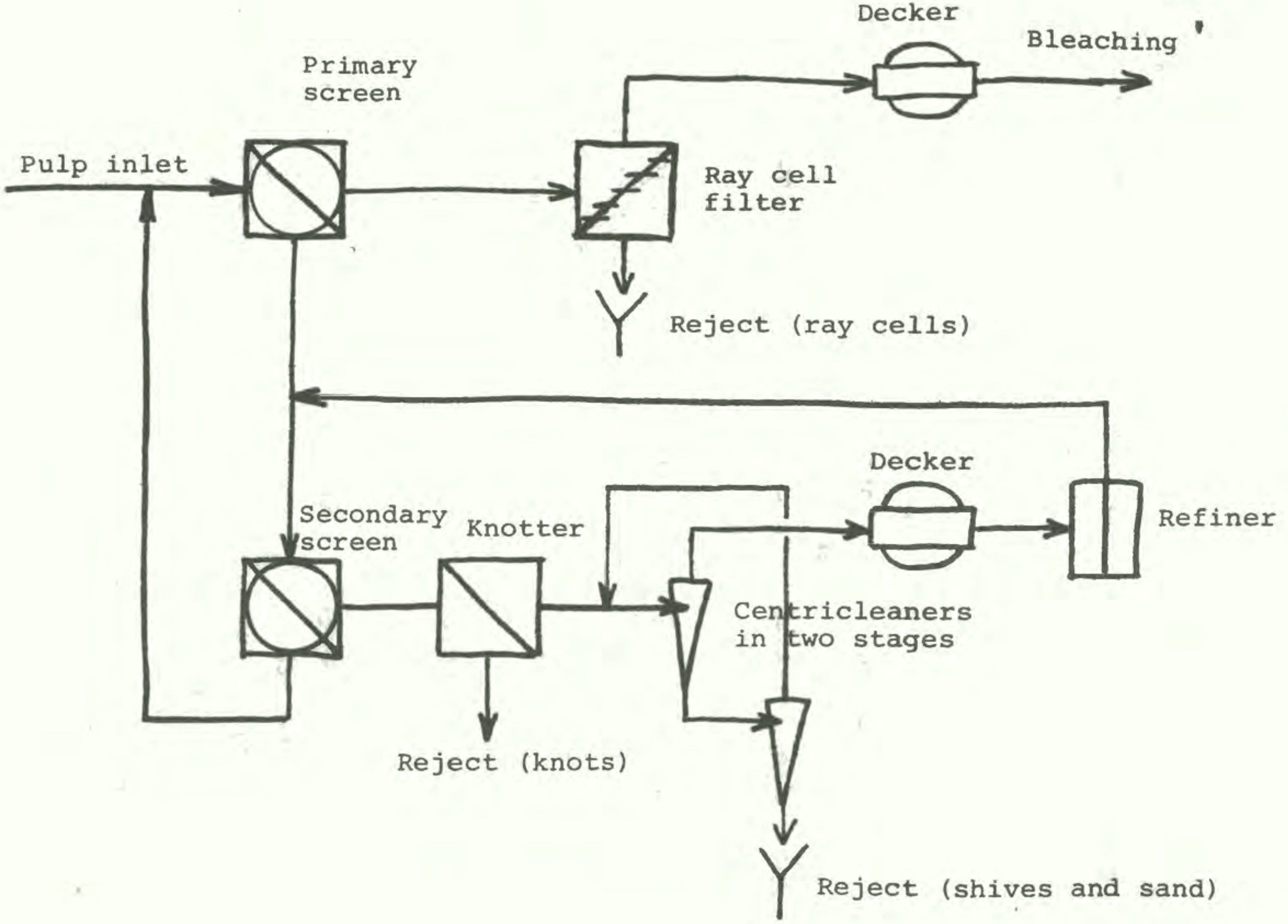


FIGURE 4.3 Schematic flow sheet of modern sulphite pulp screening with closed reject handling

the pulp or white water system, that can clog the pipes, valves, pumps etc of the washing and screening departments, in the bleachery or in the paper mill. As the deposits flake off, they give rise to dirt specks in the final product (pulp or paper).

The resin content of most wood species is concentrated in ray cells and in the bark. A careful debarking of the wood prior to chipping is in many cases an effective way to reduce the pitch problem. The trouble can also be decreased by storage of the wood or chips for a certain time. During the storage the resin is oxidized and its viscosity is changed. In this way the tendency to stick to surfaces of a different nature, and form deposits, is reduced.

Storage of the wood in logs may require several months to achieve the result desired, which is rather costly. By storage in chip piles the same effect can be reached in one or two months, but it is also possible to accelerate the oxidation of the resin in chip silos of special design.

One way by which the resin problem can be substantially reduced, is to remove the ray cells by means of a ray cell filter (fractionator). As this fractionation must be performed in a very dilute suspension, it is usually carried out after the conventional screening prior to dewatering. Modern equipment makes it possible to obtain the accepted pulp in consistencies of 3-5 %, and so the dewatering capacity required is reduced.

By ray cell fractionation the resin content of the pulp can be reduced by 40-50 %. At the same time the ash content is reduced, the brightness is increased and the consumption of bleaching chemicals is reduced. The ray cell fraction can have a resin content of 20-50 %. The separated amount normally is 15-40 kgs per ton of pulp, the highest figure refers to hardwood pulp. Depending on the high resin content and low brightness of the ray cell fraction, it cannot be used even in second grade papers. Therefore it must be disposed of, but for environmental protection reasons, it should not be released into the streams, especially as the resin is toxic to fish. However, the ray cells are easily separated from the suspension by flotation or filtration and can then be burnt.

From an economical point of view, the ray cell fractionation causes a considerable loss, corresponding to a decrease in production of 1.5-4.0 %. Therefore other ways are in many cases preferred to reduce the resin content or to prevent the formation of deposits. Thus certain chemicals (emulsifiers) are added in the cooking in order to reduce the resin content of the unbleached pulp. In some cases the resin content can be substantially reduced by an alkali treatment, which is preferably performed in connection with the bleaching, i.e. as a first bleaching stage. The addition of finely pulverized minerals (e.g. talcum powder) with very large specific surface can be an effective way to prevent the formation of resin deposits.

4.5 Closure of screening systems

In screen rooms of older mills, all the dilution water needed in the screens and most of the dilution required after the last washing stage to reach screening consistency, is made up by fresh water. In this way, a great surplus of water has to be discharged from the screening, and as a consequence the fibre losses can become rather high. Because of more rigorous environmental demands, there has been a trend to close up the screening systems by re-using the white water from the screening decker for dilution instead of fresh water. This trend is strengthened by economical demands to minimize the volumes of water to be treated in the effluent purification plant.

The difference between a traditionally open system and a closed screening system is schematically shown in Figure 4.4.

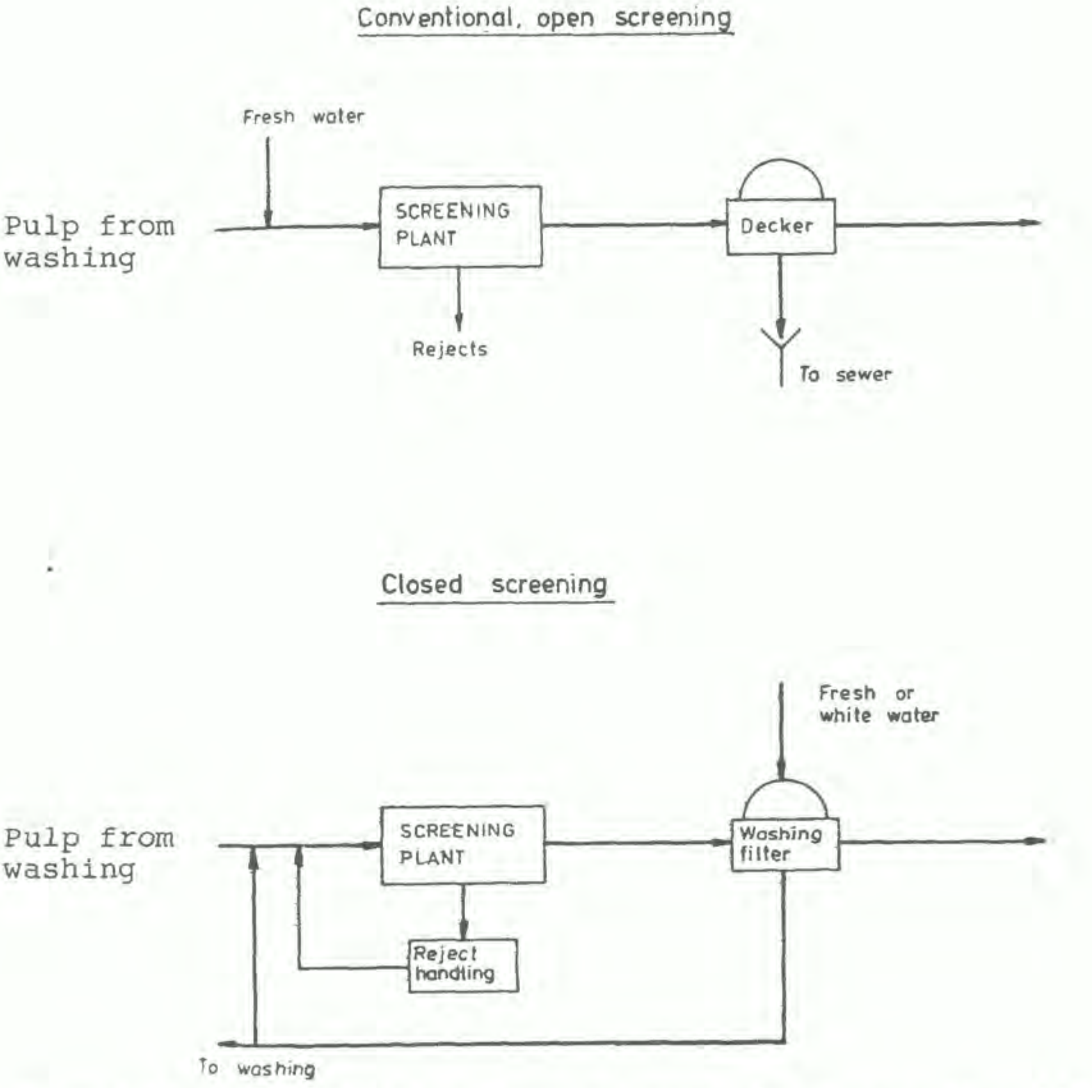


FIGURE 4.4 Simplified process schemes for conventionally open and closed screening systems

In many cases the re-use of white water in screen rooms of conventional older design is limited by certain factors, such as:

- accumulation of dry solids from the spent cooking liquor has a tendency to cause foaming

- the pulp leaving the screen room may become too hot for the following chlorination stage

- the content of spent cooking liquor dry substance may become too high for the following process of bleaching or paper making

- a higher temperature in the screen room may give an obnoxious smell in the screen room.

When the screening process is integrated in a multistage washing, the demand for closure of the system is even greater, and the inconveniencies mentioned must be avoided by choosing other equipment and processes.

The integration of the screening in the washing process is advantageous from several points of view:

- if presses are used, as is the case when oxygen bleaching is part of the washing-bleaching process, coarser impurities should be removed prior to the pressing in order not to damage the equipment

- the dewatering after screening can be used as a washing stage, if performed on a washing filter

  the heat contained in the washed pulp can be utilized in a following process, e.g. in paper making, if not lost in an intermediate low temperature screening.

In an integrated screening process, closed (pressure) screens are practically indispensable. Modern pressure screens have so many advantages that they are often preferred also in non-integrated screening systems. The only disadvatange of importance is a slightly increased energy consumption compared to open screens. It is also necessary to design the screen room in such a way that the admixture of air can be avoided. Furthermore, the screening decker must be replaced by a conventional washing filter, which is provided with a comparatively large filtrate tank and a ventilation hood. Attention should also be paid to the fact that the reject too contains residues of spent liquor, and must be treated in a way to prevent the dry substance from being sewered to any greater extent. Actually, designing the reject handling system may be the most tricky problem in integrated screening.

4.6 Screening at higher consistency

The tremendous amount of water that is involved in the screening due to the low consistency required, is a major cause of the difficulties encountered in trying to close the systems and thereby reduce the water pollution. A new knotter screen under development by the Swedish Forest Products Research Laboratory in co-operation with Sunds Defibrator AB, could hopefully contribute to reducing these difficulties (4).

The new screen is called the Disc Knotter and was originally designed for barrier screening in front of high consistency headboxes. The pulp enters the screen through a tangential inlet. In the inlet compartment heavy contaminants (e.g. stones and tramp metal) are separated. The fibre suspension accepted by the screen passes through continuous (cylindrical) slots, the width of which is adjustable. A high flow velocity through the slots results in a compact screening unit. Material that does not penetrate the screen slots accumulates in the inlet compartment and passes tangentially into the rejects compartment in the bottom of the screen.

The first full scale installation has been in operation at a Swedish sulphate pulp mill since February 1979. This unit is handling the whole mill production capacity of about 140 tons per day. Unbleached and unscreened pulp is pumped through the screen from a high-consistency tower. The inlet flow is 3-4 m^3 per minute and the consistency is about 4 %. The pressure drop is 20 kPa (corresponding to 2 m water column), and the energy consumption is less than 3 kWh per ton of pulp. The reject flow is about 10 % and may contain as much as 50 % knots. The consistency is the same in the inject, accept and reject.

When tested in the laboratory, the capacity of the Disc Knotters was 300-350 tons per day. The maximum capacity in a pulp mill aplication, however, is not yet known.

Figures 4.5 and 4.6 illustrate two alternative installations of new screen. In the first application it is used to separate knots and heavy trash after a blow tank before the pulp is washed. The reject from the Disc Knotter is sent to an open type Jönsson vibratory screen. Figure 4.6 shows a fine screening system. The coarse screening is performed with a Disc Knotter at a higher consistency than the subsequent fine screening. The operation of the pressure screen used for fine screening is safer when coarse material has already been eleiminated by the Disc Knotter.

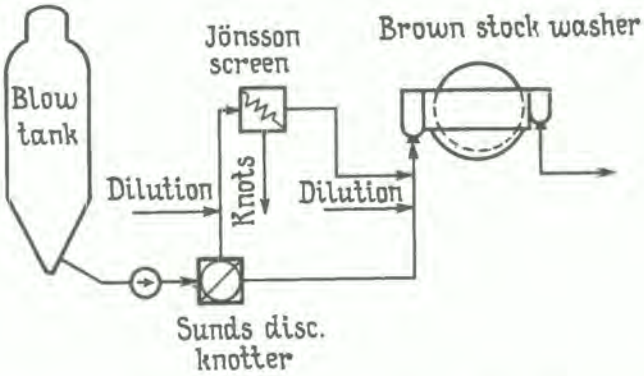


FIGURE 4.5 Typical system for hot stock knotting

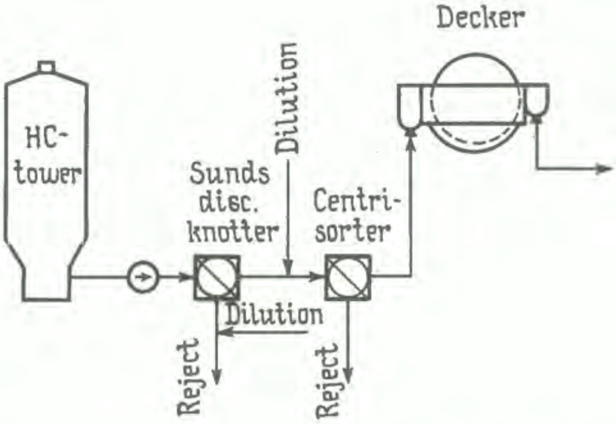


FIGURE 4.6 Typical knotting and fine screening system

Literature reference list, Chapter 4

(1) Rydholm, S.
Pulping processes
Interscience Publishers, New York 1965

(2) SSVL
The environmental care project, Technical Summary,
Stockholm 1974

(3) Sveriges Skogsindustriförbund
Yrkesbok Y-207 Silning (in Swedish)
Markaryd, Sweden, 1976

(4) Gurndström, K-J, Norman, B and Pettersson, B.
A knew knotter
Swedish Paper Journal No 8(1980) Vol. 83, 220

5. BLEACHING

5.1 Introduction

The main purpose of bleaching is to give the pulp a brightness and purity that is required for its final use. Also in other respects the physical and chemical properties are adjusted to desired levels during the bleaching process. Viscose (rayon) pulps for example are submitted to special treatments in order to give them an alfacellulose content (alkali resistance), as well as a resin content and a viscosity that are in accordance with specification.

To serve this manifold purpose, bleaching is usually performed in a multistage process. Successively the pulp is treated with various bleaching agents, of which chlorine, hypochlorite and chlorine dioxide are the most frequently used. In intermediate stages, alkali (usually sodium hydroxide) is used for dissolution of the lignin degradation products formed in reactions with the chlorine compounds.

In ordinary bleaching of chemical pulps the aim is to remove the lignin that remains after cooking, as completely as possible. Consequently the bleach plant effluent contains great quantities of organic substances, some of which is chlorinated. Thus the bleach plant is in many cases the dominating source of water pollution from a pulp mill.

The bleaching agents mentioned above have a lignin removing effect. However, for certain pulp qualities a lignin-preservative bleaching effect is preferred, as is the case for mechanical and some semichemical pulps.

This is achieved by using bleaching agents such as bisulphites, dithionites and peroxides.

There are basically three ways to reduce the water pollution from bleach plants:

a) introduction of bleaching processes and agents that permit recycling to the recovery system, e.g. oxygen bleaching

b) use of bleaching chemicals that give rise to less polluting material

c) external material of the effluent.

In the following paragraphs some examples of the categories a) and b) will be discussed. External treatment methods are dealt with in UNEP Manual, Part 8 (Volume 5).

Recycling of bleach plant effluent containing chlorine compounds to the recovery system, is limited by the chloride build-up. Though methods have been developed to remove chlorides from recovery systems, (these have also been proved to work in full scale applications (1,7,11)), this is a serious complication and should be avoided if possible. Bleaching with chlorine-free bleaching agents, such as oxygen, ozone and peroxides, are of great advantage to recycling.

Replacing part of the elemental chlorine by chlorine dioxide in the initial bleaching stage, has the advantage to recycling, that the amount of chlorine in the recycled liquor can be decreased without losing bleaching effect. It is also of advantage to the pulp quality in certain respects.

In the following different bleaching stages are referred to by using the initial letters of the active agent as indicated below:

C - chlorination
H - hypochlorite
D - chlorine dioxide
E - alkali extraction
O - oxygen
P - peroxide

5.2 Oxygen bleaching

Since delignifying bleaching is often achieved by oxidation it is natural that efforts should be made to use oxygen as an agent for delignification. The first attempts within the textile and wood pulp industries encountered difficulties with low strength properties of the products. This was due to inadequate control of the bleaching conditions. However, some twenty years ago a series of investigations reported very encouraging results on oxygen bleaching of wood pulps. Especially important was the discovery that addition of magnesium carbonate decreased the cellulose degradation. Since then the development has been very rapid, and oxygen delignification of chemical pulps is nowadays a commonly accepted technique.

Oxygen bleaching is in principle a treatment with gaseous oxygen at high pressure and high temperature in the presence of alkali. The cellulose degradation is prohibited or at least reduced by the addition of magnesium compounds. Compared to conventional bleaching technique, the use of oxygen bleaching has great advantages from the environmental protection point of view, provided that the oxygen stage is integrated in a closed washing-screening system. In this way, the organic material dissolved and the inorganic chemicals added in the oxygen stage, can be recovered and made use of in the ordinry recovery system of the mill, without the introduction of chlorine compounds from subsequent bleaching stages to the recovery cycle.

The first commercial oxygen bleaching installations were built for high consistency technique, operating at pulp consistencies between 20 and 30 % (10). The pressure is 0.8-1.0 MPa (8-10 atm) and the temperature 110-120°C. Using these conditions, the reaction time required to give a 50 % reduction of the Kappa number is 30-50 minutes, when softwood and hardwood sulphate pulps with initial Kappa numbers of 30-35 and 20-22 respectively, are bleached.

Oxygen is only slightly soluble in water. Thus a large reaction surface of the pulp and a high oxygen pressure are essential for the rate of reaction. The reaction surface is obtained with high consistency and the accessibility of the surface is further promoted by fluffing the pulp before it enters the oxygen reactor.

The oxygen reactions with pulp require a strongly alkaline environment, the pH should normally be above 11. To provide this, sodium hydroxide is usually added and mixed into the pulp after the presses which have brought the consistency up to the desired level.

The magnesium inhibitor used to prevent too great a loss of pulp viscosity during the oxygen bleaching, is usually added as a magnesium sulphate solution prior to pressing to ensure a uniform mixing.

Figure 5.1 shows a principle flow sheet of an oxygen bleaching stage. In this case it is the MoDo-CIL-Sunds system, which is one of the two major commercial processes for oxygen bleaching. Unbleached pulp, previously treated with a magnesium sulphate solution as mentioned above, enters a high-consistency cylinder press, where the consistency is raised to about 32 %. Sodium hydroxide is added and the pulp is presteamed in a screw mixer. The consistency drops down to 30 % entering a second screw feeder, which feeds directly into the top of the reactor, where a fluffer breaks up and distributes the pulp.

In the bottom of the reactor there is a dilution zone and the pulp is discharged at about 5 % consistency to a blow tank. The oxygen reactor itself operates much like a digester - a continuous fluffy pulp mass flows down inside. This contrasts with the competing SAPPI-Air Liquide process in which the Kamyr-built oxygen reactor contains a series of rotating trays, on which layers of pulp rest, the pulp falling from tray to tray down the reactor.

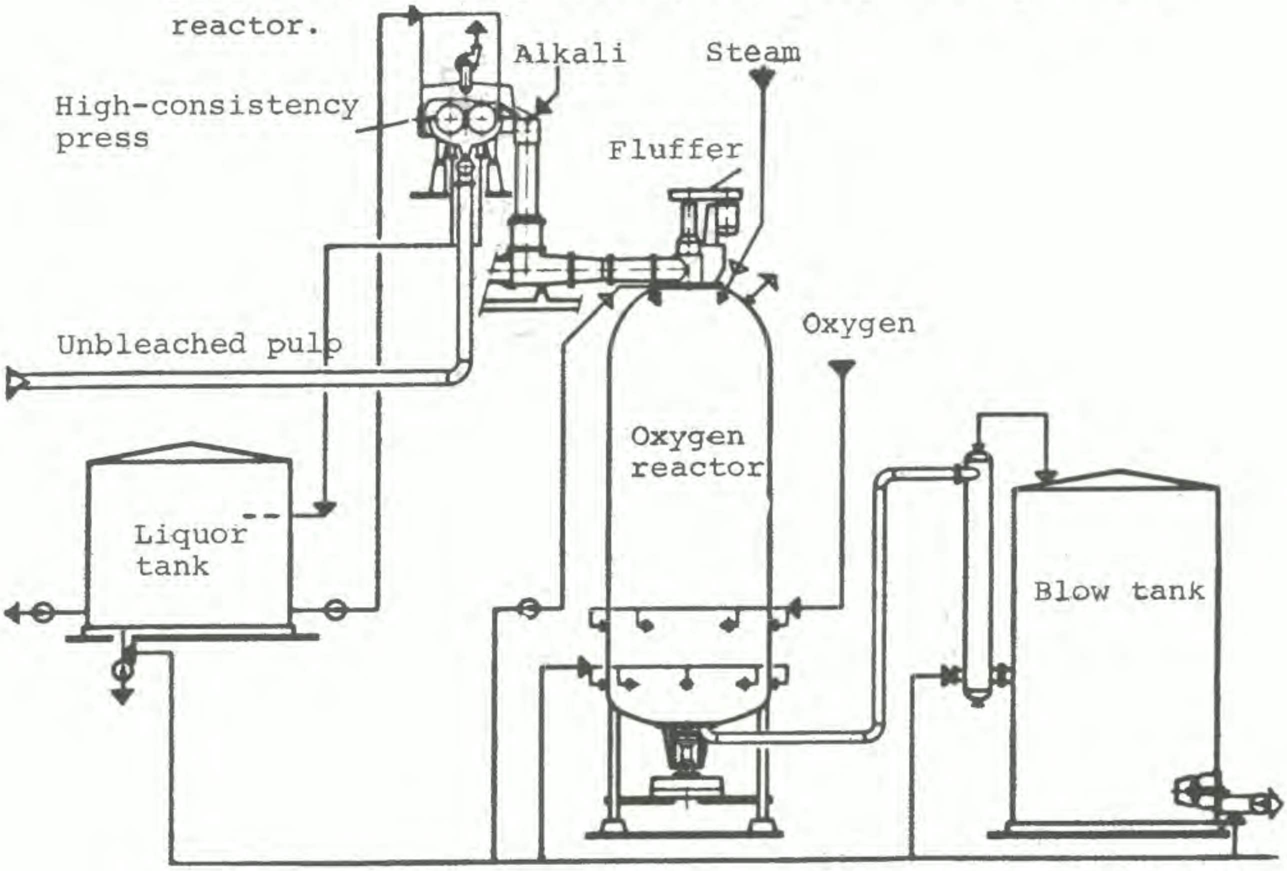


FIGURE 5.1 Oxygen bleaching system according to MoDo-CIL-Sunds

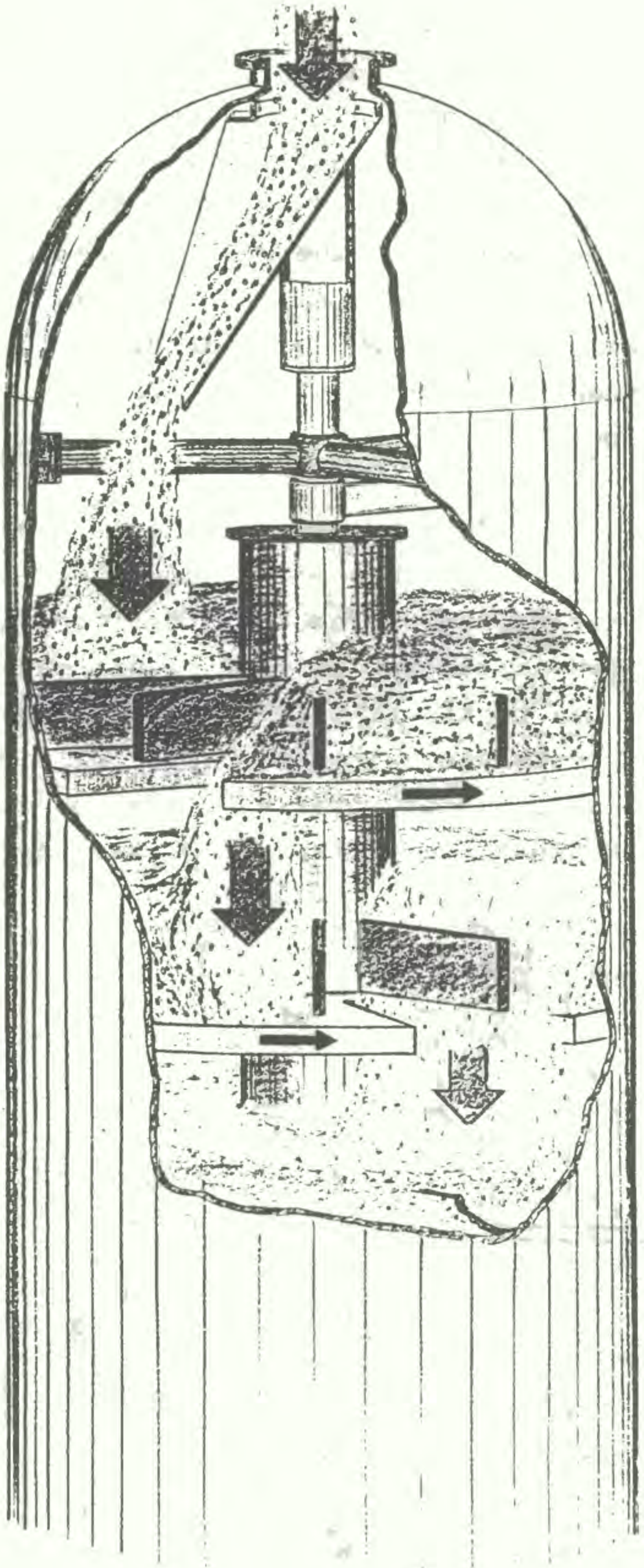


FIGURE 5.2 Kamyr oxygen reactor used in the Sapoxal (SAPPI- L'Air Liquide-Kamyr) oxygen bleaching system

A principle sketch of the Kamyr reactor is shown in Figure 5.2. In Figure 5.3 the same reactor is shown as part of the Sapoxal (SAPPI-L'Air Liquide-Kamyr) oxygen bleaching process integrated in a closed washing-screening system. The partly washed and prescreened unbleached pulp is pumped to two parallel wash presses. Here the pulp is further washed and dewatered to a consistency of about 34-35 %. Screw conveyors take the high-consistency pulp to steam mixers and after that it is fed to the top of the oxygen reactor by means of high-consistency stock pumps. Entering the reactor, the pulp is broken up by built-in fluffers and falls down on the first horizontal tray. As mentioned above, there is a series of horizontal trays or stages mounted on a vertical shaft inside the reactor. Each tray has a cut-out sector through which the pulp can fall to the tray below. Above each tray is a divider assembly which separates the layers of pulp into pie-shaped sections. The trays rotate in intermittent steps, each movement allowing a section of pulp to drop to the tray below. In this way a step-wise downward movement of the pulp is achieved.

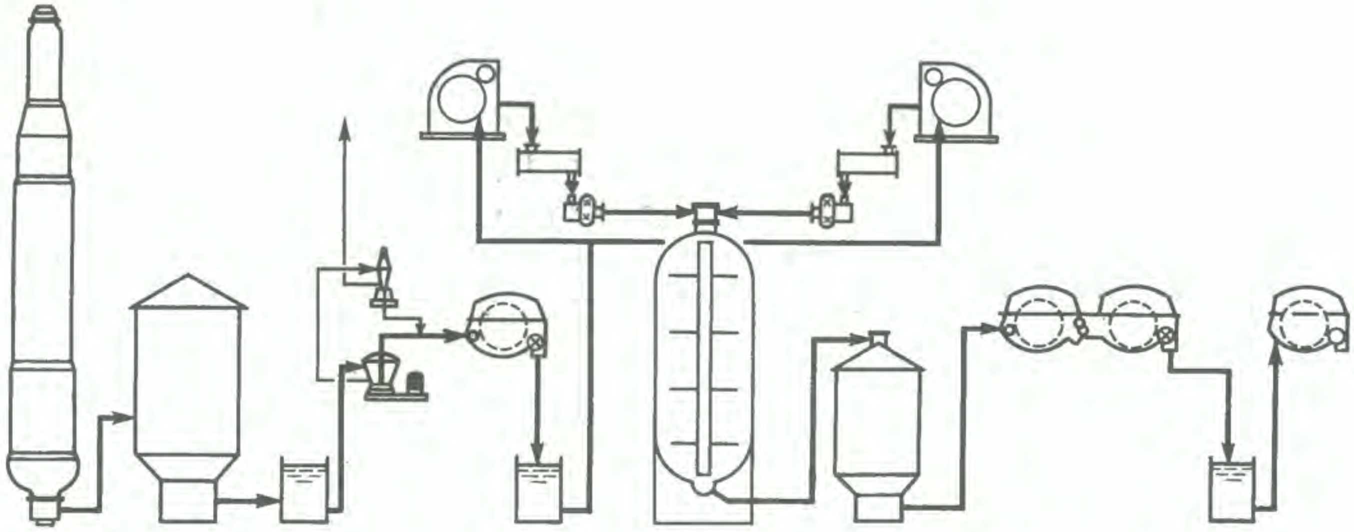


FIGURE 5.3 The Sapoxal oxygen bleaching process in a closed washing-screening system

Although the Kamyr reactor is a bit more complicated in its mechanical design than the simpler MoDo-CIL-Sunds reactor, it has a better distribution of the pulp within the reactor and thus an improved control of both the reaction time and the temperature (10). This enables working with lower pulp consistencies, down to 20 % has been achieved.

From an environmental point of view, the full advantage of oxygen bleaching is obtained when the chemicals (alkali) used in the oxygen stage can be recovered together with the cooking chemicals. This is the case, for instance, when oxygen bleaching with sodium hydroxide used as alkali is applied to sulphate pulps and sulphite pulps cooked with sodium base.

It has been reported (3), that oxygen bleaching of magnesium sulphite pulps with sodium hydroxide as alkali in the oxygen stage, can bring about a considerable reduction of the bleach plant pollution. The discharges of COD and BOD are said to be reduced by 50 % and the colour is reduced by 70 % in comparison with a conventional five stage, C-E-D-E-D, bleaching sequence.

It is also claimed that the oxygen stage spent liquor can be recovered and burnt together with spent magnesium sulphite cooking liquor in a conventional recovery boiler. The sodium introduced in the oxygen stage, is removed from the recovery cycle by rejecting sodium sulphate from the ash filter. The system has been tried in commercial scale experiments in a Swedish magnesium based sulphite mill (3,4).

In spite of the findings reported above, it is usually not satisfactory to use sodium hydroxide in the oxygen delignification of magnesium based sulphite mills. In these cases, the alkali should instead be supplied in the form of a magnesium compound, of which the oxide, MgO, or the hydroxide, $Mg(OH)_2$, are readily available in a magnesium base sulphite mill. They have, however, a very low solubility in water, which means it is not possible to reach as high a pH level as is usually applied in oxygen bleaching with sodium hydroxide, pH 11. The lower rate of delignification caused by the lower pH level, can be compensated for by a higher reaction temperature and a longer reaction time. It has been reported (6), that encouraging results have been achieved with magnesium hydroxide added in the form of a suspension to compensate for the low solubility. The oxygen bleaching was then carried out at 140°C with a reaction time of 90-120 minutes to reach a Kappa number of 5-10 from an original Kappa number around 30.

A reduction by 70-80 % of the lignin content in the oxygen bleaching stage, will roughly give a corresponding reduction of organic material in the spent liquor from the remaining stages of the bleach plant, provided that all the spent liquor from the oxygen stage is returned to the chemical recovery system of the pulp mill.

A fully bleached pulp is easily obtained with several two-stage bleaching processes after the oxygen delignification of sulphite paper pulps with magnesium hydroxide used as alkali. With chlorine dioxide and hydrogen peroxide in the final bleach stages, and a countercurrent wash in the bleach plant, a bleaching system is obtained which produces a minimum of chlorinated organic compounds for the effluent. Calculated discharges of chlorine compounds from different bleaching sequences (6) are shown in Figure 5.4.

SULPHITE PULP BLEACHING

Kappa	Cl—Discharge			Kg/ton pulp
25	C-E-H-D	50+0+15+2	=	67
6—7	O-C-H	0+13+10	=	23
6—7	O-D-E-D	0+3,5+0+2	=	5,5
6—7	O-D-P	0+3,5+0	=	3,5

FIGURE 5.4 Calculated discharges of chlorine compounds from different bleaching sequences

Reactors for high-consistency oxygen bleaching are comparatively expensive, and so is the equipment required for dewatering pulp ahead of the reactor. Development work has been carried out in the laboratory as well as in pilot plants, with the purpose of finding system solutions for oxygen delignification which at medium pulp consistencies, i.e. 10-15 % (9.13). For instance a major simplification of the system would be achieved if the oxygen delignification could follow close to a continuous digester, using the same pulp consistency as in the digester blow line.

This has for some time been successfully tried in a Norwegian sulphate pulp mill (13).

Working at a lower pulp consistency also has the advantage that the risk of deflagration of the pulp due to an accidental excess of the upper pulp consistency limit, can be avoided.

It has, however, been reported (9), that oxygen delignification at medium pulp consistencies has a slower rate of reaction and requires somewhat more steam per ton of pulp compared to the high-consistency systems now in commercial use. Thus it is said, that for the time being, one system cannot be categorically recommended over the other.

Oxygen bleaching plants are presently being installed in two sulphite mills working with magnesium base, one in Norway (Hunsfos) and one in West Germany (Kelheim). In both cases the pulp bleaching capacity is around 200 tons per day.

The main reason for the installation of an oxygen bleaching plant at Hunsfos is to decrease the amount of chlorine and poisonous chlorinated compounds in the effluent. Because of the limited space available an existing batch digester has been rebuilt to serve as an oxygen reactor. For this purpose it has been provided with a mixer on the top and a discharging device in the bottom of the type that is used in ordinary down-stream bleaching towers. For obvious reasons the digester was not suited for conversion to a "tray reactor" of the type described above. At 25 % pulp consistency the reaction time is expected to be about 90 minutes. The system is illustrated in Figure 5.5.

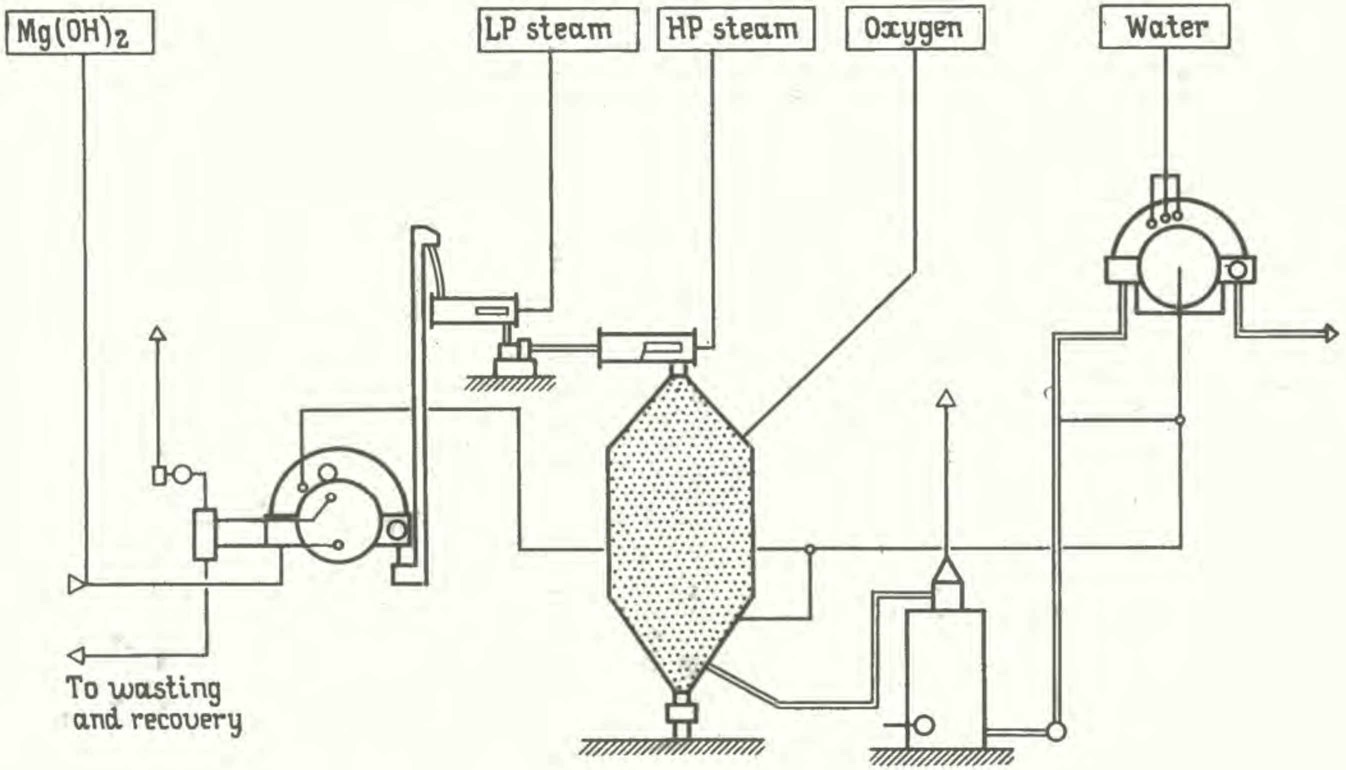


FIGURE 5.5 Oxygen bleach plant at the Hunsfos sulphite mill (6)

The Hunsfos plant will start up during autumn 1980. In the beginning, i.e. as long as the system has not been fully closed, sodium hydroxide will be used as alkali and the bleach plant effluent will be sewered. In a second phase a complete closure of the screening-oxygen bleaching-washing systems is planned. The sodium hydroxide will then be replaced by magnesium hydroxide and the oxygen bleach plant effluent will be recovered together with the spent cooking liquor. The reaction time is expected to be sufficient also with magnesium hydroxide as alkali if the temperature is raised to 135°C.

The Kelheim oxygen reactor is equipped with intermediate bottoms, trays, like the one in Figure 5.2. This makes the operating conditions very flexible, so that pulps with different Kappa numbers can be bleached with different reaction times. It is planned to start up at the beginning of 1981.

5.3 Modified bleaching technology using high amounts of chlorine dioxide or reversed pre-bleaching

After oxgyen delignification, a further reduction of the effluent load can be obtained by using chlorine dioxide instead of chlorine in the final bleaching. This is demonstrated in Figure 5.6.

Kappa number	Bleaching sequence	Discharge, kg/t BOD_7	Colour	Org Cl
28	CEDED	14.5	105	8
	OCED	6.5	55	3
	ODED	6.2	25	0.5
19	CEDED	12.2	75	5
	ODED	5.2	20	0.5

FIGURE 5.6 The discharge of BOD, colour and organic chlorides from the bleaching of acid sulphite softwood paper pulps. 85 % recovery of oxygen stage effluent

Bleaching acid sulphite paper pulps with the sequence O-D-E-D instead of O-C-E-D has reduced the colour load by over 50 % and the amount of organic chlorine compounds from 3 to less than 0.5 kg per ton of pulp. The influence on the BOD values is of minor importance (4,5).

Figure 5.6 also shows that a decrease in unbleached Kappa number gives a reduction primarily of the colour and the amount of chlorinated organic compounds, when the same bleaching sequence is used. All data refer to pulps with the same brightness (89 % ISO).

It has been reported (1) that a reversed pre-bleaching, with the sequence E-C-H-D has been successfully applied at a Swedish sulphite mill using a two-stage sodium based cooking process for the production of either paper grade pulp with an unbleached Kappa number of 10-12, or viscose pulp with an unbleached Kappa number of 6-8. The original sequence used was C-E-H-D. By changing to the sequence mentioned above, it was possible to return the alkali extraction stage effluent via the screen room to the recovery furnace. The extent of pollution abatement that may result from this change is dependent on the washing efficiency for the extracted pulp. With a displacement ratio of 0.7 for the washer after the E-stage, the pollution from the bleach plant is shown in Figure 5.7.

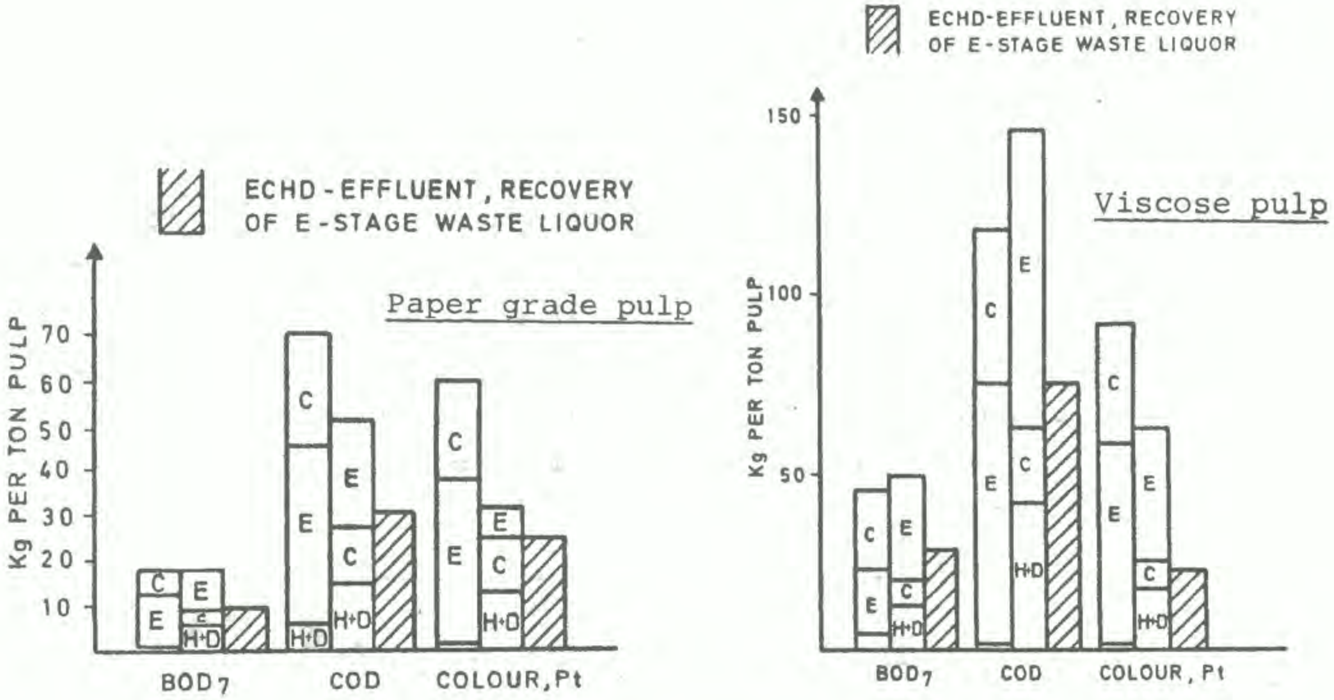


FIGURE 5.7 Comparison of effluent streams C-E-H-D and E-C-H-D sequences when bleaching paper grade and viscose pulps

Effluent colour and COD quantities have been significantly reduced compared to the previous C-E-H-D sequence. The BOD reduction is not so impressive, but is at least equivalent to that leaving a sulphate pulp bleachery (C-E-H-D-E-D) incorporating ion exchange treatment of the first extraction stage effluent, Figure 5.8.

	BOD_7	COD	COLOUR	(Kg PER TON PULP)
ECHD	9	31	26	PAPER GRADE PULP
	23	75	29	VISCOSE PULP
CE_1HDE_2D	9	-	23	SULPHATE PULP. ION EXCHANGE OF E_1

FIGURE 5.8 Effluent from E-C-H-D sequence with 70 % recovery of the E-stage spent liquor

Figure 5.9 shows the comparative BOD and colour loadings of bleached sulphite and sulphate effluents. The colour loading for the E-C-H-D sulphite sequence is about 80 % lower than that for the conventional C-E-H-D-E-D sulphate sequence. It has also been reported (2) that the E-C-H-D sequence has a 30 % lower capital cost than the O-C/D-E-D sequence for a sulphate mill.

Sequence	BOD_7 kg/a.d. ton	Colour kg/a.d. ton
	Kraft	
CEHDED	12	154
OC/DED	10	36
	Sulphite	
CEHD	13	61
ECHD	9	26

FIGURE 5.9 Effluent quality of modified sulphite bleaching sequences for full-bleached paper grade pulps

5.4 Possible reduction of polluting discharges

Bleaching according to traditional methods with an introductory chlorination stage is one of the most polluting processes in modern sulphite pulp manufacture. This statement is based on an evaluation of discharges from sulphite mills using available in-plant control technologies to reduce the pollution (4). In the examples given in Figure 5.10 a washing efficiency of 95 % has been assumed as well as treatment of condensates and an effective system for spills collection. Measured as BOD_7 bleaching is responsible for over 35 % of the total polluting discharges from a magnesium based sulphite paper pulp production.

Position	Sulphite paper pulp CEDED	OCED
Washing-Screening	15	2
Condensates	6	6
Spills	5	5
Bleaching	15	6
Total	41	19

FIGURE 5.10 Total discharge of BOD_7 in kg ptp from magnesium sulphite pulping with two different bleaching sequences (4)

By introduction of oxygen bleaching with recovery of chemicals and dissolved substance from this stage - 85 % recovery is assumed - the BOD of the bleach plant effluent can be reduced from 15 to 6 kg ptp. At the same time the 15 kg BOD_7 discharged from washing-screening is reduced to 2 kg leaving the mill system via the open stages in the bleach plant, provided that the screening system can be closed. Thus there is 50 % reduction of the total BOD discharged from the mill as indicated in Figure 5.10

Literature reference list, Chapter 5

(1) Brännland, R. et al
New in-plant technology to reduce pollution from a sodium base sulphite mill
Svensk Papperstidning 79(1976):18, 591

(2) Kalish, J.
Pulp & Paper Journal 51(1977):10

Wong, A.
Sulfite - an option whose time has come again
TAPPI April 1980 Vol. 63, No. 4, 53

(3) Ivnäs, L. and Lekander, K-E
Zellstoffqualität und Umweltschutz durch die Sauerstoffbleiche für die Herstellung von gebleichtem Magnesiumsulfitzellstoff
Das Papier 32(1978) Heft 10A, V19

(4) Ivnäs, L. and Norrström, H.
Reduced effluent load from Mg-sulphite pulp bleaching by system closure and recycle to the recovery Preprint from the 1979 international pulp bleaching conference in Toronto, Canada

(5) Ivnäs, L. and Norrström, H.
How to reduce effluent load in closed systems
Pulp & Paper Magazine of Canada

(6) Christensen, P.K
Bleaching of sulphite pulp with oxygen and magnesium hydroxide
Paper presented at the 1978 SPCI annual meeting in Stockholm, Sweden

(7) SSVL
Klorid i återvinningssystem (in Swedish)
Stockholm 1977

(8) Almberg, L., Croon, I. and Jamieson, A.
Oxygen delignification as part of future mill systems
TAPPI June 1979 Vol. 62, No. 6, 33

(9) Näsman, L. and Annergren, G.
Medium-consistency oxygen bleaching
TAPPI April 1980 Vol. 63, No. 4, 105

(10) Anon.
Oxygen bleaching
Pulp & Paper International March 1975, Vol. 22, No. 3, 53

(11) Reeve, D., Rowlandson, G., Kramer, J. and Rapson, W.H.
The closed-cycle bleached kraft pulp mill - 1978
TAPPI August 1979 Vol. 62, No. 8, 51

(12) Sveriges Skogsindustriförbund
Yrkesbok Y-208 Blekning (in Swedish)
Markaryd 1978

(13) Kleppe, P., Backlund, Å. and Schildt, Y.
Oxygen/alkali delignification at Kamyr digester blowline consistency - a status report
TAPPI November 1976 Vol. 59, No. 11, 77

(14) Christensen, P.K.
Oxygen delignification of sulphite pulp with $Mg(OH)_2$ as base
Preprint from the 1976 international pulp bleaching conference, Chicago, Ill

(15) Warnqvist, B. and Norrström, H.
Chlorides in the recovery boiler and a mechanism for chlorine removal
TAPPI November 1976 Vol. 59, No. 11, 89

6. SPENT LIQUOR EVAPORATION

6.1 Introduction

Organic substances dissolved in the cooking process represent a considerable value as fuel. The quantity of this substance can be as much as half the wood consumption for paper-grade pulps, and even more for dissolving pulps. In addition, they would cause serious water pollution, corresponding to 300-500 kg BOD_7 per ton of pulp, if they are not recovered and destroyed.

Furthermore, it is of vital economical interest for the process to recover as much as possible of the chemicals remaining in the spent liquor for re-use in the preparation of new cooking liquor, especially if a soluble base like magnesium or sodium is used.

The concentration of dry solids (DS), i.e. used chemicals and dissolved organic substance, in the spent liquor, is usually rather low. Thus the liquor has to be concentrated prior to further processing. This concentration is usually performed in evaporation stations. In some cases the final concentration is carried out by direct evaporation with flue gases from the liquor burning boiler.

The huge amounts of water in the dilute spent liquor coming from the pulp washing, require great quantities of heat in the form of steam for evaporation. This steam is supplied from boilers where the concentrated liquor is being burnt. The combustion of the organic matter is necessary also from the point of view of pollution abatement.

Thus the spent liquor recovery consists essentially of two processes, viz. the concentration of spent liquor from the cooking-washing process, and the burning process which is closely connected to the preparation of new cooking liquor.

The spent cooking liquor from the NSSC process, usually called red liquor, is quite often evaporated and burnt together with sulphate black liquor, so called cross recovery. If this is not possible, because of geographical or other reasons, the red liquor must be recovered by separate evaporation and burning. However, the fuel value is low and the recovery systems applicable are complicated and expensive, which can render recovery unprofitable. But it may be necessary to take care of and destroy the red liquor for environmental protection reasons.

6.2 General principles

Depending on the type of cooking process and especially the pulp yield, the spent sulphite liquor has a concentration of 11-17 % DS (dry solids) in the digester, i.e. before the inevitable dilution during the washing. After washing the concentration has normally decreased to 10-15 % DS. In the main combustion processes the DS content should be 55-58 % to enable a proper ignition and burning with good heat economy. Therefore the liquor has to be concentrated before it can be burnt. This concentration is usually performed in the same type of multiple effect evaporation station as is used for sulphate black liquor. However, some construction and operating modifications have been necessary due to problems with deposits (scaling) on the heating surfaces, especially in the case of calcium base liquors.

Moreover, the acidic sulphite spent liquors require acid resistant steel in the evaporation plant. Details of construction and operation will not be given here, but some fundamental principles and aspects will be discussed.

The quantity of water to be evaporated and how it depends on the concentration of incoming liquor, will be illustrated by an example. Suppose that the DS concentration of the liquor entering the evaporation station is 15 %, the water content being 85:15 = 5.67 tons per ton of DS. With a DS concentration of 55 % in the liquor leaving the station, the water content is 45:55 = = 0.82 ton per ton of DS. Thus the amount of water to be evaporated is 5.67 - 0.82 = 4.85 tons per ton of DS.

If the concentration of incoming liquor decreases to 12 %, e.g. because of a demand for better washing, the water content increases to 88:12 = 7.33 tons per ton of DS. The evaporated water quantity will in this case be 6.51 tons per ton of DS, i.e. an increase of 34 % over the previous example.

As in evaporation of sulphate black liquor, spent cooking liquor from the sulphite process usually is evaporated in multiple effect stations with 4-6 effects. Live steam is supplied to the first effect only, and evaporated liquor vapour from this one is used for heating effect no. 2, etc. The consumption of live steam is thereby reduced considerably, and is only about 25 % in a five-effect station compared to that of one stage evaporation. Thus the heat consumption is about 560 MJ (135 Mcal) per ton of water evaporated.

6.3 Evaporation apparatus and practice

In principle the equipment used for evaporation of sulphite spent liquor is the same as described for sulphate black liquor evaporation in volume 3 of this series.

An evaporation effect (evaporator) mainly consists of a heat exchanger and an expansion vessel (separator) as is shown in Figure 6.1.

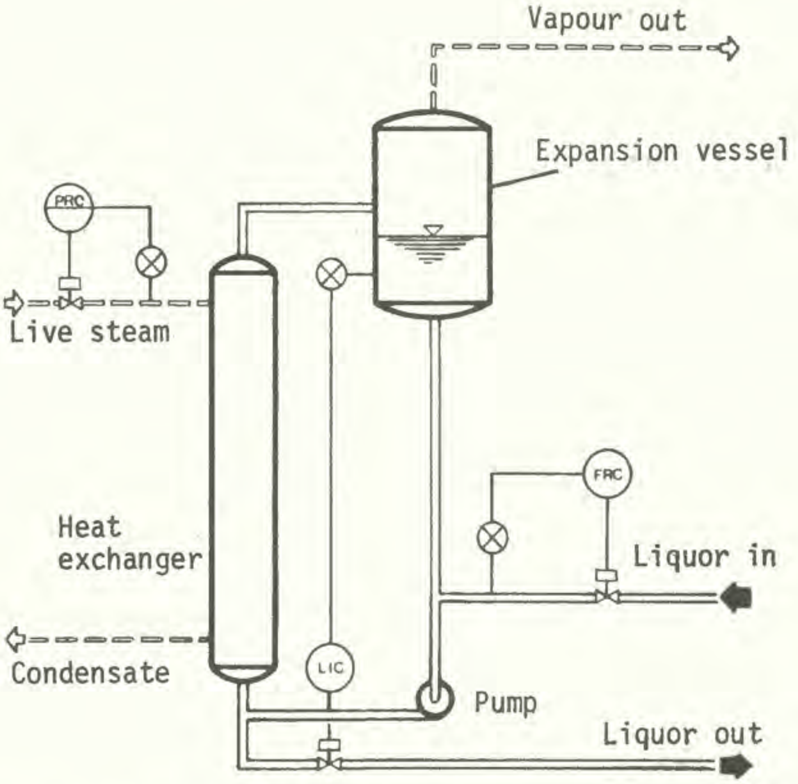


FIGURE 6.1 Schematic flow sheet of forced circulation evaporator according to Rosenblad

In the heat exchanger the liquor is heated to boiling point by means of live steam or liquor vapour with a higher pressure than in the expansion vessel. In sulphite liquor evaporation the circulation is often forced by pumps in order to reduce the effects of scaling, Figure 6.2.

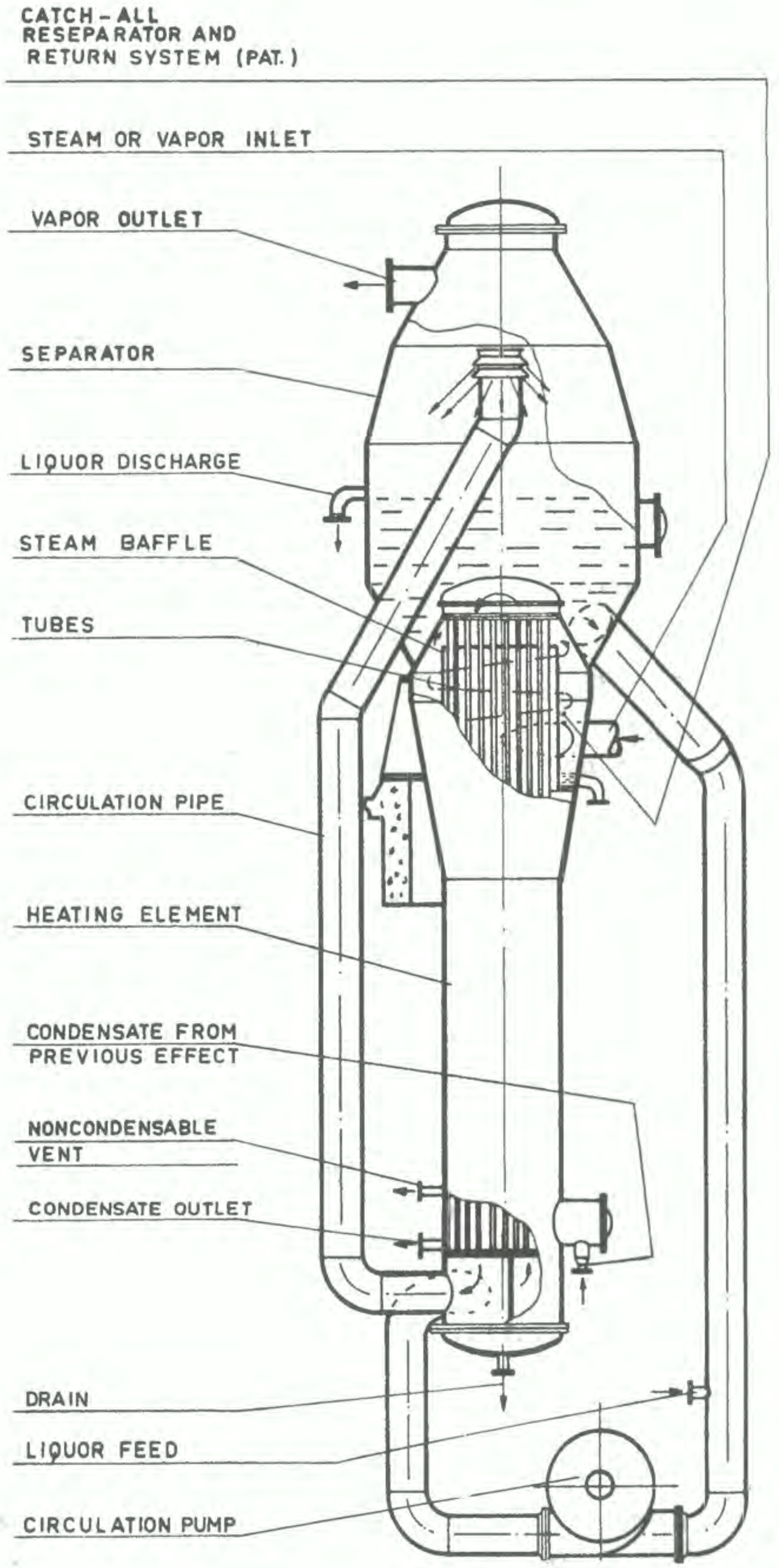


FIGURE 6.2 Swenson forced circulation evaporator (Rosenlew)

The evaporators principally operated in principally three different ways, viz. as vacuum, back pressure or thermo-compression stations. The choice between these ways of operation is mainly governed by the relation of fuel to electric energy prices and the risk of scaling trouble.

The most common method of operation is vacuum evaporation, where most of the process is performed under vacuum, whereby lower temperatures can be used, 120-125°C, which decreases the risk of deposits of calcium sulphate scales. The vapour from the last effect has a temperature around 50°C and is usually condensed in a surface condenser. The use of direct condensers should be avoided for environmental protection reasons, as they create great quantities of contaminated cooling water.

As a rule the heat economy is better in a back pressure station than in a vacuum station. The evaporation is performed above the atmospheric pressure, which enables the vapour from the last effect to be used for other heating purposes in the mill, as for instance in cooking. However, the vapour is acidic, so the equipment where it is used must be made of acid resistant steel. The use of back pressure evaporation for sulphite liquors is limited by sensitivity to higher temperatures, which may cause decomposition (condensation) of the organic substance. Besides for calcium base liquors, the scaling tendency is very disturbing.

If the price of electric energy is low compared to other fuel prices, thermo compression can be a favourable alternative. Vapour from the expansion vessel is compressed and then used for heating the liquor in the heat exchanger. The main part of the energy consumed is supplied as electric energy to the compressor.

The evaporator construction has to consider the scaling problem that is always present in sulphite liquor evaporation. For this purpose special washing systems have been developed in order to facilitate the removal of deposits. In the first place scaling occurs on the heating surfaces but also liquor pipes, pumps and valves have a tendency to be clogged by deposits.

Thus sulphite liquor evaporation usually is performed in evaporators with heat exchangers built up by equally spaced parallel steel plates (lamellae). This construction permits the use of washing systems in which the liquor and steam/vapour channels are interchanged at intervals. The deposits formed on the liquor side of the heat exchanger surface, are dissolved by the acidic condensate, when the channels are switched. Such a construction is illustrated in Figure 6.3.

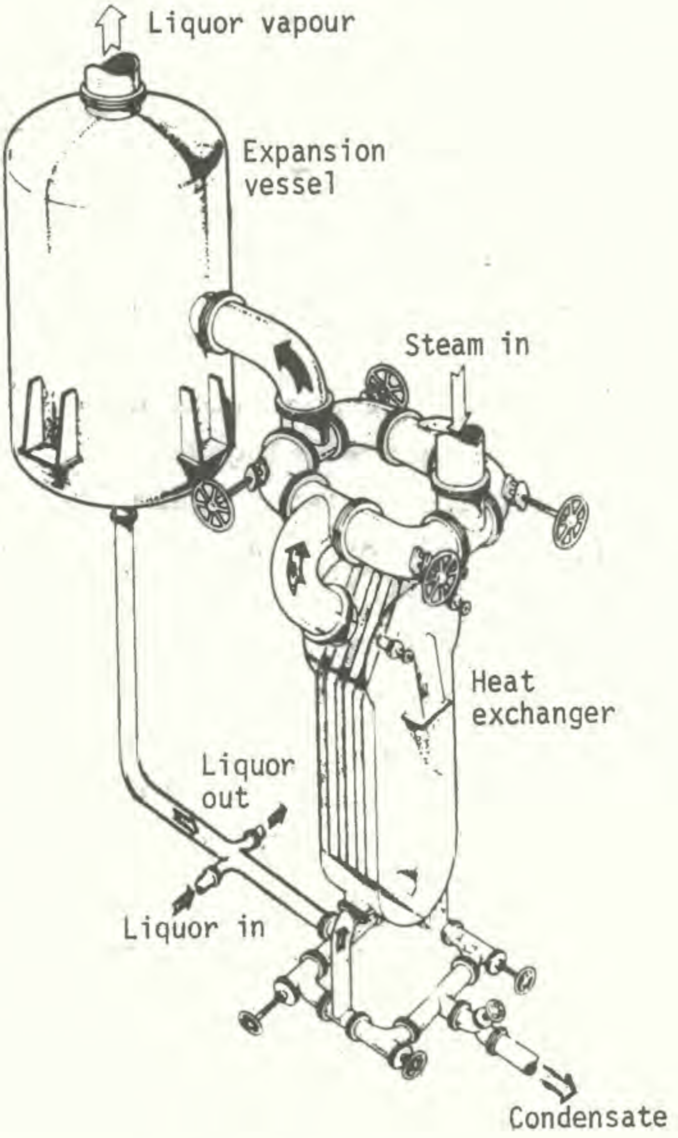


FIGURE 6.3. Evaporator with natural circulation and channel switching system

It is quite common that the capacity of an existing evaporation station need to be increased as a consequence of pollution abatement measures undertaken in other departments of the mill. Under these circumstances it has in some cases been found advantageous to install a multiple expansion or multi-flash evaporation station according to Lockman, Figure 6.4.

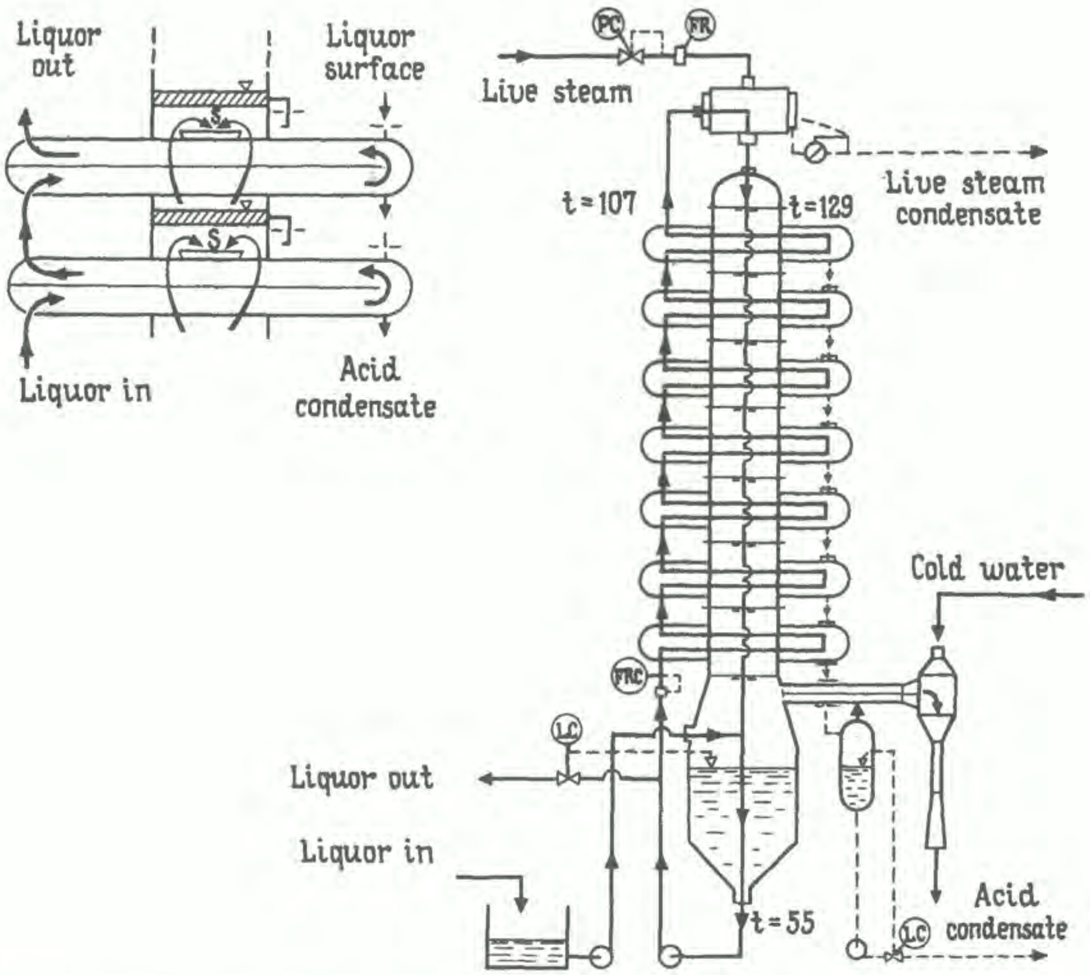


FIGURE 6.4 Lockman evaporator with details of construction

The Lockman evaporator has the shape of a distillation tower (still) with the effects one above the other. Thus the floor space requirements are comparatively small and the capacity can easily be extended simply by adding more effects at the top of the evaporator column. The pre-heated liquor is allowed to expand stepwise as it flows downwards in the column. From the bottom it is pumped through a series of heat exchangers and returned to the top again. Each heat exchanger is supplied with vapour from a corresponding expansion effect.

The Lockman evaporator is predominantly used as a pre-evaporator, as shown in Figure 6.5. Here the liquor is pre-heated by flasch vapour from a continuous digester, which saves energy. The flow sheet also shows how a conventional evaporation effect can be installed between the digester and the steaming vessel. This evaporator as well is also supplied with flash vapour from the digester.

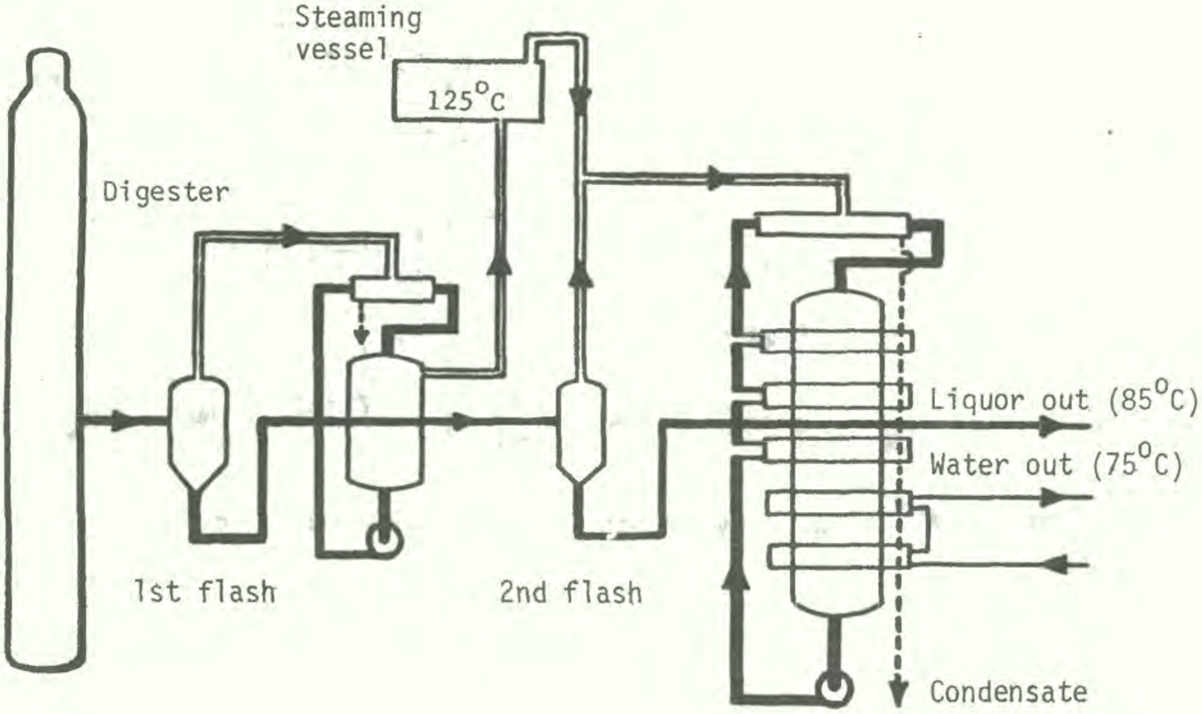


FIGURE 6.5 Lockman evaporator in combination with a continuous digester

6.4 Aspects of pollution problems

The evaporation station is a vital part of the liquor recovery system. It should have a capacity sufficient to take care of the normal flow of liquor from washing as well as accidental discharges from various departments. In addition to a sufficient capacity, the station must have appropriate equipment and a suitable design with regard to liquor quality and operating circumstances.

In planning an evaporation station various aspects must therefore be considered. Besides the usual questions regarding heat economy, capacity etc, the following items are of vital importance from the environmental protection point of view:

- scaling and liquor quality
- cleaning of evaporators
- carry over of dry substances in separators
- operating control
- separation and purification of condensates
- bases for capacity calculations.

The main polluting discharges from the evaporation station itself, are the contaminated condensates. The dominating impurities are acetic acid, methanol and furfural as well as liquor dry matter caused partly by carry over in the separators and partly by the cleaning of heating surfaces from scales. These questions will be discussed below and the treatment of contaminated condensates, in paragraph 6.5.

Scaling_and_liquor_quality

Not only in the case of calcium base, but also when soluble bases are used, the liquor contains certain amounts of calcium as well as sulphate ions. As soon as the product of these two ion concentrations exceeds a certain value, depending on the temperature among other factors, there is a precipitation of calcium sulphate. Experience shows that such precipitation occurs in any sulphite liquor evaporation plant. Due to the fact that the solubility of calcium sulphate is lower at higher temperatures, the risk for precipitation (scaling) is less pronounced in low temperature evaporation such as vacuum stations.

Although other types of deposits occur in sulphite liquor evaporation plants, the precipitation of calcium sulphate on the heating surfaces is the most serious one. Thia has enforced modifications in operation and equipment construction as shown in the following.

Other types of deposits that may occur on the liquor side are calcium sulphite and silica. If fibres are present in the liquor they have a tendency to mix with other components and reinforce the deposits making them much more difficult to remove by washing. It is therefore recommended that the fibres be filtered off on a special fibre filter so that the fibre content of the liquor can be kept below 20 milligrams per litre.

Scalings may occur also on the vapour side caused by volatile organic compounds following the vapour to the next effect, where they condensate to form deposits with a low heat transfer value.

Cleaning of evaporators

Scalings caused by calcium sulphate can be removed by frequent washing with acidic condensate according to a certain programme. In natural circulation plants this is normally accomplished by channel switching, see Figure 6.3. In forced-circulation plants extra evaporation bodies are used so that one effect at a time can be out of operation for washing. Routine systems have been developed for this purpose.

Deposits of organic substances on the vapour side, as well as on the liquor side, can be removed by periodic washing with nitric acid. Silica containing deposits may be removed by alternate washing with nitric acid and sodium hydroxide solution. Deposits of elementary sulphur that can occur under certain conditions are also treated with sodium hydroxide solution.

During the washing a substanctial quantity of liquor dry matter can be lost with the remaining liquor in the evaporator, which may cause serious water pollution. However, the loss could be reduced if the liquor is first displaced by weak liquor and condensate. For very obvious reasons this method leads to an increasing demand for evaporator capacity and a higher steam consumption.

Carry over

Carry over is caused by incomplete separation of small liquor droplets accompanying the vapour to the separator. As they end up in the condensate, this will be contaminated with liquor dry matter.

The loss of liquor dry matter by this phenomenon can be as much as 5-10 kg per ton of pulp. This loss can be reduced by installation of larger separators, which means lower vapour velocity, or by insertion of specially designed shields and baffles in the separator or in the vapour line. Preferably these measures should be undertaken in the last evaporation effect, as the carry over problem is greatest there.

Operating control

Appropriate instrumentation is a pre-requisite for proper control and easy operation of an evaporation plant. By this means operating disturbances can be minimized and carry over reduced. Of direct interest from the environmental protection point of view, are conductivity meters in the condensate output lines. The instruments should be equipped with automatic valves switching it to a collecting vessel if the conductivity is too high.

Air pollution

The non-condensable gas in the liquor vapour contains small quantities of sulphur dioxide, that leaves the system via the vacuum pump if not adsorbed in water and collected.

6.5 Treatment of contaminated condensates

Introduction

Various volatile organic compounds are formed during the sulphite cooking process, such as acetic acid, methanol, furfural, formic acid and others. These compounds consume oxygen if discharged to the streams and they are also toxic to some extent. It has been reported (1) that the formation of these compounds can be in the order of 45 to 60 kg per ton of softwood sulphite pulp, corresponding to approximately 50 kg of biological oxygen demand (BOD) ptp. Up to 50 % higher values have been found for hardwood pulps.

An example of quantities and distribution is shown in Figure 6.6, which refers to acid sulphite cooking of dissolving and paper grade pulps (of softwood).

Compound	Total amount formed		Corresponding amount of BOD kgs ptp			
			Total amount		With condensate	
	Dissolving	Paper	Dissolving	Paper	Dissolving	Paper
Acetic acid	45	35	38	29	28	19
Methanol	9	7	11	9	10.5	8.5
Furfural	6	2	6	2	5.5	2
Formic acid	0.9	-	0.04	-	0.01	-
Total	-	-	55	40	44	30

FIGURE 6.6 Volatile organic compounds in the sulphite process, kgs per ton of pulp (1)

A small part of these compounds is found in the cooking condensates from top relief and blow down gases. Most of them, however, remain in the spent cooking liquor and are vapourized during liquor evaporation, thus contaminating the evaporation condensates.

About 95 to 100 % of the methanol and furfural content of the incoming liquor is vapourized during the evaporation, ending up in the condensate. Under normal conditions the corresponding vapourization factor for acetic acid is between 50 and 70 % depending on the liquor pH.

Several methods have been developed and some of them are in practical use to reduce environmental pollution from condensates:

- Neutralization of the liquor prior to evaporation.

- Re-use of contaminated condensates instead of discharging them to the effluent.

- Purification of condensates by stripping with steam.

- Stripping of liquor with steam prior to evaporation.

- Purification of condensates by various methods such as ion exchange technique, reversed osmosis, biological treatment etc.

Composition of condensates

The main chemical components of condensates from the evaporation of acid sulphite spent liquor are, acetic acid, methanol and furfural (5). Quite obviously the total amount and the relation between these compounds depends on the cooking process and the fibre raw material. However, the pre-treatment of the liquor to evaporation and the conditions in the evaporation process are of great importance for the content of contaminating substances in the condensate.

It has been shown that furfural is formed during the evaporation process, especially at high temperature and low pH. Thus the formation predominantly occurs in the last (thick liquor) effect and in back pressure stations with high temperatures. It has also been found that the furfural formation is decreased by a neutralization of the liquor to higher pH values. Moreover, there is decomposition of already present furfural, if the liquor is stored for a couple of hours at 80-85°C and a pH of 8-9. Storing at pH below 7 is of less importance to the BOD reduction.

Formic acid may cause a catalytic decomposition of sulphite cooking acid. The content of this compound in evaporation condensates is, however, too low to be of practical importance in the re-use of condensates in cooking liquor preparation (5). Other organic compounds are normally present in negligible proportions only.

Due to the circumstances, the volatile com pounds will concentrate to certain fractions of the condensate. This fact is illustrated by Figure 6.7, which gives calculated values for methanol and furfural contents in various fractions of condensate (7). The practical consequence of this is that the main part of these compounds can be caught by collecting just the fractions that have the highest contents.

Type of condensate	Amount of condensate tons ptp	Share of total condensate quantity %	Share of methanol formed %	Share of furfural formed %
Cooking	0.6	7	50	50
Evaporation				
Effect no. 4	1.4	17	26	23
Effect no. 5	1.5	18	13	14
Surface condensor	1.6	19	6	7

FIGURE 6.7 Calculated values for the distribution of methanol and furfural in various fractions of condensate (7)

Neutralization prior to evaporation

In order to reduce the vapourization of acetic acid and the formation of furfural, thin liquor from the pulp washing is neutralized with alkali prior to evaporation.

The pH of spent liquor coming from the washing of acid sulphite pulp is about 2-2.5. Acetic acid is almost undissociated at that pH. At $pH = pK_s = 4.76$, acetic acid is 50 % dissociated and at pH above 7, practically all acetic acid is dissociated into acetate ions. Only the free acetic acid is volatile, and the distillation factor is obviously pH dependent, which is illustrated by Figure 6.8.

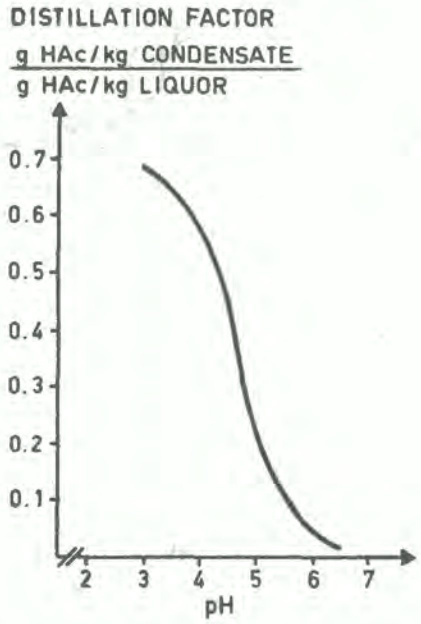


FIGURE 6.8 The distillation factor for acetic acid as a function of pH (1)

Addition of alkali to the spent liquor before evaporation can therefore decrease the transfer of acetic acid to the condensate, though neutral substances such as methanol are not affected. At a Swedish sulphite mill working with sodium base and the STORA Recovery Process, evaporation takes place both before and after an alcohol plant, alkali being added prior to both evaporation sections (4).

The pre-evaporation in this mill is conducted in a Lockman evaporator. To reduce the consumption of alkali, the unevaporated spent liquor is first stripped of sulphur dioxide before alkali is added. This reduces the alkali requirement by about 7 kg Na_2O per ton of pulp. Sodium bicarbonate can be obtained from the reaction tower of the STORA Recovery Process and is used to raise the pH to 4.5-5.0, which is suitable for the fermentation in the alcohol plant, <u>Figure 6.9</u> and <u>6.10</u>.

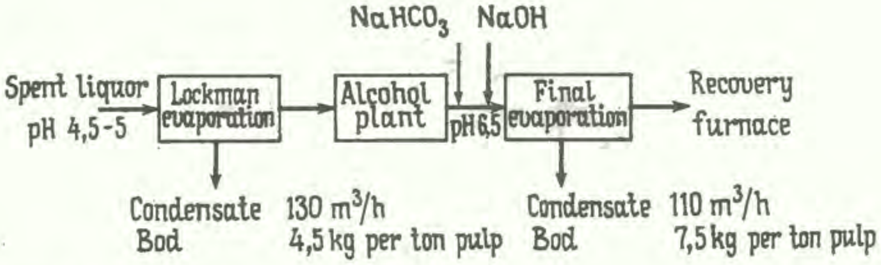


FIGURE 6.9 Flow of spent liquor and condensate at Domsjö sulphite mill (4)

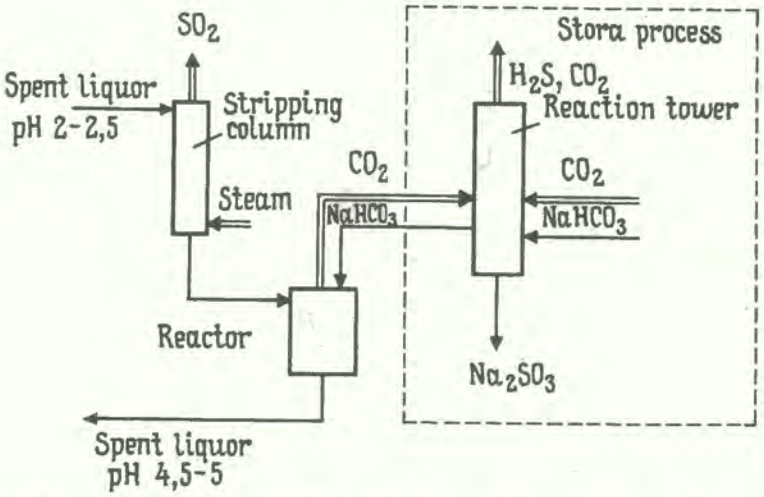


FIGURE 6.10 Stripping of sulphur dioxide and use of sodium bicarbonate from the STORA process for pH adjustment of spent liquor (4)

For the final evaporation a higher pH, about 6.5, is necessary. This can be achieved either with a mixture of sodium bicarbonate and sodium hydroxide or with oxidized green liquor. The pH levels used in both evaporation sections have decreased the acetic acid content in the total condensate by 70 % and the BOD_7 load has decreased from 25 to 12 kg per ton of pulp. One drawback with the neutralization is that more inert chemicals are circulated in the liquor which reduces the fuel value.

For very obvious reasons, the alkali used for pH adjustment of thin liquor prior to evaporation should preferably be the same as the base used for cooking.

Experience shows that the pH of neutralized liquors decreases during storing or in the evaporation, probably due to a slow decomposition of certain organic substances in the liquor (1). The decrease can be up to 2 pH units. But when CaO is used as neutralizing agent, the opposite has been observed, i.e. pH increases after the addition.

It has been reported that a pH value of 6.5 is required to get the maximum reduction of acetic acid transfer to the condensate (6). This value refers to the pH of thick liquor after evaporation, which means that the pH of thin liquor immediately after the addition of alkali should be 1-1.5 units higher if sodium hydroxide, magnesium oxide or ammo-nia is used as neutralizing agent. The quantity of alkali required is said to be 1.6 gramequivalents per kg of dry substance in the liquor for acid sulphite liquors and 1.0 gramequivalent per kg DS for bisulphite liquors. This means that the following quantities are needed, expressed in kg agent per ton of acid sulphite paper grade pulp of softwood:

MgO	35	kg per ton of pulp
NaOH	70	- " -
CaO	50	- " -
NH_3	30	- " -

The increased amount of inorganic material due to thin liquor neutralization decreases the heat value of the liquor and changes the behaviour of the liquor in some ways. In some cases the installation may have to be changed and the operational cost will increase. To compensate for the decreased heat value it may be necessary to add some fuel oil to get stable conditions for the combustion.

The neutralization can also require an expansion of the chemical recovery plant, as the content of inorganic chemicals is increased by 75 % for acid sulphite and by 25 % for bisulphite liquors. If the neutralizing agent contains water, an additional evaporation capacity can be required as well.

Magnesium based liquors can be neutralized with magnesium oxide (MgO) in dry form. The dissolution of dry MgO in thin liquor, however, has proven to be rather troublesome and is not recommended. This can be avoided by using a slurry of magnesium hydroxide ($Mg(OH)_2$) instead, which is readily available in the recovery system. The control of the addition is a well established technique and the system is not very complicated, but extra evaporation capacity of 0.5-1.0 ton of water per ton of pulp will be required, see Figure 6.11.

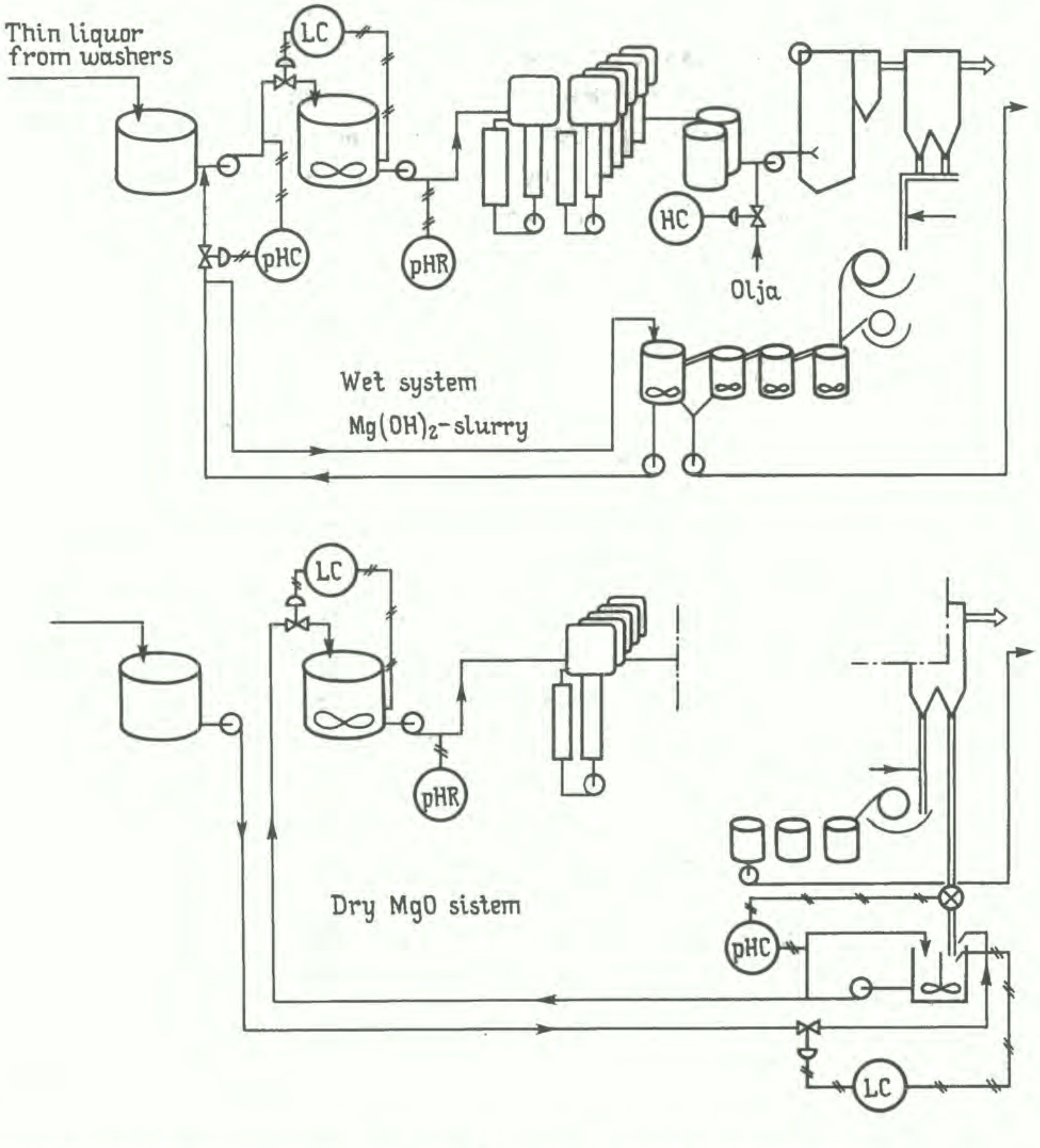


FIGURE 6.11 Systems for thin liquor neutralization in magnesium base sulphite mills. Shadowed parts indicate additional equipment required

Depending on the type of chemical recovery system used in sodium base sulphite mills, sodium carbonate or bicarbonate solution is available for neutralization. The former should not cause any problems, the latter, however, is not sufficient to achieve pH values above 6. Thus the neutralization has to be carried out in two stages, the final stage being performed with sodium hydroxide. This means an extra addition of sodium to the recovery cycle. The first stage is complicated by foaming caused by evolution of carbon dioxide, which should be collected and returned to the system.

In calcium based mills the neutralization can be performed with calcium hydroxide, burnt lime or ammonia. The only extra equipment is that for control of the addition, as there is no question of recovery.

Stripping of condensates

By treatment of condensate with steam in a stripper, volatile substances such as methanol and furfural can be removed. This is frequently practised for sulphate condensate and the same technique can also be applied on sulphite condensate. For heat economy reasons the stripper is preferably connected to the evaporation station.

Stripping of thin liquor prior to evaporation

If the thin liquor is used for alcohol production, the methanol and furfural will be completely stripped off in the alcohol distillation and are obtained as by-products. Even if alcohol is not produced the same distillation technique can be applied with the sole purpose of reducing the methanol and furfural content of the liquor prior to evaporation. This is, however, rather expensive if live steam has to be used.For a good stripping effect about 150 kg of steam is neded per ton of thin liquor. The cost is considerable even if the vapour from the distillation tower is used for heating in evaporation heat exchangers.

Stripping of thin liquor is sometimes used to remove sulphur dioxide and thereby reduce the required amount of neutralizing agent. With as little as 20 kg steam per ton of liquor, 1-2 kg sulphur dioxide per ton of liquor can be stripped off.

Ion exchange technique

Acetic acid and certain other substances in the condensates can be absorbed on an anionic exchanger saturated with OH-ions, which is then eluated with ammonia. The eluate with the contaminating substances is destroyed, e.g. by burning in the recovery boiler.

It has been reported (6) that 70-90 % of the acetic acid can be removed from the condensate by this method.

Reversed osmosis

It has been suggested that sulphite evaporation condensates should be purified with reversed osmosis. However, the process is complicated and expensive. Very high pressure and a large membrane surface are required. So far this technique has not been applied on a commercial scale.

6.6 Re-use of condensates

In acid sulphite pulping, blow down gases and condensates are normally returned to the cooking liquor preparation, the main object being to recover sulphur dioxide. If a trhee-stage countercurrent system with pressure acid tanks is applied, the gas does not have to be cooled first and there is no condensate appears to be taken care of. However, the same amount of liquor is of course transferred to the new cooking liquor as if the gas were first condensed.

This is important as only limited quantities of contaminated condensates can be re-used because of liquor balance restrictions in mills with closed recovery cycles. This balance allows the following quantities of liquor to be added:

- cooking liquor preparation: max 2-3 tons/ton of pulp
- last washer of liquor recovery: approx. 2 tons/ton of pulp replacing hot water.

It has been demonstrated in practice (6) that 60-80 % of the methanol and furfural content of evaporation condensates can be withdrawn from the effluent by re-using the condensate fractions from effects number 4 and 5, which is about 1/3 of the total volume.

Methanol and furfural are not effectively destroyed when the condensate is re-used in cooking liquor preparation and pulp washing. By circulating the methanol rich condensate, its concentration in the liquor is gradually increased, and the main part will probably leave the system and causing an air pollution instead. This is, however, comparatively harmless.

Re-using part of the contaminated condensate in the hot water section of a flue gas scrubber after the recovery

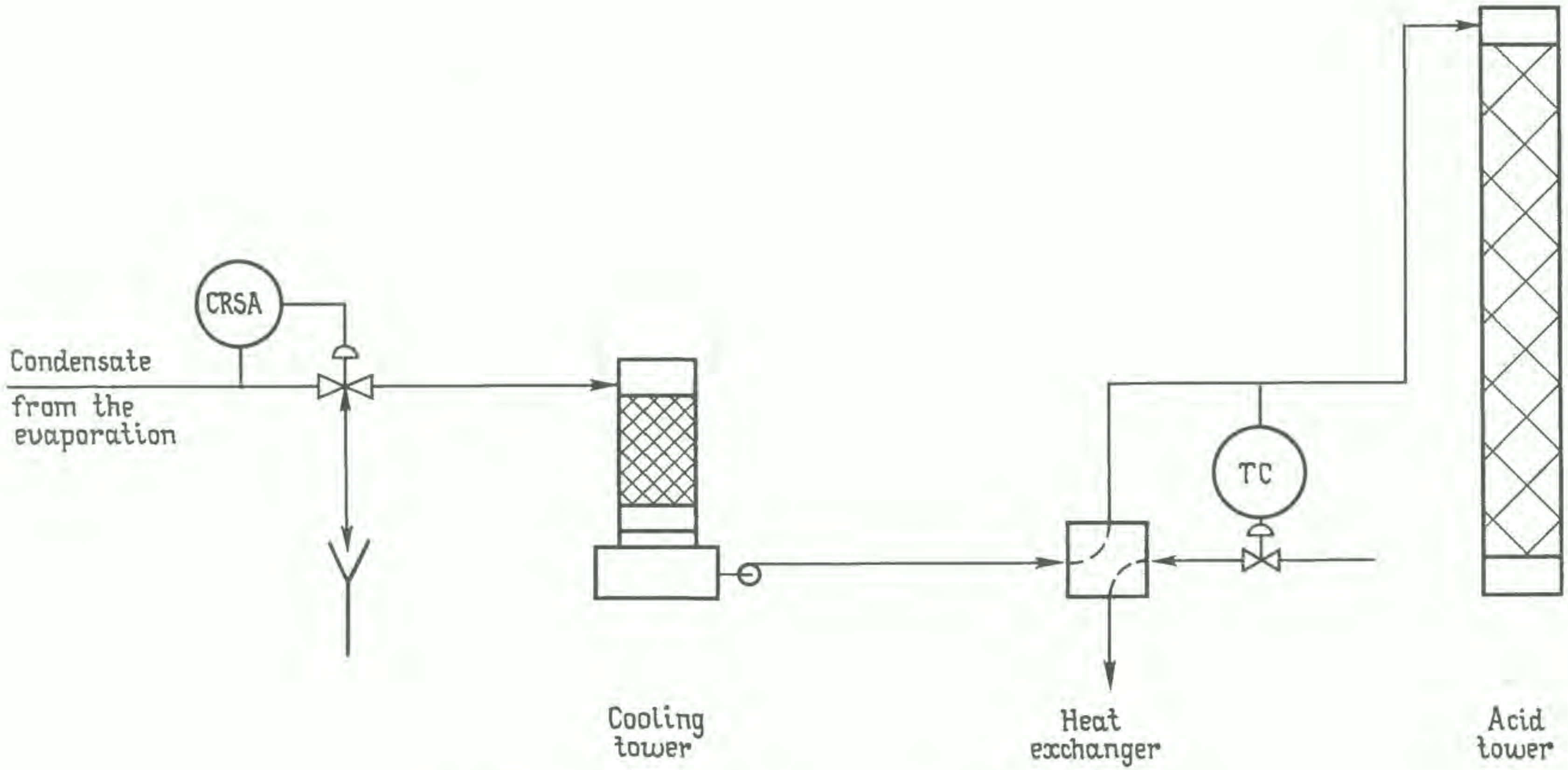


FIGURE 6.12 Re-use of condensate for acid preparation

boiler has been tried (4). In this case the methanol is partly stripped off, and the BOD of the effluent is correspondingly reduced. Stripping effects of 70-90 % have been achieved.

A suggested arrangement for recycling of condensate to the cooking liquor preparation is shown in Figure 6.12. The condensate has to be controlled continuously by a colorimeter to avoid that dry solids forming the liquor (carry over) from entering the acid tower. This would seriously disturb the operation of the tower by foaming and could initiate a decomposition of the acid. The instrument should be connected to a valve, switching the condensate to the sewer, if polluted by liquor solids.

Literature reference list, Chapter 6

(1) SSVL
The environmental care project, Technical Summary,
Stockholm 1974

(2) Rydholm, S.
Pulping processes
Interscience Publishers, New York 1965

(3) Sveriges Skogsindustriförbund
Yrkesbok Y-211 Lutindunstning (in Swedish)
Markaryd, Sweden, 1978

(4) Brännland, R. et al
New in-plant technology to reduce pollution from a sodium base sulphite mill
Svensk Papperstidning 79(1976):18, 591

(5) Rexfelt, J. and Samuelson, O.
The Composition of Condensates from the Evaporation of Sulfite Spent Liquor
Svensk Papperstidning 73(1970):21, 689

(6) SSVL

The environmental care project, Project no. 3:3
Sulphite condensates (in Swedish)
Stockholm 1973

(7) Axelsson, O. and Wahlund, L-G
Volatile oxygen demanding compounds in the sulphite process (in Swedish)
Svensk Papperstidning 75(1972):8, 287

7. COMBUSTION OF SULPHITE LIQUORS AND REGENERATION OF CHEMICALS

7.1 Introduction

Liquor combustion has a two-fold purpose, to make use of the fuel value and to regenerate the cooking chemicals. The fuel value of thick liquor (evaporated spent cooking liquor) is considerable and could in certain processes be sufficient to cover the total steam consumption of the mill and, in addition, part of the electric energy consumption via steam turbine generators. At 55 % dry solids concentration the effective heat value of evaporated spent sulphite and NSSC cooking liquors is 6-9 GJ (1400-2200 Mcal) per ton of liquor, Figure 7.1.

Process	Effective heat value
Acid sulphite, dissolving	9.3 GJ (2200 Mcal) per ton liquor
Acid sulphite, paper	8.9 GJ (2100 Mcal) - " -
Bisulphite, paper	7.0 GJ (1700 Mcal) - " -
NSSC	5.9 GJ (1400 Mcal) - " -
Heavy fuel oil	40.8 GJ (9800 Mcal) per ton

FIGURE 7.1 Effective heat values of thick liquors at 55 % DS concentration compared to heavy fuel oil

The combustion conditions determine the type of chemical reactions that will occur and thereby the form in which the cooking chemicals can be recovered. Especially important is the amount of air and how it is furnished, which decides whether oxidation or reduction reactions will dominate.

7.2 Calcium sulphite

The combustion of concentrated calcium-based spent liquors is usually performed in primary furnaces attached to ordinary steam boilers. The primary furnace can be of the Loddby or the Lurgi type, the former being shown in Figures 7.2-7.4. The ashes from the combustion, containing a mixture of calcium sulphate and oxide in about equal amounts, as well as small amounts of carbon (soot), cannot be re-used in the cooking process, but have sometimes to be recovered in dust collectors in order to reduce air pollution.

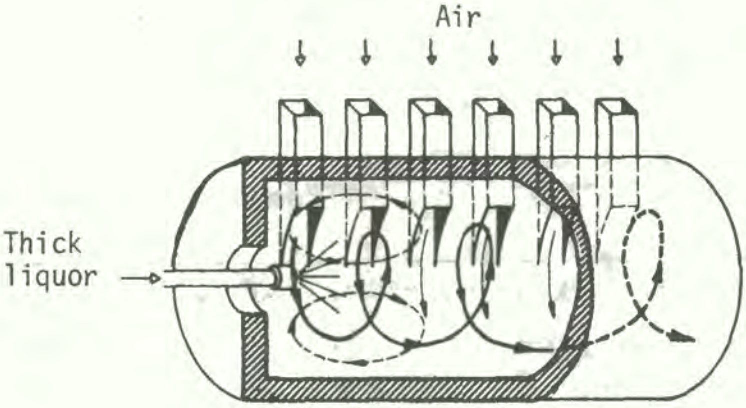


FIGURE 7.2 Loddby furnace

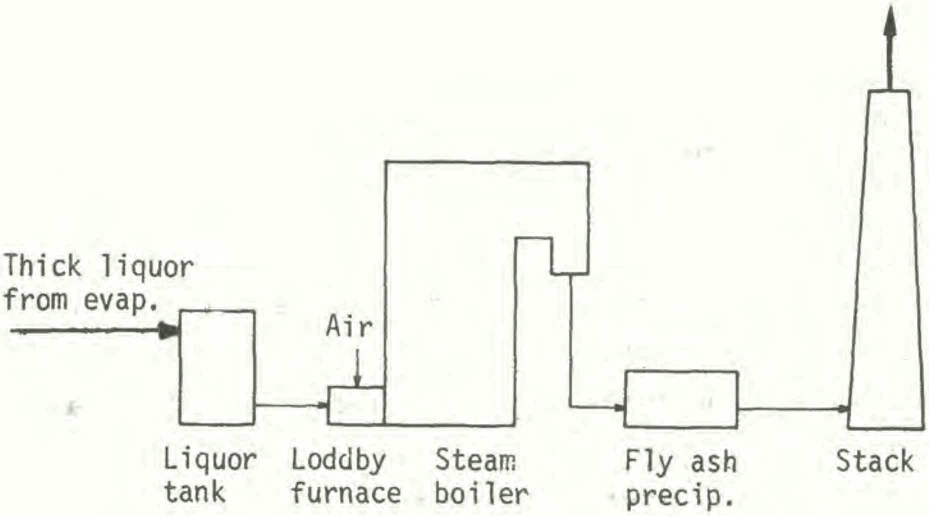


FIGURE 7.3 Schematic flow sheet of liquor combustion system with Loddby furnace

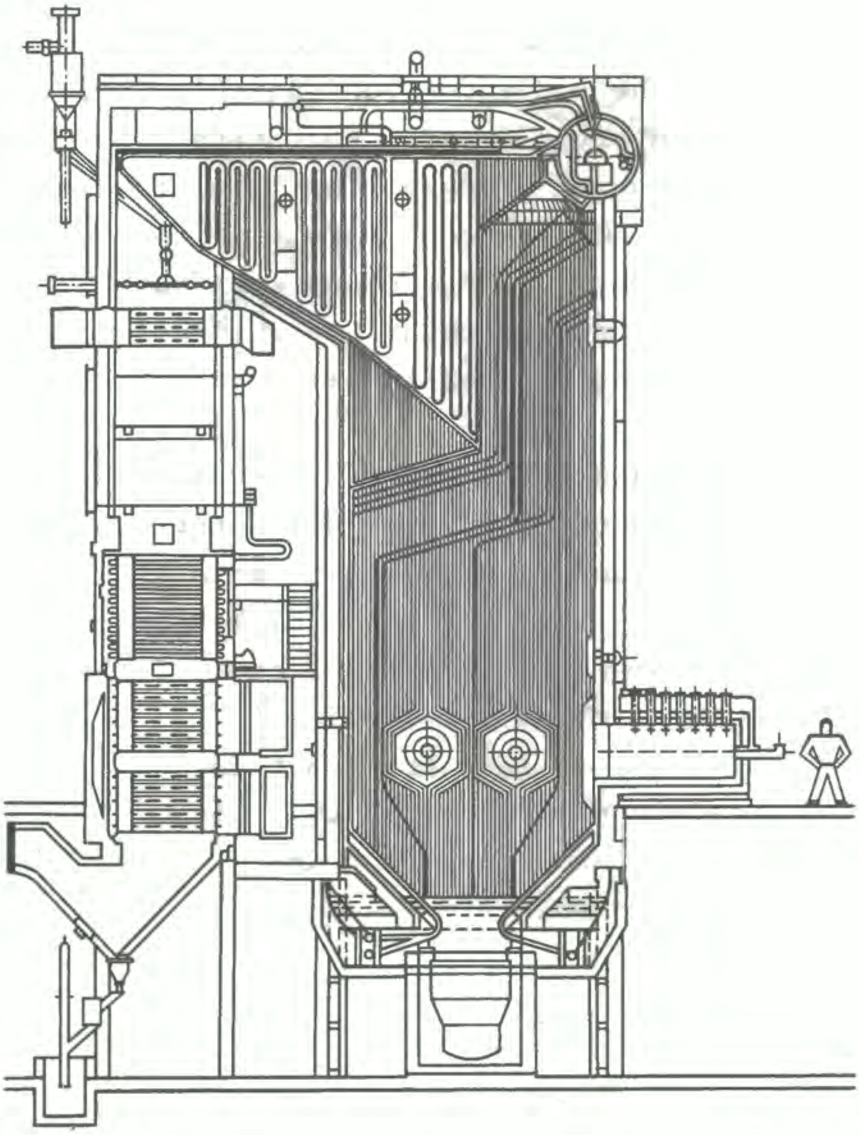


FIGURE 7.4 Loddby extension furnace attached to an ordinary boiler for the combustion of calcium-base sulphite spent liquor

The purification of flue gases from ashes is carried out either in mechanical dust separators, electrostatic precipitators or in wet separators, scrubbers. In the latter case sulphur dioxide is absorbed as well to some extent. Usually the ashes are discharged wet condition and are disposed of on the land. The quantity is quite considerable, about 250 kg (calculated as 50 % dry content) per ton of pulp. Even small sulphite mills will thus produce great amounts in a few years time.

About 70 % of the sulphur content in calcium liquors will leave the combustion furnace as sulphur dioxide, SO_2. the concentration is too low (about 0.5-1.0 % SO_2 on dry flue gas) to motivate recovery for re-use in the cooking process. The total quantity, however, can be 130 kg SO_2 per ton of pulp in the acid sulphite process for paper grade pulp and will cause serious air pollution if not thoroughly washed out. This subject will be discussed further in paragraph 7.6.

The Loddby furnace was originally developed for combustion of calcium liquors, but has proven suitable for magnesium and ammonium liquors as well. Its rather small capacity (about 10 tons of liquor at 55 % DS per hour, corresponding to a production of 110 tons per day of acid sulphite paper pulp) is of course a limitation, but two or more furnaces can be attached to the same steam boiler, provided that the volume of its combustion chamber and flue gas channels are sufficient for the flue gas volume produced.

7.3 Ammonium sulphite

In comparison to calcium sulphite the sulphur recovery of ammonium based liquors is simplifed in two ways. All sulphur is contained in the combustion gases as sulphur dioxide and can be absorbed in aqueous ammonia. Besides there is little or no fly ash present to complicate the absorption. Aqueous ammonia is a more ideal medium for absorption than milk of lime (or even milk of magnesia), but it presents a problem because of its volatility, which puts a limit to the alkalinity allowable.

To recover ammonia from the spent liquor, on the other hand, is very difficult. Unless removed previously, it will decompose and burn during combustion, leaving water and nitrogen as products.

A number of processes for the recovery of ammonia from spent sulphite liquors by means of ion exchange have been studied (5), but so far this technique has not been practised commercially. In such processes, ammonia is absorbed from spent liquor on strongly acidic cation exchange resins and subsequently displaced by hydrogen ions from a fresh solution of sulphur dioxide to regenerate the resin and to produce an ammonium bisulphite solution suitable for use as cooking liquor.

7.4 Magnesium sulphite and magnefite

Magnesium-based liquors are usually burnt in combustion furnaces similar to those used for sulphate black liquor combustion. The process differs from the latter in that the chemicals are not converted to a smelt on the bottom of the furnace, but rather are swept through the boiler with the flue gas in the form of magnesium oxide ash and sulphur dioxide gas. Thereby the combustion products are in a form that is very suitable for a simple cooking liquor regeneration process.

The design of the combustion chamber is important if required properties in the ash are to be obtained. Combustion must be complete to produce an ash that is essentially free of carbon. On the other hand, the formation of overheated "dead burned" magnesium oxide, which is unsuitable for subsequent liquor generation, must be prevented. The amount of air used in the combustion must also be carefully controlled to prevent sulphate formation.

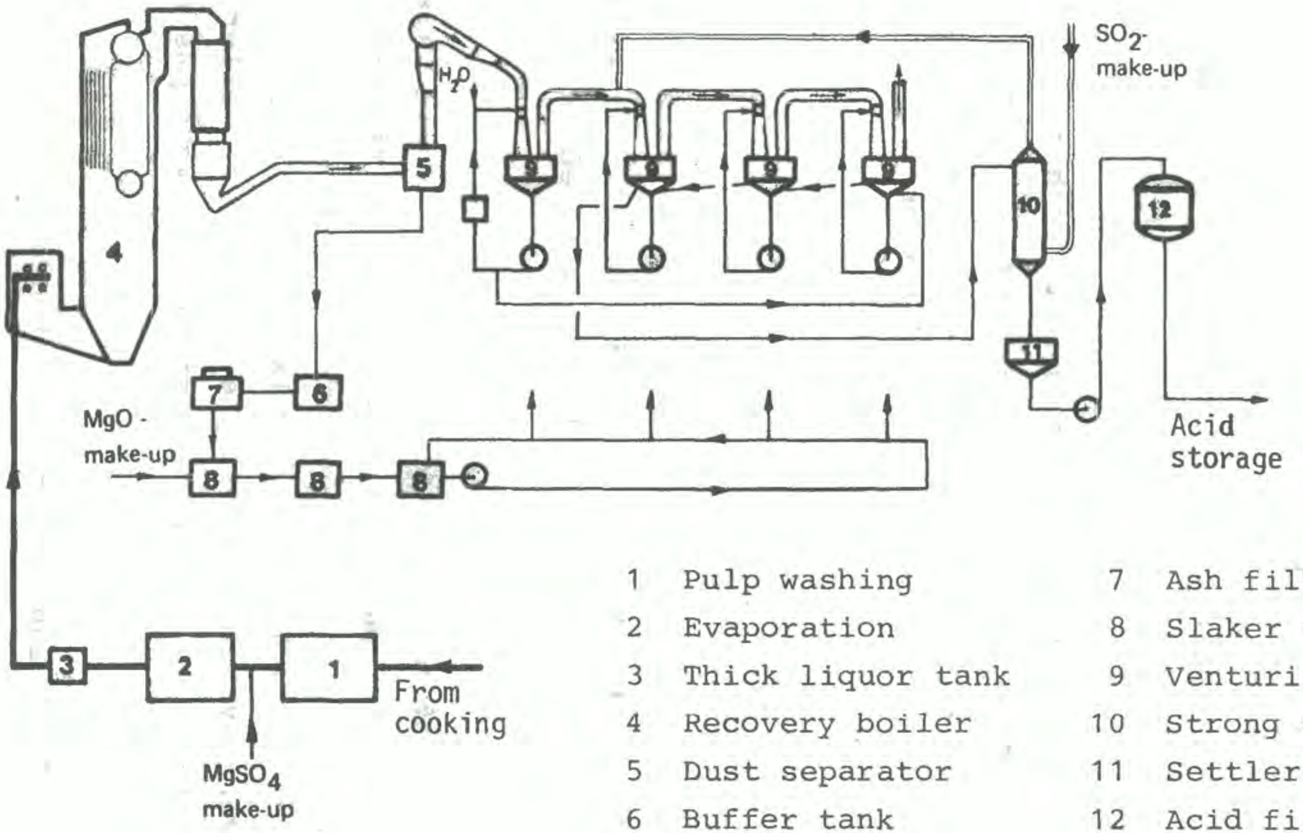
The principles of a magnesium liquor recovery system is shown in Figure 7.5. Concentrated liquor is sprayed into the combustion furnace, where magnesium compounds are converted mainly to oxide fly ash separated from the flue gas in dust collectors and the gas is then cooled with water in a cooling tower, or in a cooling venturi as in the figure. The sulphur dioxide is subsequently absorbed with a circulation solution of magnesium sulphite and bisulphite, the pH of which must be carefully controlled by addition of a magnesium hydroxide slurry. In the system illustrated in Figure 7.5 the absorption is performed in three venturi absorbers following the cooling venturi.

The raw acid produced in a system like this consists mainly of magnesium bisulphite and is ready for use in magnefite pulping after filtration. For acid sulphite pulping the raw acid has to be diluted with sulphur dioxide water, and is then fortified in a cooking liquor preparation plant using the same principles as for calcium base cooking (paragraph 2.4).

Magnesium oxide separated from the flue gas in an electro-precipitator or in a mechanical separator, is fed to a buffer tank, where eventually magnesium oxide make-up is added as well. Cold water is added under stirring and impurities such as chlorides, calcium and potassium compounds as well as to some extent magnesium sulphate, are dissolved and can be removed on the following ash filter.

The purified magnesium oxide is treated with warm water in a series of three to four slakers, where it is converted to a hydroxide slurry, which is used for absorption of sulphur dioxide from the flue gas as already mentioned.

Magnesium make-up is added either as sulphate to the thin liquor prior to evaporation, or as oxide to the buffer tank before the ash filter.



1	Pulp washing	7	Ash filter
2	Evaporation	8	Slaker tanks
3	Thick liquor tank	9	Venturi absorbers
4	Recovery boiler	10	Strong acid tower
5	Dust separator	11	Settler
6	Buffer tank	12	Acid filter

FIGURE 7.5 Schematic flow sheet of magnesium liquor recovery system

A number of magnesium recovery systems have been developed, the essential difference being the equipment for sulphur dioxide absorption. Instead of venturi absorbers, various types of ball scrubbers are used, as shown in Figures 7.6-7.8.

The lowest reported discharge of sulphur dioxide with the flue gas is 5 kg SO_2 per ton pulp (3).

Operating experience in modern plants has shown that the magnesium recovery process is very stable compared to the operation of a sulphate black liquor recovery boiler. This means less risk of air or water pollution problems.

7.5 Sodium sulphite and NSSC

There are basically three different ways for the recovery of sodium sulphite and NSSC liquors, viz. smelt-based, pyrolysis-based and fluidized bed-based processes.

Recovery of sodium liquors based on a smelt is rather complex in comparison to, for example, magnesium recovery. Consequently it is normally more expensive, so that small mills in particular cannot afford a complete recovery system and the type of recovery boiler required. Thus a number of simplified versions have been developed.

In the following some of the processes will be surveyed and schematic flow sheets given as they are of importance for the discussion of pollution abatement measures.

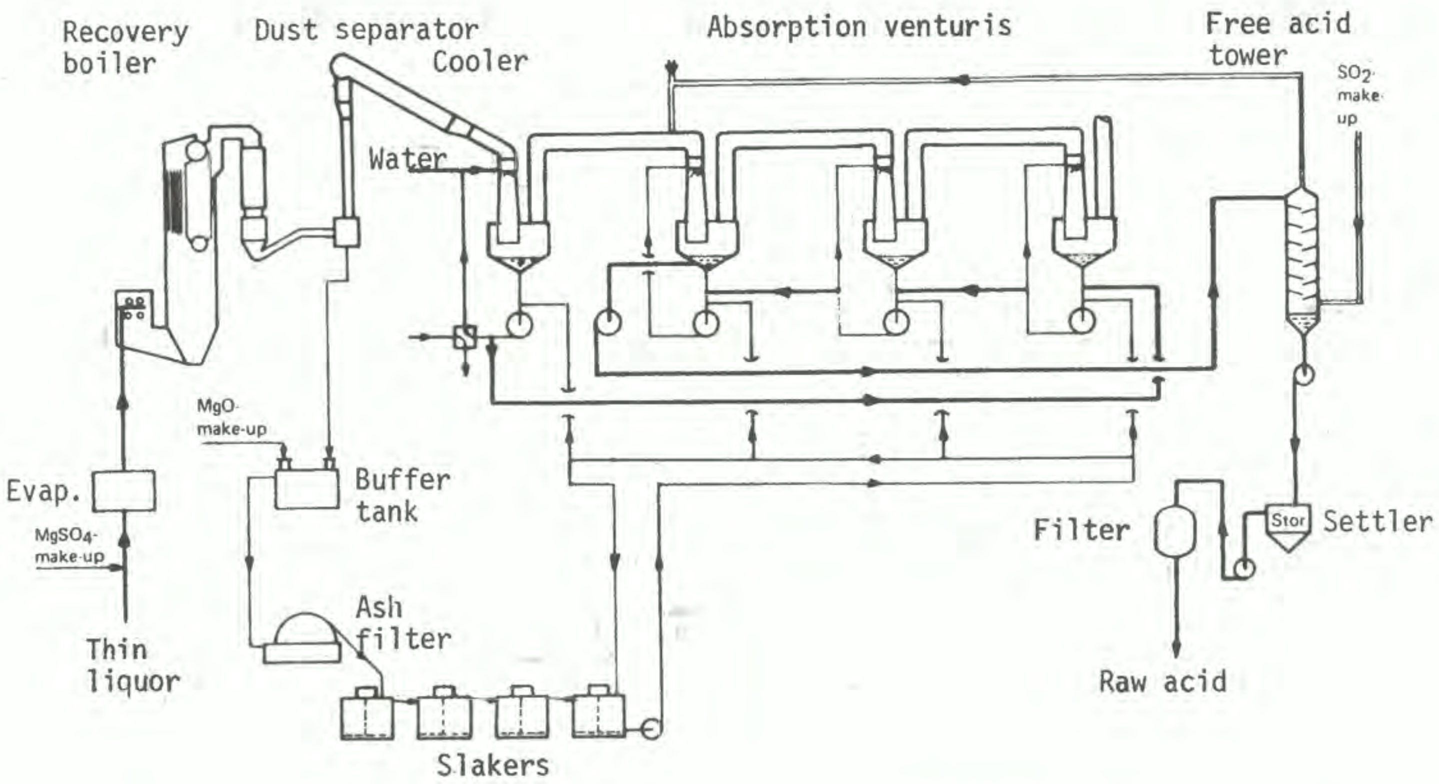


Figure 7.6 Magnesium recovery system according to B&W-Nordström

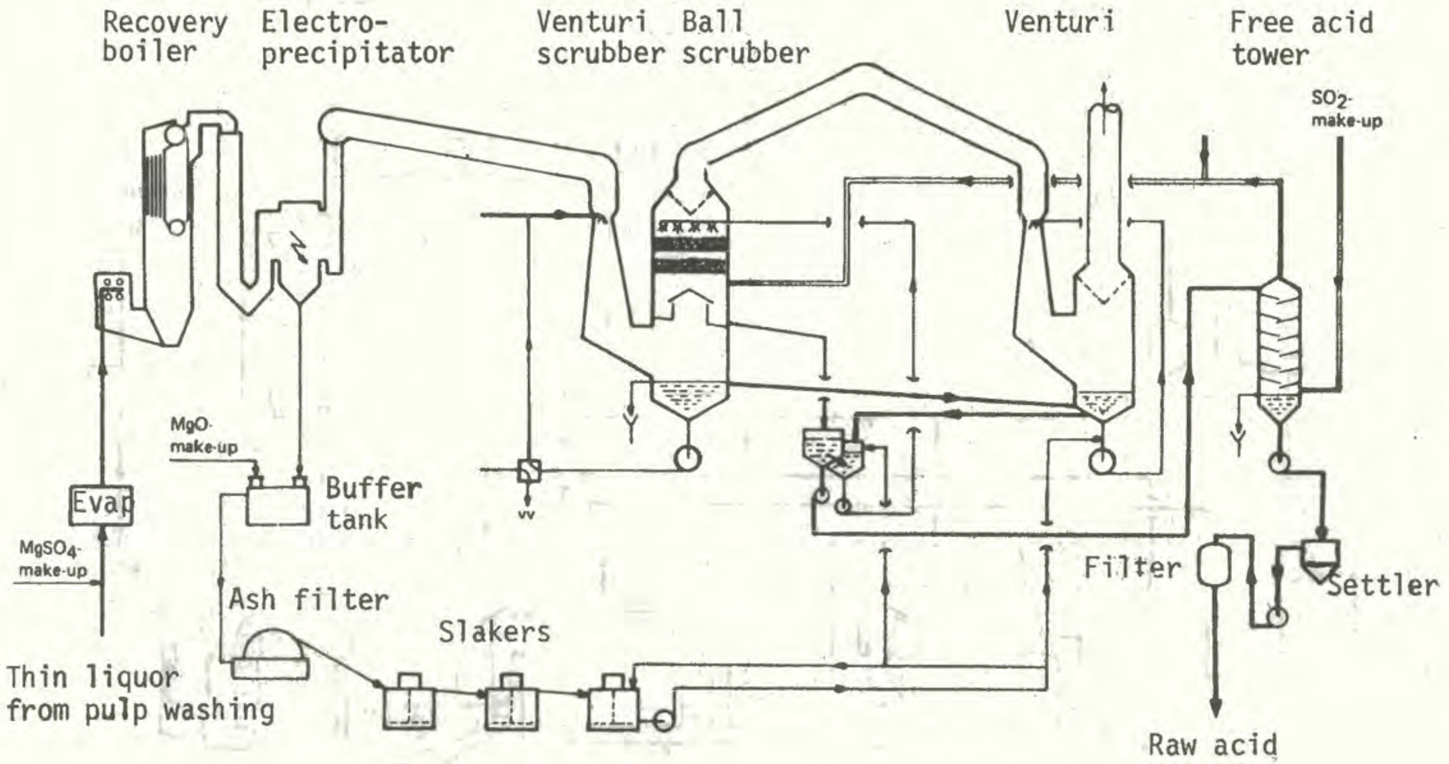


Figure 7.7 Magnesium recovery system (Ahlström)

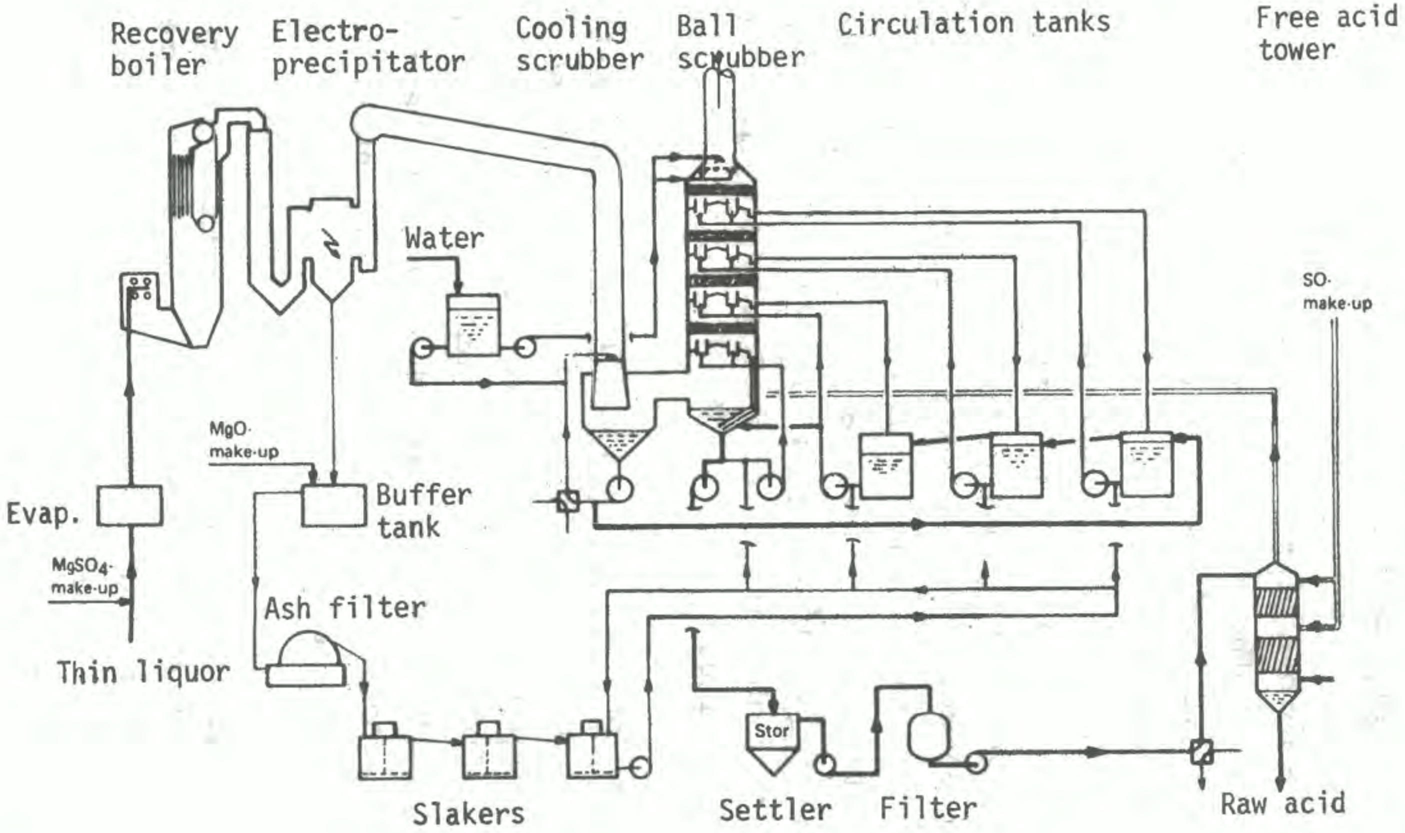


Figure 7.8 Magnesium recovery system according to SF

Smelt-based processes

A large number of the processes proposed for the recovery of pulping chemicals form sodium-based spent sulphite liquors are based on the combustion of the concentrated liquor in a recovery boiler of the type used for sulphate black liquor. The products obtained are similar to those from sulphate liquor combustion, a smelt consisting primarily of sodium carbonate and sulphide with small amounts of sulphate and thiosulphate, and a flue gas containing sulphur dioxide. The most significant difference is that the sulphidity of the smelt and the sulphur dioxide content of the flue gas are higher in the case of sulphite liquor than for sulphate liquor.

Recovery of the sodium and sulphur compounds from the combustion products for generation of cooking liquor is based on the conversion of the chemicals in the smelt to some combination of sodium carbonate, sodium sulphite and sulphur dioxide. These chemicals can be combined to produce cooking liquor for any of the neutral or acid sulphite processes.

In the STORA Recovery Process, Figure 7.9, the smelt from the recovery furnace is dissolved to a green liquor which is clarified and then carbonated with a recycled stream of pure carbon dioxide, thus converting the green liquor to a solution of sodium bicarbonate. The exit gas from this "reaction tower" is a mixture of hydrogen sulphide in carbon dioxide, which is fed to a "Claus-reactor" where the hydrogen sulphide reacts with sulphur dioxide gas to produce elemental sulphur.

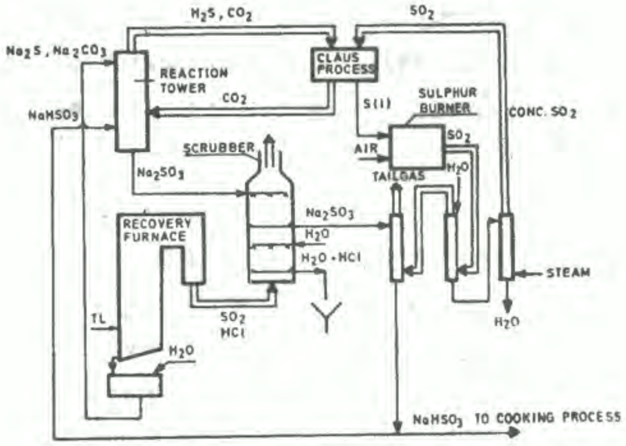


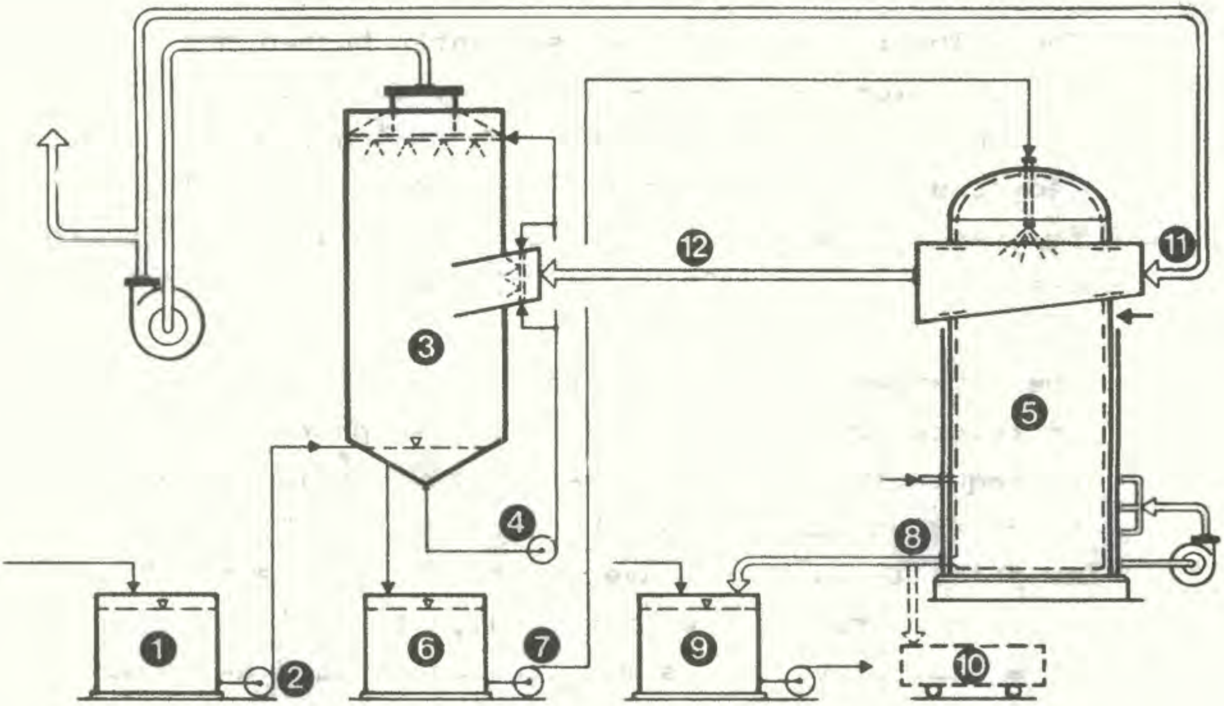
FIGURE 7.9 The STORA recovery process for sodium-based liquors

The sulphur produced is subsequently burned and the sulphur dioxide is concentrated by solution in water and stripping with steam. Part of the sulphur dioxide is recycled to the Claus reactor and part can be liquified for use in the second stage of a two-stage cooking process.

The bicarbonate solution produced in the reaction tower is reacted with recycled sodium bisulphite, produced subsequently in the process, to give sodium sulphite and more carbon dioxide for the carbonation. The sodium sulphite is in turn converted to a sulphite/bisulphite mixture by reaction with the sulphur dioxide containing flue gas. Part of this mixture can be used as cooking liquor in the first stage of the two-stage process. Another part is fortified with residual sulphur dioxide from the liquification process to form the recycled bisulphite solution.

As described above the STORA process produces chemicals for a two-stage process, but with suitable modifications it can be adapted to conventional acid sulphite or NSSC pulping.

A modification of the Stora process is the STORA-BROBY process operating with a BROBY SMELTER, Figure 7.10. The Broby Smelter is a less expensive combustion equipment consisting of a cylindrical brick-lined furnace designed to burn a pre-evaporated liquor with 22-25 % dry solids content. The combustion capacity is about 6 tons of dry solids per hour, corresponding to a pulp production capacity of 150 tons ordinary chemical pulp per day or 300-350 tons per day of semichemical pulp.



Key

1 Pre-evaporated liquor
2 Dosing pump
3 Cyclone evaporator
4 Circulation pump
5 Broby smelter
6 Thick liquor
7 Injection pump
8 Smelt outlet
9 Smelt dissolver
10 Solidified smelt
11 Exhaust gas from evaporator
12 Blended gas to evaporator

FIGURE 7.10 The BROBY system for combustion of sulphite liquors

No steam is produced in the application as shown in the figure, but the combustion gas is used for final evaporation of the liquor in a direct-contact evaporator, where the concentration is raised to about 55 % DS. The smelt obtained is processed in a suitably modified Stora process to regenerate cooking liquor.

However, the smelter can be attached to a low pressure steam boiler to produce steam enough for the pre-evaporation of thin liquor up to 30 % DS content, provided that the heat value and the original DS content are sufficiently high. If the heat value is too low, fuel oil must be added to the concentrated liquor prior to combustion.

The Broby system with a direct-contact cyclone evaporator is advantageous in case of high silica content in the liquor, which is usual in pulping tropical hardwoods and non-wood raw material. In order to avoid the heavy air pollution that normally occurs in direct evaporation processes, a two-stage wet scrubber is attached to the evaporator (not shown in the figure).

Basical features of the Tampella Recovery Process are illustrated in Figure 7.11 and a schemtaic flow sheet is shown in Figure 7.12.

The used cooking liquor is concentrated by evaporation and then burned in a recovery furnace. The smelt obtained from the furnace is dissolved and the green liquor is clarified by conventional means.

The green liquor is pre-carbonated with gases carrying carbon dioxide (usually recovery boiler flue gases) to form bisulphide and bicarbonate. This solution is fed to a stripper-evaporator, where bicarbonate is added at the same time. The sulphur is stripped as hydrogen sulphide and the carbonate crystallizes as monohydrate. Part of this monohydrate is withdrawn and circulated through a carbonator, where new bicarbonate is formed and returned to the stripper-evaporator. The process is controlled by regulating the sulphidity of the liquor leaving the stripper-evaporator by means of the amount of bicarbonate added.

The hydrogen sulphide and sodium carbonate obtained from the process can be converted to cooking liquors of any desired type by conventional methods. In sulphite pulping the hydrogen sulphide is burned to sulphur dioxide and adsorbed in the sodium carbonate solution to form sodium bisulphite. In NSSC cooking the absorption is carried out only to the extent need to reach the proper soda/sulphite proportion.

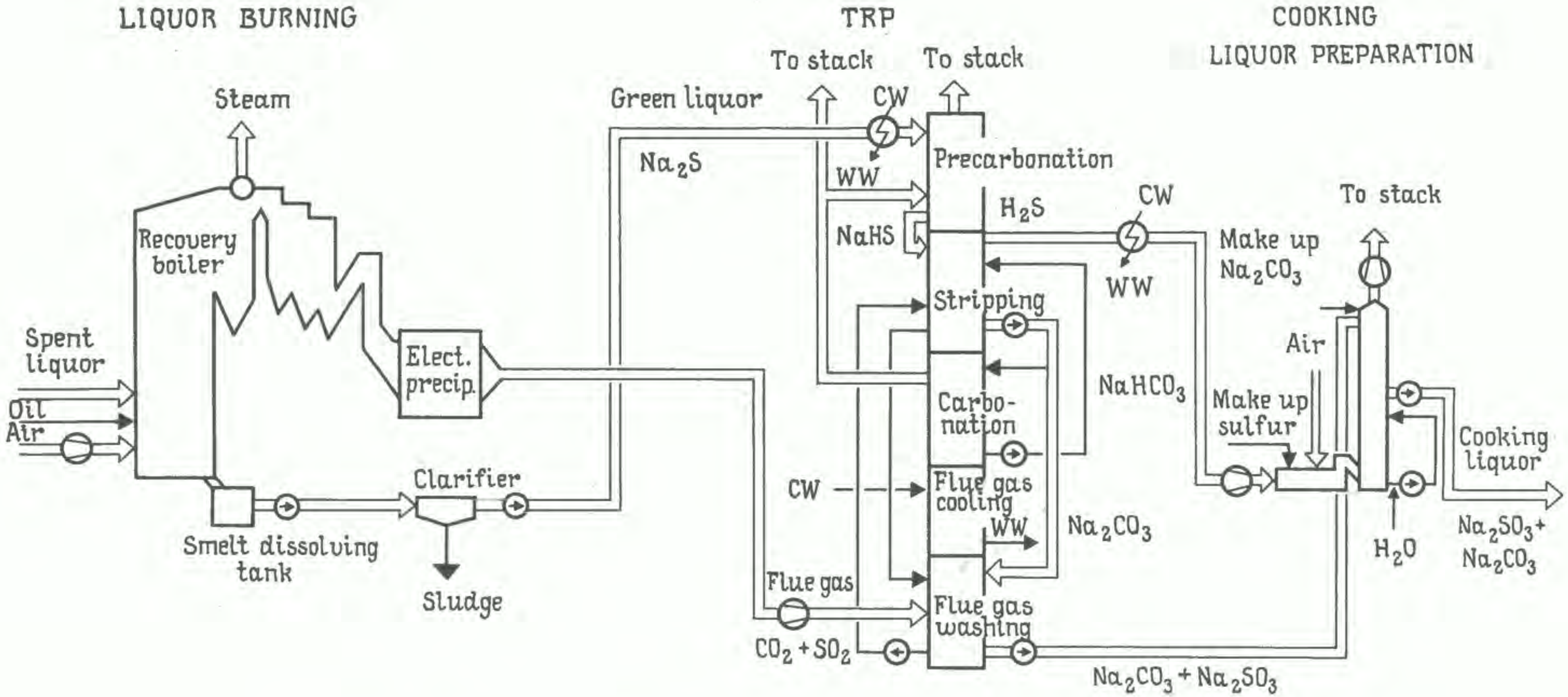


Figure 7.11 The Tampella recovery system for sodium-based sulphite liquors

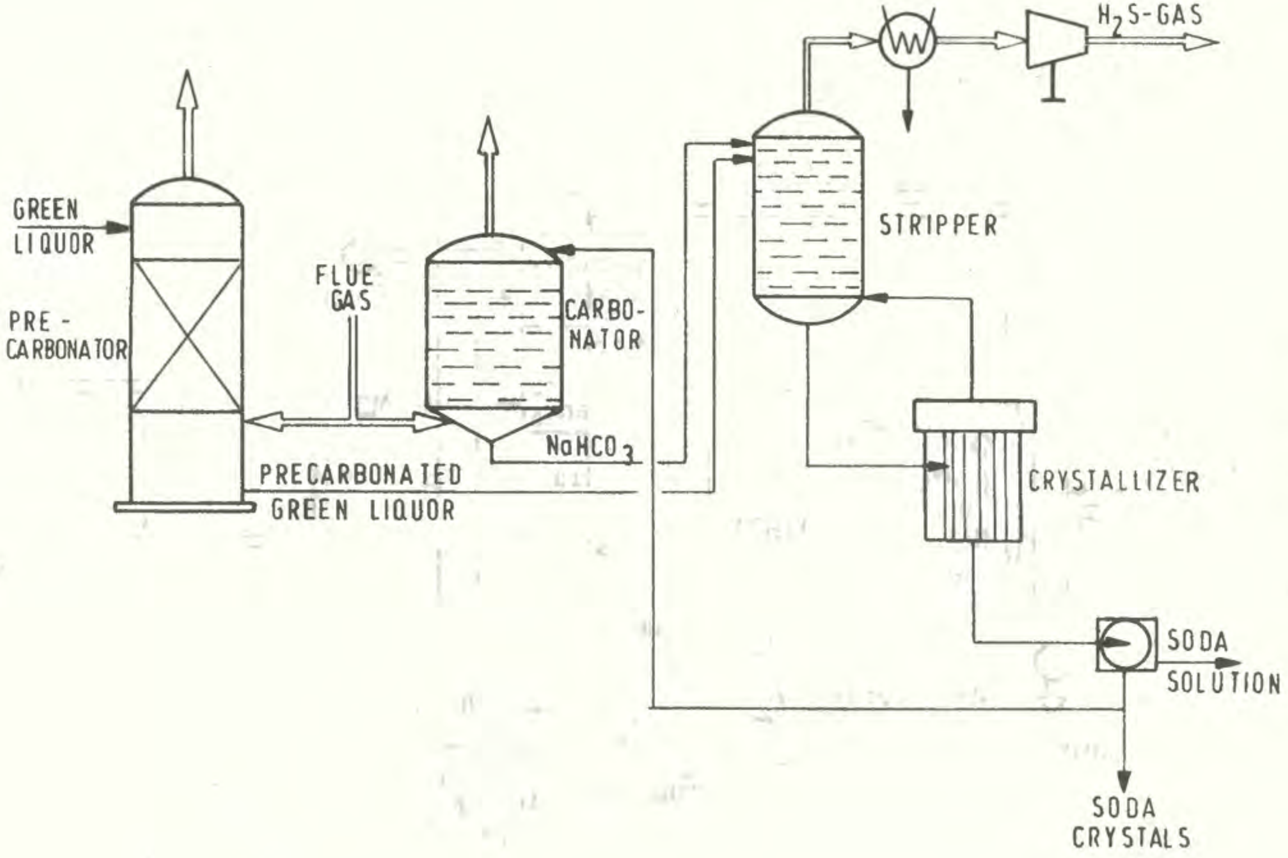


Figure 7.12 Principal flow sheet of the Tampella recovery process

Pyrolysis-based process

Of the processes proposed for recovery of sulphite liquors, which are not based on a smelt procedure, the most interesting probably is the pyrolysis process. It is characterized by its dry end products, soda (sodium carbonate) and sulphur dioxide gas, which can be directly used for generation of cooking liquor.

The pyrolysis processes will be exemplified by the SCA--Billerud process, Figure 7.13, which is in use commercially in a few European mills, one of them producing high yield bisulphite pulp.

The first stage of this process is a pyrolysis of the concentrated liquor, which is performed in a specially designed reactor, Figure 7.14. In an almost instantaneous reaction the sodium salts of the spent liquor are converted into sodium carbonate, and the sulphur compounds into hydrogen sulphide. As the temperature is kept between 700 and 760°C, i.e. below the melting point of sodium carbonate, the reaction products are a dry powder and a combustible gas. The sulphur is in the gas phase and the sodium in the powder.

In the second stage the gas is burnt after separation from the powder. By this combustion the hydrogen sulphide is converted to sulphur dioxide.

After separation the powder is leached with water. The carbon contained in the powder is filtered off and returned to the pyrolysis reactor. The pure sodium carbonate solution is used for absorption of the sulphur dioxide, resulting in a sodium sulphite solution, which is used as cooking liquor.

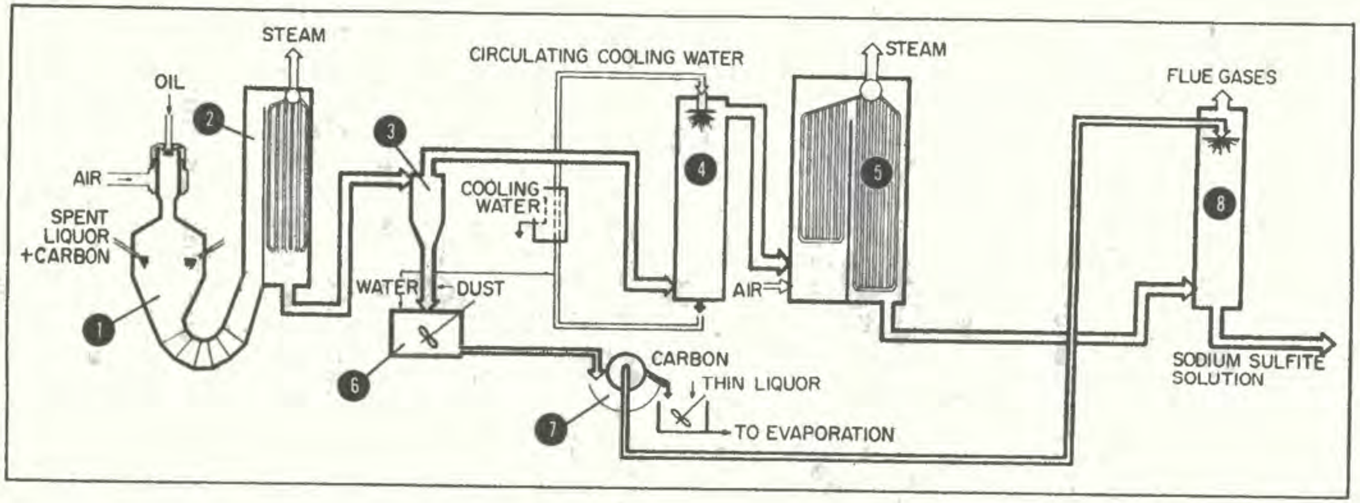
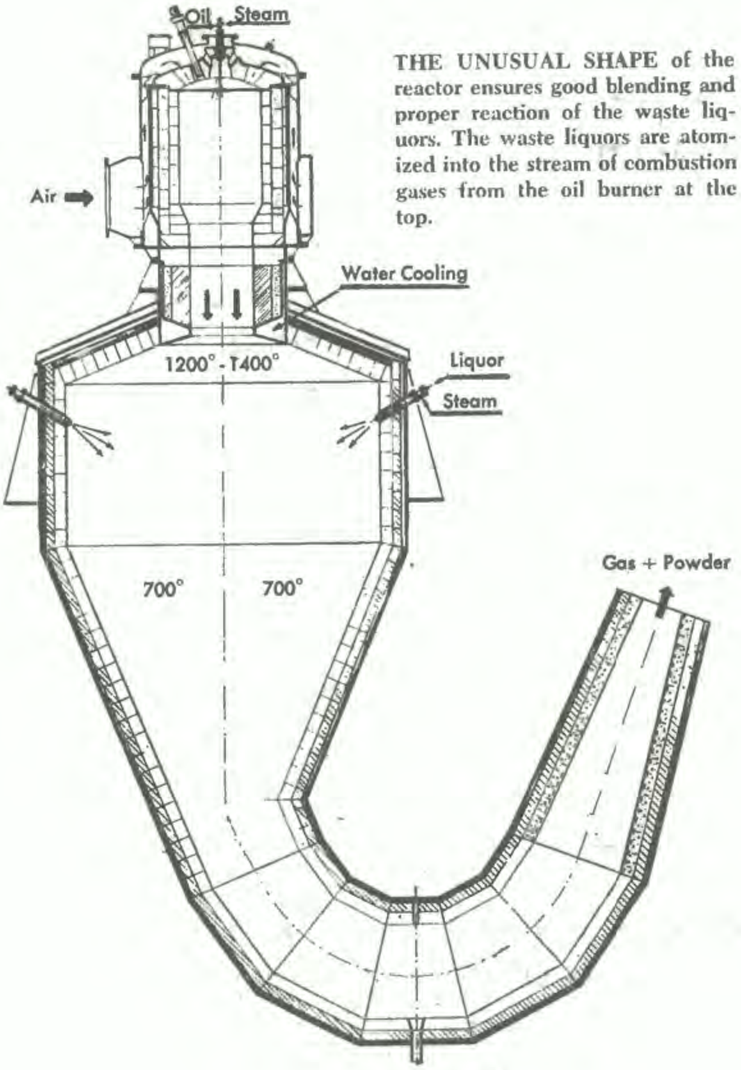


FIGURE 7.13 The SCA-Billerud recovery process adapted to a high-yield bisulphite mill



THE UNUSUAL SHAPE of the reactor ensures good blending and proper reaction of the waste liquors. The waste liquors are atomized into the stream of combustion gases from the oil burner at the top.

FIGURE 7.14 Details of the reactor used in the SCA-Billerud recovery process

The heat produced in the pyrolysis process and in the combustion of hydrogen sulphide can be recovered in boilers for production of superheated high-pressure steam. In addition, warm water at 70°C is produced in a gas cooler-condenser.

Fluidized bed based combustion

While not resulting in the regeneration of cooking liquor, fluidized bed processes are being used for the destruction of the organic content of NSSC spent liquor for purposes of pollution control (5). In these pro cesses, the organic portion of the spent liquor is converted substantially to a sulphur-free mixture of carbon dioxide and water and the inorganic portion to a mixture of sodium sulphate and sodium carbonate. This latter material is suitable for use as a make-up chemical in sulphate mills.

Examples of this process are the Container-Copeland process and the FluoSolids process of Dorr-Oliver Inc.

7.6 Flue gas purification

Flue gas from the combustion of sulphite liquors contains dust as well as gaseous contaminations that will create pollution problems if they are not removed before the gas is discharged to the atmosphere. The chemical recovery systems used for magnesium and sodium based liquors are very effective as pollution abatement measures. In the case of calcium-based liquors, on the other hand, a flue gas purification is required, which is not motivated from the chemical recovery point of view.

The removal of hydrochloric acid or chlorides will be a requirement in many mills as a consequence of increased system closure.

Dust separation

The fly ash formed in the combustion of calcium liquors can be separated from the flue gas by means of mechanical separators (e.g. small cyclones), in wet scrubbers or in electro-precipitators.

The Varkaus venturi scrubber, Figure 7.15, can be used for separation of fly ash from the combustion of calcium sulphite liquors. At the same time the separated calcium oxide serves as an absorption agent for sulphur dioxide. The scrubber water is injected into the venturi under high pressure to get a fine dispersion (mist) of droplets, on which dust particles are absorbed. The calcium oxide absorbed is converted to hydroxide in the water and reacts with sulphur dioxide to form calcium sulphite. Part of this sulphite is oxidized to sulphate.

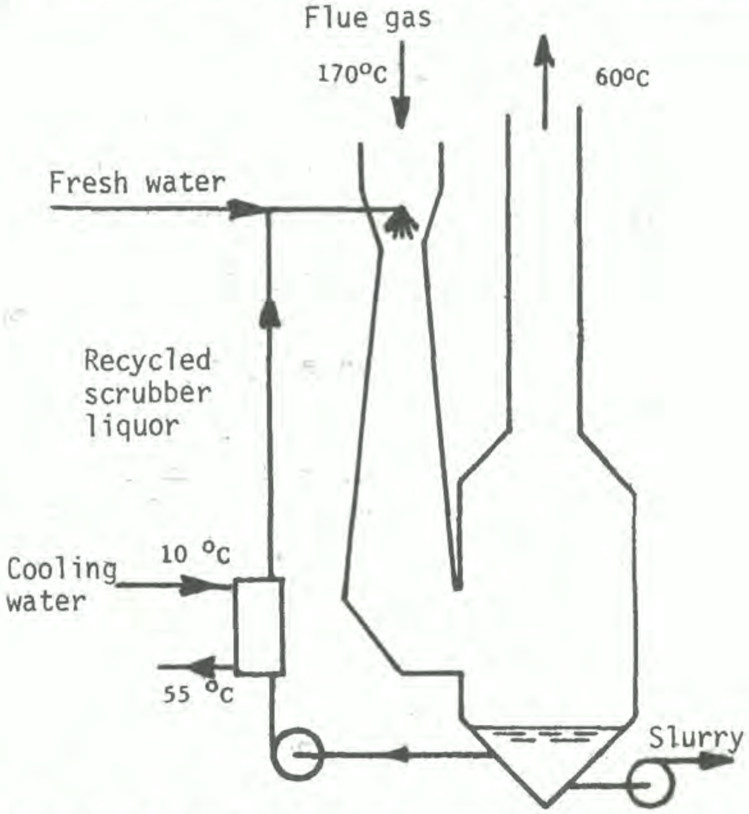


FIGURE 7.15 The Varkaus venturi scrubber

The following data have been reported from a Swedish installation in connection with calcium liquor combustion (6):

Content of dust in flue gas	
before scrubber	17.0 g/m^3 norm
after scrubber	0.3 - " -

Content of sulphur dioxide in flue gas	
before scrubber	70 kg/ton pulp
after scrubber	41 kg/ton pulp

Sulphur dioxide absorption

The concentration of sulphur dioxide in flue gas from the combustion of calcium sulphite liquors is usually in the range of 0.5-1.0 % by volume, depending on the pulping conditions. This corresponds to 60-120 kg of sulphur dioxide in the flue gas per ton of pulp.

The concentration is too low to motivate a sulphur recovery as the base does not contribute to the economy of such a process, but on the contrary the sulphur dioxid is a burden. Thus sulphur dioxide absorption is motivated solely by environmental protection considerations.

The Bahco SO_2-scrubber, Figure 7.16, was developed during the SSVL Environmental Care Project in Sweden 1970-73, and was tried in a pilot plant project having a capacity of 30 000 m^3 norm flue gas per hour which corresponds to about 150 tons pulp per day.

The dust separation efficiency was good (99 %), but sulphur dioxide absorption was not considered sufficient until milk of lime (calcium hydroxide) was used as absorption media. With powdered lime stone the absorption was only 65 %. This makes the process rather expensive considering that the calcium sulphite/sulphate slurry obtained is useless and must be disposed of at an extra cost.

The best results obtained were (3):

Dust concentration in flue gas after scrubber	0.15 g/m^3 norm
Content of sulphur dioxide in flue gas after scrubber	25 kg/ton pulp

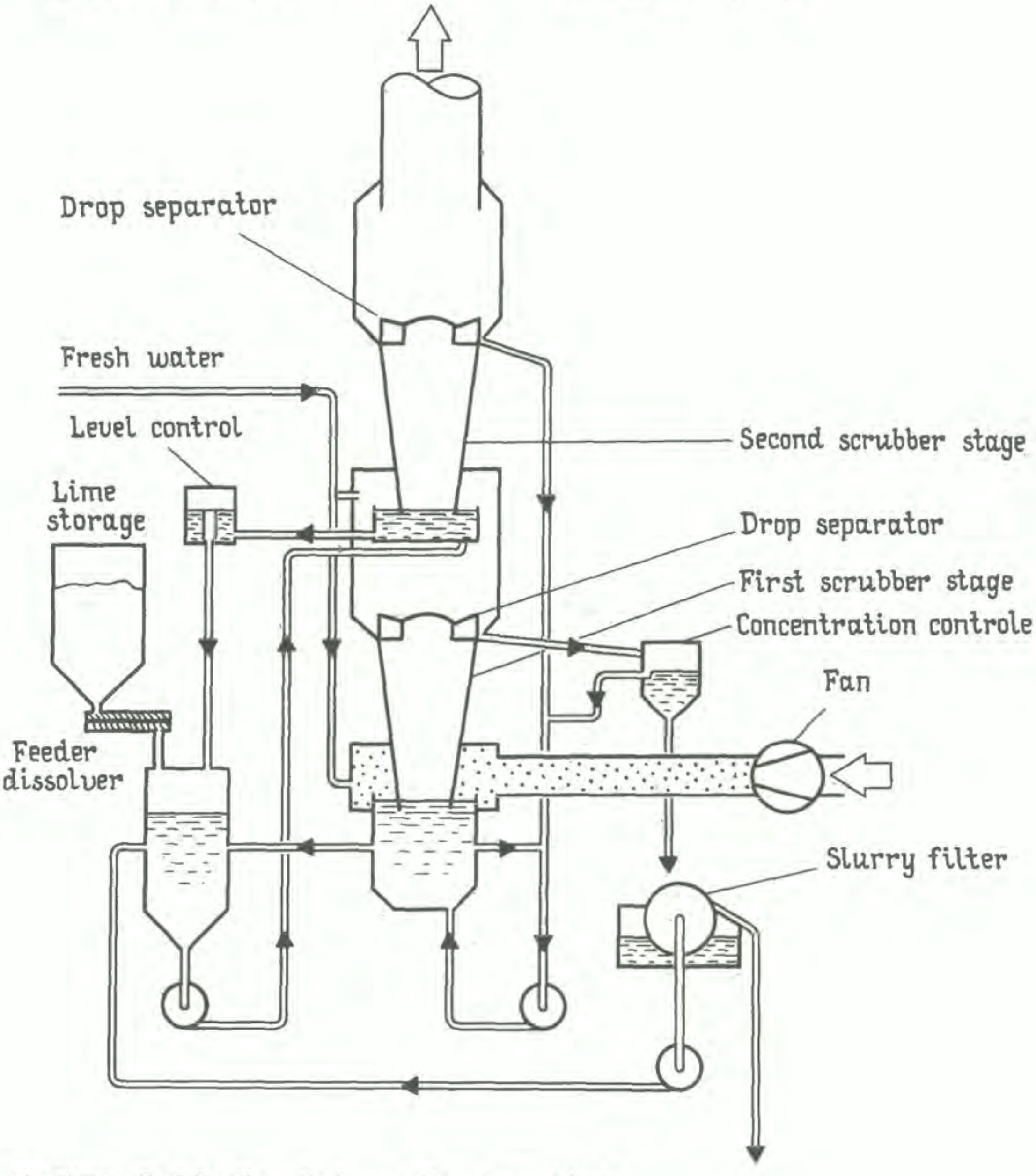


FIGURE 7.16 The Bahco SO_2 scrubber

The Tampella flue gas scrubber, Figure 7.17, is designed specially for removal of sulphur containing compounds such as sulphur dioxide and hydrogen sulphide from flue gas. The scrubber can be fitted with a heat recovery stage if required.

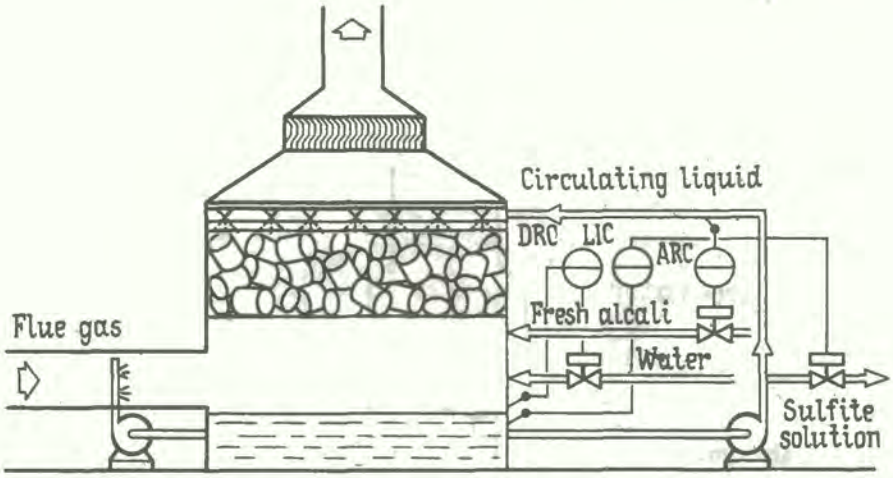


FIGURE 7.17 The Tampella flue gas scrubber

Hot flue gas is fed from the bottom or from the side into the scrubber, where it is precooled by spraying a part of the circulating washing liquor into the gas.

The flue gas is then washed in a packing section where efficient contact is reached between gas and washing liquor. The washing liquor is distributed evenly by means of a special distribution system giving low pumping power consumption.

Sulphur dioxide removal efficiency is claimed to be 95-98 %, but this obviously depends on the concentration of incoming gas.

Chloride removal

The major sources of chlorides in the cooking chemical cycle are the wood (especially if sea-floated logs are used), chloride containing make-up chemicals and recycled bleaching liquors. A requirement for effective recovery of chemicals is that the chloride concentration in the cooking liquor can be kept at a low level. Reported experience has shown (8), that this concentration should not exceed 0.8 kg NaCl per litre of cooking liquor.

The chloride concentration in cooking liquor depends on the relation between total chloride input and chloride lost in various parts of the chemical cycle. An illustration of this relation is shown in Figure 7.18.

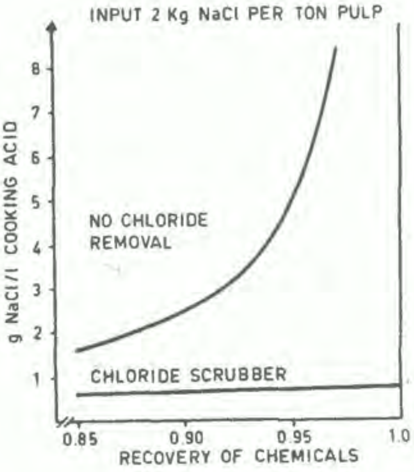


FIGURE 7.18 Concentration of sodium chloride in the cooking acid as a function of the recovery of chemicals

Chlorine compounds in thick liquor in combustion leave the furnace partly with the flue gas (mainly as hydrochloric acid) and partly with the smelt or ash (as chlorides of sodium, magnesium etc). Hydrochloric acid is formed in the flue gas by a reaction between sulphur dioxide and sodium chloride, Figure 7.19. Consequently the formation is favoured by a high concentration of sulphur dioxide in the flue gas.

$$1/2\ O_2\ (g) + SO_2\ (g) + 2NaCl\ (s) + H_2O\ (g) \rightarrow$$
$$2HCl\ (g) + Na_2SO_4\ (s)$$

FIGURE 7.19 Reaction formula for the formation of hydrochloric acid in flue gas

In magnesium-based sulphite mills chlorides are discharged via the ash filter, as chlorides are easily soluble in cold water, while magnesium oxide is not.

An interesting method for chloride removal from flue gas is practised in a Swedish sodium sulphite mill (8), where a special hydrochloric acid washing stage has been installed in the flue gas scrubber, which is shown in Figure 7.20. It is reported that about 40 % of the input chloride leaves in the flue gas as hydrochloric acid, up to 80 % of which is washed out in the washing stage.

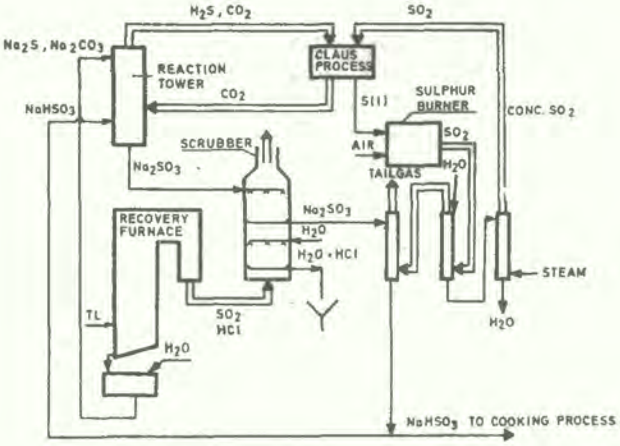


FIGURE 7.20 Recovery system with a special hydrochloric acid washing stage in the flue gas scrubber

Literature reference list, Chapter 7

(1) Horntvedt, E.
A Sodium-Base Sulfite Recovery Process Based on Pyrolysis
TAPPI November 1970 Vol. 53, No. 7, 1074

(2) Jönsson, S-E
Pollution problems in small sulphite mills (in Swedish)
Norsk Skogsindustri No. 11, 1971, 336

(3) SSVL
The Environmental Care project, Technical Summary
Stockholm 1974

(4) Lundén, B.
Stora-Broby Recovery Process for Semichemical Pulp Mills
TAPPI September 1970, Vol. 53, No. 9, 1726

(5) Whittle, D.J.
Sulfite and Bisulfite Pulp Mill Recovery Systems
TAPPI July 1971 Vol. 54, No. 7, 1074

(6) Sveriges Skogsindustriförbund
Yrkesbok Y-212 Lutförbränning (in Swedish)
Markaryd, Sweden, 1979

(7) Keef, R.C.
Magnesium Bisulfite Recovery Startup
TAPPI April 1971 Vol. 54, No. 4, 564

(8) Brännland, R. et al
New in-plant technology to reduce pollution from a sodium base sulphite mill
Svensk Papperstidning 79(1976):18, 591

(9) Warnqvist, B. and Norrström, H.
Chlorides in the recovery boiler and a mechanism for chloride removal

TAPPI November 1976 Vol. 59, No. 11, 89

(10) SSVL
Final report from SSVL 7 "Klorid i återvinningssystem"
(in Swedish)
Stockholm 1977

PART IV - IN-PLANT MEASURES FOR SULPHATE PULPING AND RECOVERY

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1 COOKING

1.1 The cooking process

In the sulphate or soda cook wood or other fibrous material is treated with an alkaline cooking liquid, called white liquor, at 160-180°C for 30 to 200 minutes. Most of the lignin in the wood is then dissolved and the fibres liberated. The fibres are separated from the cooking liquor and dissolved wood constituents by washing. Solid impurities and undissolved wood components are separated by screening.

The various operations and the discharge points in the sulphate process are shown in Figure 1.1.

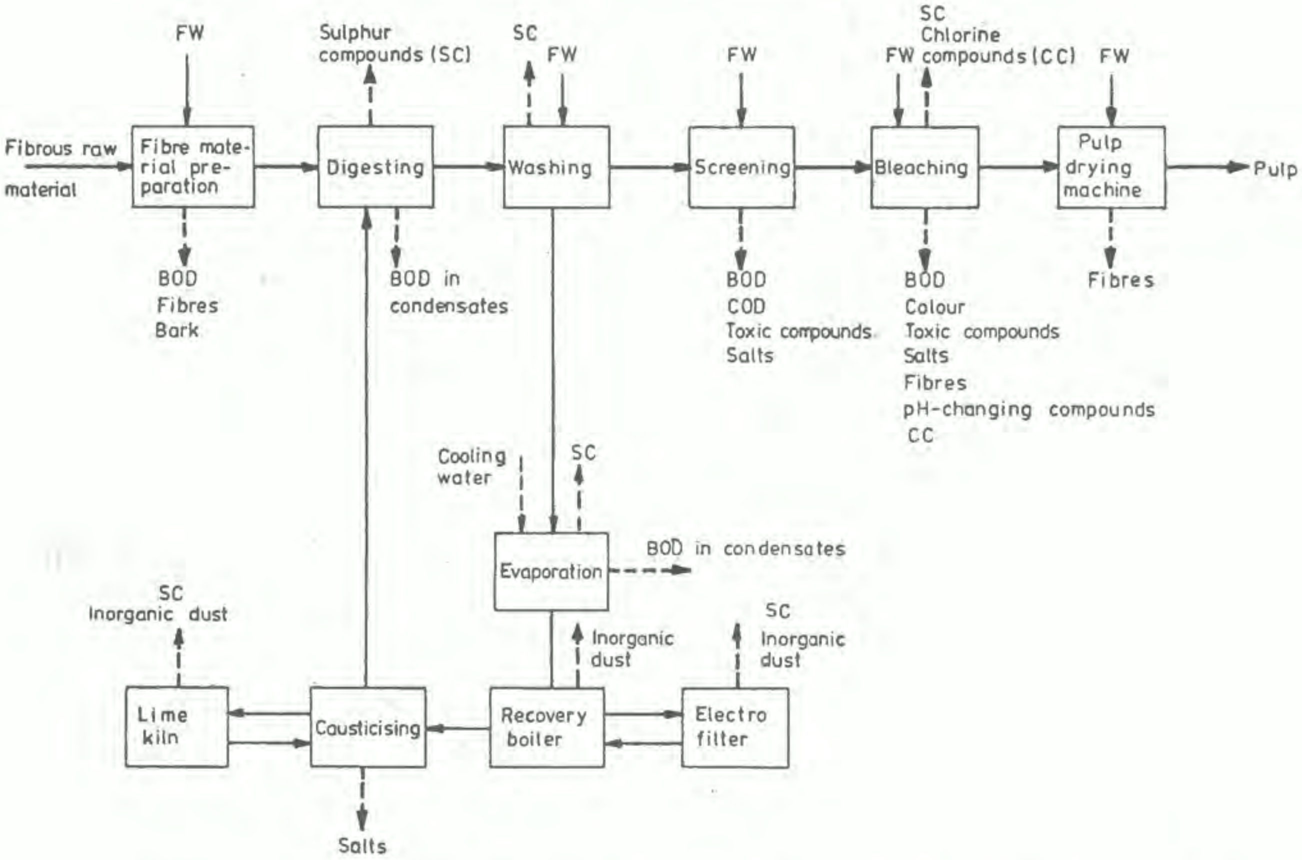


Figure 1.1. Principal flow sheet of bleached sulphate pulp mill

The active chemicals in the sulphate cooking are sodium hydroxide, NaOH, and sodium sulphide, Na_2S. In a soda cook sodium hydroxide alone is used, but the lignin dissolves more rapidly in the presence of sulphide, moreover, the carbohydrates are better preserved, giving a higher yield and a stronger pulp. In the sulphate cook a certain level of "sulphidity" is thus desirable, which is provided by the sodium sulphide. The white liquor also contains certain sodium compounds as inactive ballast - for instance, sodium carbonate Na_2CO_3, sodium sulphate Na_2SO_4, sodium sulphite Na_2SO_3, sodium thiosulphate $Na_2S_2O_3$ and sodium chloride NaCl.

The composition of white liquor can vary considerably in both concentration and the proportions of the various chemicals. Approximate values for the main components are the following (sulphate cooking liquor) (1):

Sodium hydroxide, NaOH	100-120 g/l
Sodium sulphide, Na_2S	20-40 g/l
Sodium carbonate, Na_2SO_3	20-30 g/l
Sodium sulphate, Na_2SO_4	10-20 g/l

Terms and definitions used in sulphate and soda cooking are given in Table 1.1.

Table 1.1. Terms and definitions in sulphate and soda cooking

Effective alkali	$NaOH + \frac{1}{2} Na_2S$
Active alkali	$NaOH + Na_2S$
Total titrable alkali	$NaOH + Na_2S + Na_2CO_3$

These quantities are expressed as percentage of the wood charge (grams of alkali · 100)/(grams of wood) per cent

$$\text{Sulphidity} = \frac{Na_2S \cdot 100}{Na_2S + NaOH} \text{ per cent}$$

$$\text{Causticizing efficiency} = \frac{NaOH \cdot 100}{NaOH + Na_2CO_3} \text{ per cent}$$

$$\text{Degree of reduction} = \frac{Na_2S \cdot 100}{Na_2S + Na_2SO_4} \text{ per cent}$$

or

$$\frac{Na_2S \cdot 100}{\text{total S (as } Na_2S)} \text{ per cent}$$

Liquor-to-wood ratio = (liquid volume)/(dry wood weight)

In the calculations the quantities of all sodium compounds are expressed as the corresponding amounts of NaOH.

The main factors governing the cooking process and the lignin content of the final pulp (degree of delignification) are the wood properties and chip quality, the alkali to wood ratio, the liquor-to-wood ratio, the sulphidity and the time/temperature relationship. The result of the cook is determied by the interaction between the temperature and the chemical concentration throughout the cook. The degree of delignification is often expressed as the Roe number, which is defined as the number of grams of chlorine absorbed by 100 grams of bone-dry pulp in 15 minutes at 20°C. The value corresponds roughly to the percentage of lignin in the pulp. The degree of delignification can also be expressed as the Kappa number; this is the permanganate consumption of the pulp under specified conditions. The approximate relationship between the Kappa and Roe numbers is shown in Figure 1.2.

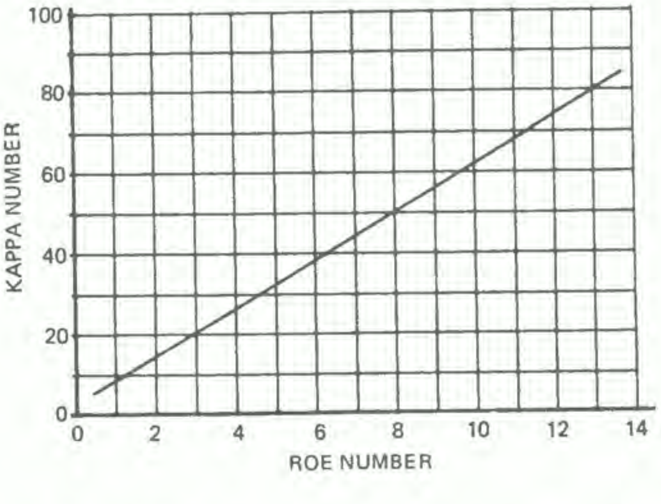


Figure 1.2. Relationship between Kappa number and Roe number for kraft pulp (1)

If the alkali charge is increased and other conditions are kept constant the Roe number falls, and vice versa. The effective alkali-to-wood ratio normally ranges from 17 to 27 percent for cooking the normal types of kraft pulp. If too much alkali is added there will be severe degradation of the cellulose while for an alkali-to-wood ratio below about 17 per cent, delignification to normal kraft pulp will not occur. If, in the latter case, the cooking time is prolonged, previously dissolved lignin will be reprecipitated and the Roe number will rise instead of falling. The higher the alkali-to-wood ratio the more rapidly the cook proceeds and the higher the pulp production; but at the same time there is an increase in the amount of chemicals circulating in the recovery system.

The cooking liquor consists mainly of the water from the wood, and white and black liquors. The liquor-to-wood ratio can be varied, but there must be enough alkali for the delignification. The more the cooking liquor is diluted the longer will be the cooking time. Consideration of heat economy also limits the liquor volume. However, too small a volume may impair the circulation in the digester and lead to difficulties in emptying the digester.

The white liquor and the amount of water added to the cook in the form of chip moisture do not alone provide an adequate liquid volume. However, to add water would be uneconomical because later on it must be vaporized to render the liquor combustible. Instead, 20 to 50 per cent of black liquor is added. Besides combustible products, the black liquor contains a certain amount of sodium sulphide, which is involved in the cooking process.

The white liquor is diluted with recirculated black liquor and wood moisture so that its sodium hydroxide concentration at the beginning of the cook is about 40 g/litre. This applies in batch cooking where the liquor-to-wood ratio is 3.5:1, in a continuous cook a liquor-to-wood ratio of 2.5:1 is used and this can be maintained with white liquor alone.

The sulphidity of white liquor is dependent on the extent of the sulphur losses. At a sulphidity above 35 per cent the yield and the pulp properties are only slightly affected. Too low a sulphidity (below about 25 per cent) results in slow cooking, a low yield and impaired strength. An increase in sulphidity decreases the cooking time to a constant Roe number.

The relationship between Roe number and cooking time for four temperature levels is shown in Figure 1.3.

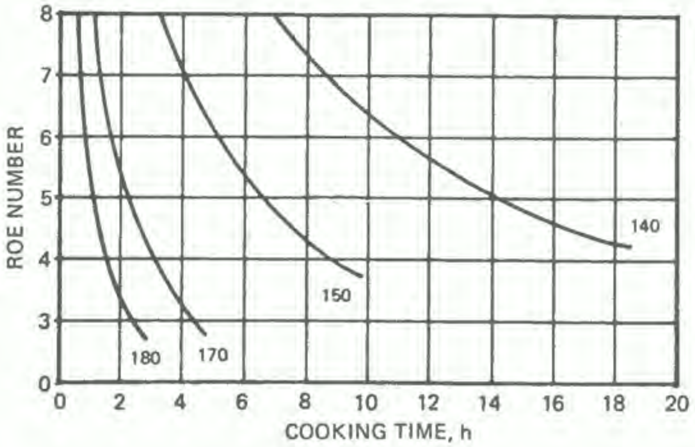


Figure 1.3. Approximate relationship between Roe number and cooking time for kraft cooking at four temperatures °C (1)

The final degree of delignification is chosen according to the desired quality of the pulp (Table 1.2).

Softwood pulp to be bleached is cooked to a Kappa number of 30-40 (Roe No. 4.5-6.5) for reasons of economy and quality. Semi-bleached kraft pulp can be cooked in the same way as bleached; alternatively, it can be cooked to a low Kappa number (bleachable kraft) and bleached in a single stage with hypochlorite.

Hardwoods and grasses are delignified more rapidly than softwoods, but to obtain fibre separation they usually require digesting to a Kappa number of about 20. The Kappa number, yield, and brightness for some sulphate pulp grades are given in Table 1.2.

Table 1.2. Kappa number, yield and brightness for various sulphate pulp grades

	Kappa number	Yield, % of dry raw material	Brightness % SCAN
Softwood pulp (pine):	70-90	55-60	16-20
Pulp for kraft liner	70-90	55-60	16-20
Unbleached market pulp	35-40	48	24-26
Pulp for bleaching	30-40	46-48	24-28
Bleached pulp (pine)	-	43	90-93
Polysulphide pulp, unbleached (pine)	30-40	48-50	24-28
Polysulphide pulp, bleached (pine)	-	44-46	90-93
Birch and Eucalyptus globulus pulp:			
Unbleached	20	54	-
Bleached	-	50-51	90-93
Beech, unbleached	20	52	-
Bamboo, unbleached	30	46	25-30
Bagasse, unbleached	18	48-50	40
Bagasse, bleached	-	45	80-90
Straw, unbleached	20	45-50	-

It should be pointed out that the lower the pulp yield the more organic material is dissolved in the spent liquor. This means that the specific BOD, COD etc. of the liquor increases and thus ultimately the effluent load.

1.2 Methods and equipment

Batch cooking

Sulphate cooking can be performed by either a batch or a continuous process. In batch cooking (discontinuous cooking) the digester is charged with chips and steam is often supplied at the same time. This steam facilitates the charging of the chips and increases the digester capacity.

The supply of steam is sometimes continued after the chips have been charged, an operation known as "steaming". Air enclosed within and between the chips is then expelled so that the cooking liquor can penetrate more completely. When the charging and steaming are complete the calculated amount of cooking liquor is added.

Heating to a specified maximum temperature follows a specific schedule and is performed by circulating the cooking liquor through an external heat exchanger. During this operation gases are released from the digester; these are passed through a liquor trap and on to a cooler (turpentine condenser), where the condensable ones are separated. In the turpentine separator the condensate is separated into a water phase, which is contaminated with odorous and oxygen consuming substances and an upper layer consisting of raw turpentine (Figure 1.4). Towards the end of the cook the pressure in the digester is lowered by gas relief.

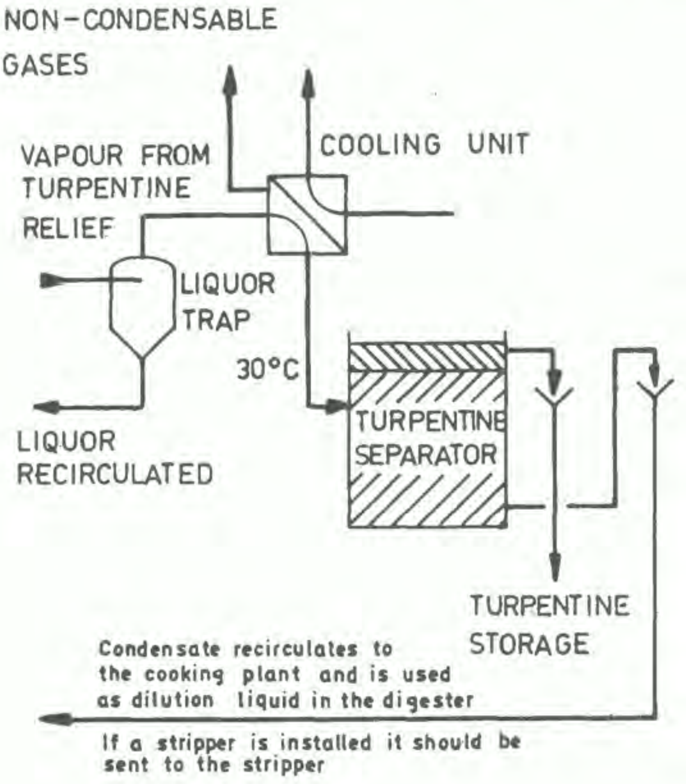


Figure 1.4. Treatment of turpentine condensate in the cooking plant

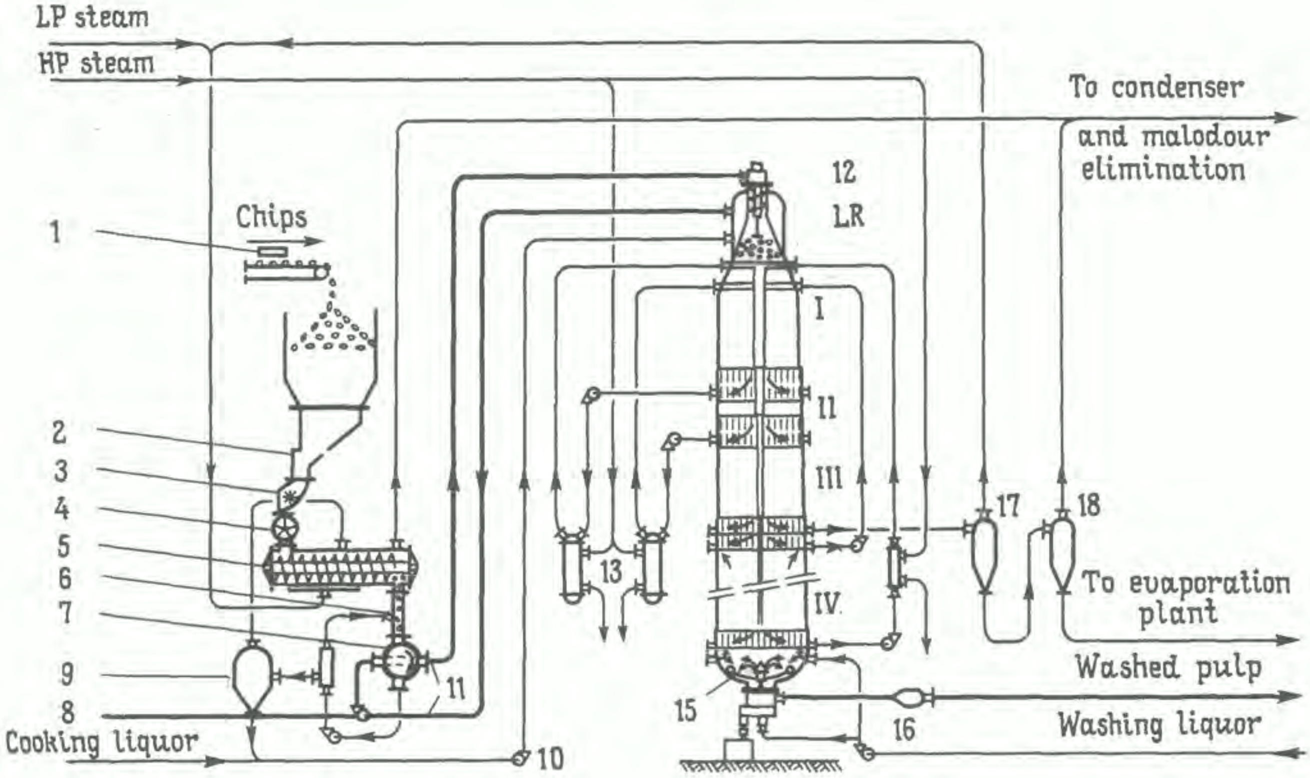
The non-condensable gases are composed mainly of nitrogen and carbon dioxide. They also contain methanol and formic acid and small amounts of hydrogen sulphide, methyl mercaptan (MM), dimethyl sulphide (DMS) and dimethyl disulphide (DMDS). The greater part of the last two compounds will have been condensed, however, and separated together with the raw turpentine phase.

When the cook is finished the contents of the digester are blown to a blow tank or to a batch diffuser (Figure 2.8). Flash steam amounting to 1-1,5 t/t of pulp is then liberated.

This contains a large quantity of heat, which is recovered in a blow condenser plant. The hot water so obtained is used for washing the pulp.

Continuous cooking in vertical digesters

In continuous cooking the chips are fed into a steaming vessel, where an over-pressure is maintained by injecting steam. Air and excess steam are vented and led to a condenser. From the steaming vessel the chips and the calculated amount of white liquor are conveyed to the top of the digester. As they move down they pass through a number of zones with separate liquor circulation systems for impregnation and cooking. Below the cooking zone there is usually a zone where the pulp undergoes counter-current washing for 2-5 hours. The wash solution consists of water or heated filtrate from the washing stage following the digester. At the bottom of the digester there is a cooling zone and a discharge mechanism for blowing the pulp from the digester to the blow tank (Figure 1.5).



1 Magnetic Separator
2 Chip Hopper
3 Chip Meter
4 Low Pressure Feeder
5 Steaming Vessel
6 Chip Chute
7 High Pressure Feeder
8 Chip Chute Circulation
9 Level Tank
10 High Pressure Pump
11 Top Circulation
12 Top Separator
13 Heat Exchangers
14 Digester
15 Outlet Device
16 Blow Unit
17 1:st Flash Cyclone
18 2:nd Flash Cyclone

Figure 1.5. Principle flow sheet of continuous digester

The black liquor from the washing zone expands in two flash cyclones. The steam from the first cyclone goes to the steaming vessel while that from the second one about 0,4 ton/t_{90} is used for water heating. From the flash steam condensate, raw turpentine can be separated. The spent liquor is concentrated and burned.

Continuous cooking in tube type digesters

These digesters consist of one or more horizontal or inclined tubes connected with short tube pieces one above the other. Inside the tubes are mechanical arrangements for the pulp transport. The tubes are very commonly used for bagasse and straw pulping. They have no built-in washing zone.

There are several makes such as Bauer, Defibrator and Pandia (Figure 1.6).

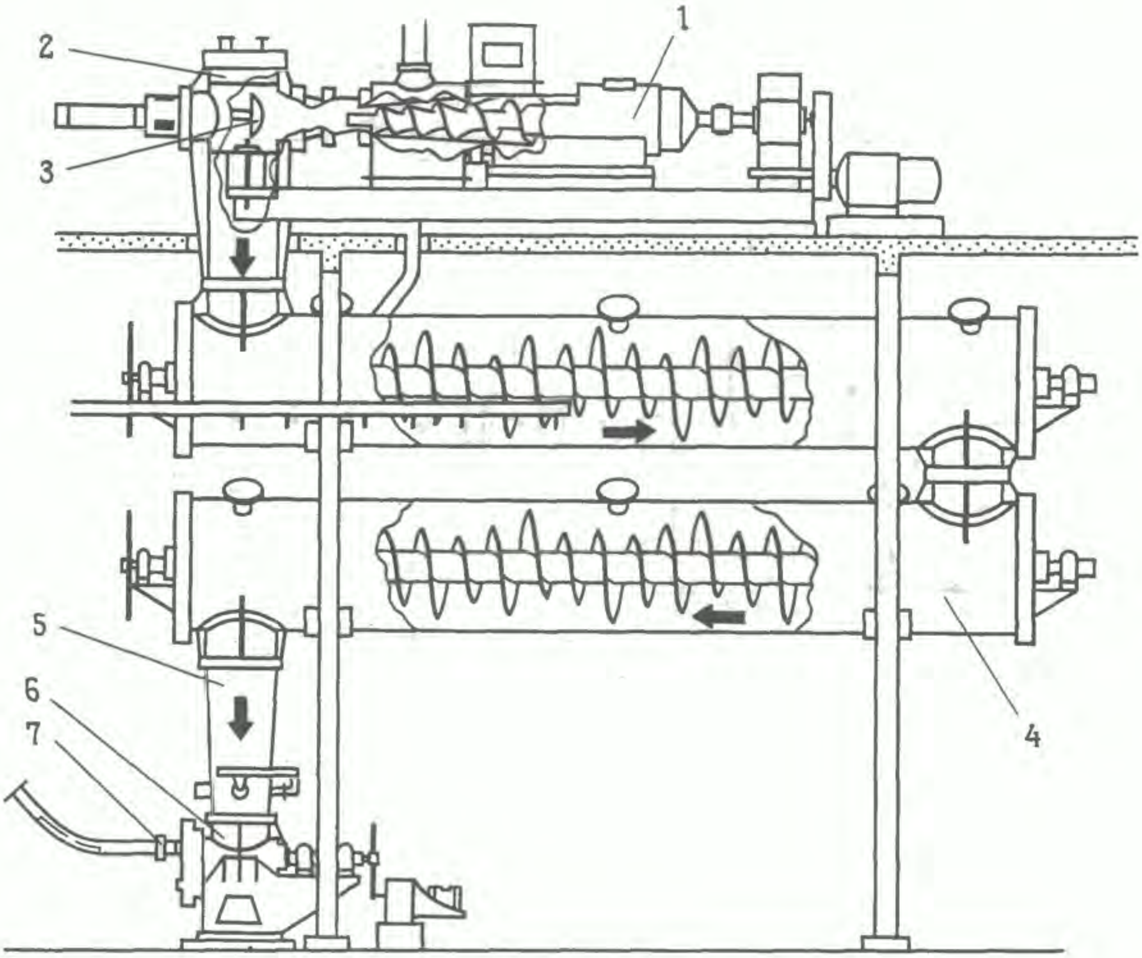


Figure 1.6. Typical pulping system

(1) Screw feeder
(2) T-pipe
(3) Blow back damper
(4) Digester tube
(5) Intermediate pipe
(6) Screw discharger
(7) Blow valve

1.3 Polluting discharges from a digester plant

The normal output from the digesting process is:

- pulp
- spent black liquor
- blow condensate
- turpentine
- turpentine condensate
- non condensable gases

Pulp and spent black liquor are sent to the washing department where the liquor is separated from the pulp. The turpentine, which is a valuable byproduct, is condensed from the relief gases, separated from the dirty turpentine condensate (Figure 1.4) and collected in a storage tank.

The blow condensate, turpentine condensate and the non condensable gases are the polluting substances from a digester house. The turpentine condensate from a continuous digester amounts to about 0,4 t/t_{90} while that of a batch plant is quite small. The amount of blow condensate from a batch plant is large, 1-1,5 tonnes per tonne of pulp.

Blow and turpentine condensates are usually heavily polluted with sulphur compounds and they also contain terpenes to an extent depending on the design and operation of the turpentine recovery system. The sulphur compounds are hydrogen sulphide and organic sulphides, which, together with the terpenes, impart a highly offensive smell to the condensates. They also contain dissolved alcohols, mainly methanol, which results in a high biological oxygen demand. The quantity of methanol amounts to a few kilos per tonne of pulp and its recovery is not normally economical.

Approximate quantities of blow and turpentine condensates and amounts of pollutants are shown in Table 1.3.

Table 1.3. Pollutant levels in blow and turpentine condensates from sulphate pulping of softwood (pine)

		Batch cooking	Continuous cooking
Approximate quantity of blow condensate	t/t of pulp	1.0-1.2	0.4
Sulphur	kg S/t of pulp	0.2	0.1
Oxygen demand	kg BOD_5/t of pulp	5	3

There are several designs of turpentine separation tank. It is important that the incoming condensate is cooled below 30-40°C in order to reduce the dissolution of turpentine compounds in the condensate. The entrance should be designed in such a way that a minimum of disturbance to the turpentine separation process occurs. The retention time should be about 4 hours for good separation. If the condensate is mixed with only small amounts of black liquor a turpentine emulsion forms and the separation is greatly reduced or fails. Therefore the turpentine vapours should pass an efficient liquor trap before being condensed (Figure 1.4).

As a rule, the sealing water for pumps and similar equipment is clean, but occasionally it is polluted owing to leaky shaft packings. The escaping substance is usually black liquor, though it may also be white liquor, turpentine or turpentine condensate.

Cooling water from condensers and liquor coolers is also normally quite clean. Hot water generated in the blow heat recovery system is used in the mill, such as in the washing and bleaching department. If there is a leak in a heat exchanger the hot water may be polluted, and thus unsuitable for its purpose in which case it is passed to the sewer.

Live steam condensate from heat exchangers is normally clean and is returned to the boiler feed-water system. In case of a leakage it may be polluted by black liquor and must then be run off to the sewer, because the feed-water system is sensitive even to low amounts of black liquor. Such pollution is detected by means of conductivity gauges. If the conductivity increases above a preset value the condensate is passed straight to the sewer. An alarm is also given so that the operators are alerted about the existence of a leak which may order maintenance assistence.

During normal conditions liquid discharges from a well run digester house, whether of the continuous or batch type, are of only small volume.

1.4 Pollution control

Common measures undertaken in a cooking plant for pollution control are:

- Treatment of blow and turpentine condensates before being discharged. Two possibilities exist; internal treatment in a stripping column (see chapter 5) or external treatment in an aerated lagoon (volume 5).
- Collection of non-condensable gases. The gases are sent to the lime kiln, or a bark (waste) boiler, or the recovery boiler or to a special incinerator for burning, thereby converting the odorous sulphur compounds to sulphur dioxide.

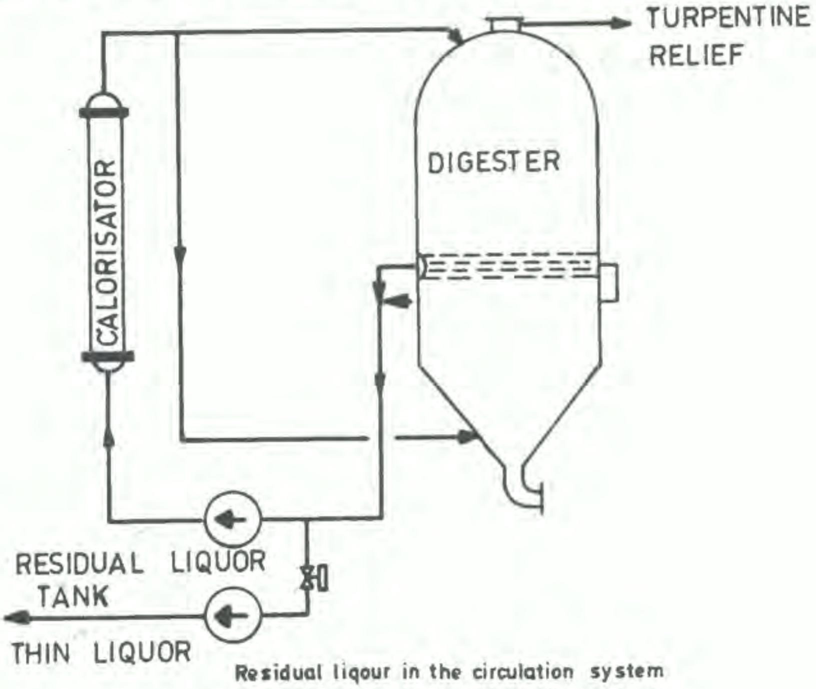
Both the blow and turpentine condensates are normally so heavily polluted by oxygen consuming and malodorous compounds, as well as toxic terpenes, that they should be treated. If the condensates are treated in a stripper the resulting cleaned condensate can be reused in the mill.

In the stripping column, which is usually coupled between two effects in the evaporation plant for better steam economy, the most polluted condensate from the evaporation plant and the blow and turpentine condensates from the digester house are freed from 75-90 % of the BOD consuming compounds mostly methanol and 98-100 % of the malodorous gases. The compounds stripped off are piped to the lime kiln for burning. Instead of the lime kiln a boiler or a separate incinerator is often used. Precautions must be taken in order to prevent explosions in the gas system. The stripping, gas transport and burning systems are described in chapter 5.

The treatment of the condensates in an aerated lagoon removes most of the BOD, malodorous compounds and terpenes from the condensate. A small part is evaporated to the atmosphere but the majority is degraded biologically. The total investment and operating costs in an aerated lagoon are often lower than the corresponding costs for a stripper per ton of BOD removed.

Collection of the malodorous, non condensable gases is more complicated and costly from batch digesters than from a continous plant because of the discontinuous nature of the former discharge. The gases collected are piped to an incinerator, the lime kiln or a boiler for burning. To even out the load on the burning system a gas holder can be used.

When emptying a batch digester system for repairs or cleaning a few cubic meters of black liquor are normally discharged to the sewer. To avoid this a small pump can be installed for pumping the residual liquor to the residual liquor tank or to the blow tank (Figure 1.7).



Residual liqour in the circulation system is pumped to the residual liquor tank

Figure 1.7. Clearing the circulation system in batch digesters

When there is a sewer collection pump connected to a conductivity meter in the digesting plant the black liquor can of course be dumped in the sewer. For more information about accidental discharges, see chapter 8.

Literature reference list, chapter·1

(1) The SSVL Environmental care project, Technical summary. Stockholm 1974.

2. WASHING

2.1 The aims of the washing operation

The spent liquor from a sulphate or soda cook contains the majority of the pollutants generated in the whole pulping and bleaching process. An effective chemical recovery and liquor combustion therefore results in a marked improvement in the environmental situation at the mill.

For a cost efficient chemical recovery the spent liquor should be delivered as concentrated as possible and as completely as possible to the recovery system. The aim of the washing operation is to separate the fibres from the spent liquor fullfilling the above criteria. Any residual spent liquor leaving the washing operation with the pulp will be washed out in a subsequent, open process stage (e.g. the screening or bleaching) and contributes to the water pollution.

The main factors influencing the results of the wash are as follows:

- type of pulp to be washed
- type of washing equipment
- dimensions of the washer
- number of washing units
- washing liquid (composition, amount, temperatures etc.)

These factors will be dealt with separately and furthermore some washing principles and definition will be given.

The possibilities of achieving any particular result in the wash are different in two cases where a) a new washing line will be installed or b) where an existing one will be upgraded. Examples given show the basic considerations and calculations that must be made in each case.

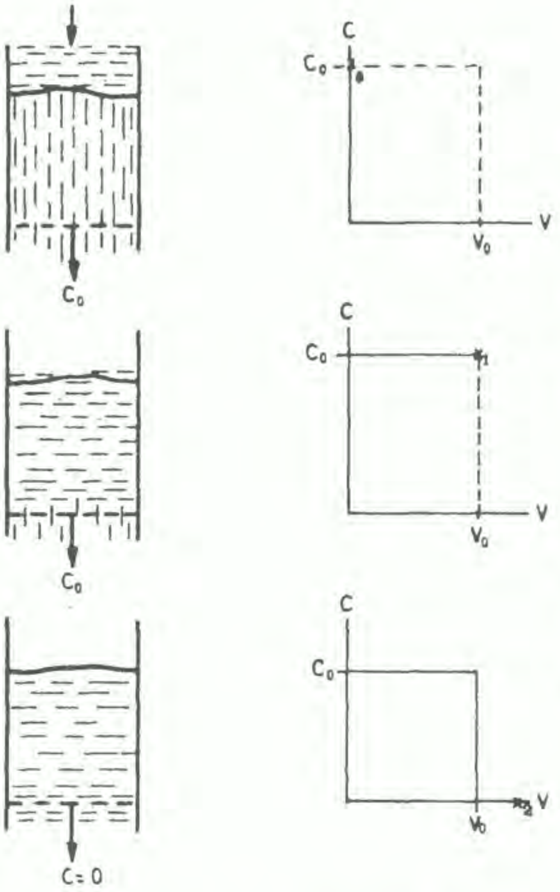
2.2 Washing principles

In a pulp suspension the liquid can be considered to be divided into one free and one enclosed liquid part. The free part is the liquid that the fibres and fibre bundles are suspended in, and the enclosed part is located on the fibre surface or inside the fibres and the fibre bundles.

The free part is evidently the most easily accessible and its separation can be carried out by a) dilution with wash liquor followed by thickening and/or by b) displacement. The ratio between the two mechanisms depends mainly on the type of washing equipment. The liquor in the enclosed part can only be extracted through diffusion and capillary flow. Both processes are slow and the result depends on the time and temperature.

In an ideal displacement the wash liquor pushes the thicker original liquor in front of it out from the pulp layer. The process can be compared to a piston pushing a gas or a liquid in front of it in a cylinder (Figure 2.1).

However, in a technical apparatus the displacement process is not ideal, partly because the liquids get mixed, one with the other at the addition, partly because the pulp layer is not homogenous.



C - Consistency of wash liquor leaving

V - Volume of wash liquor leaving

C_o - Original liquor consistency of pulp layer

V_o - Original volume of liquor of the pulp layer

X_o - First liquor displaced keeps full concentration

X_1 - Even at the end undiluted liquor is leaving the pulp

X_2 - After the washing only clean water is leaving

Figure 2.1. Ideal displacement of liquor from pulp layer (5)

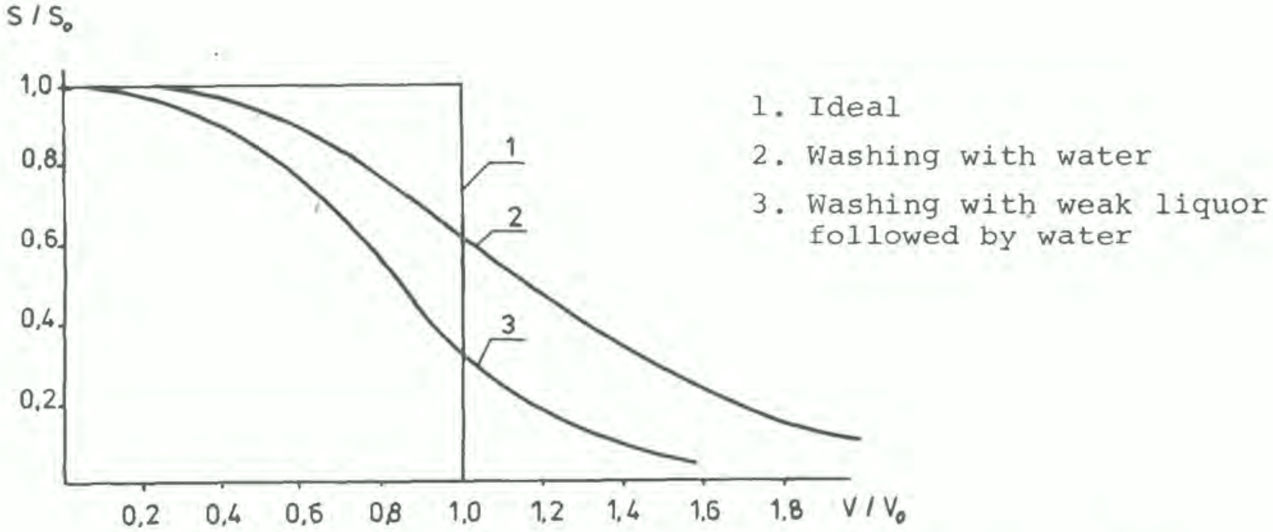
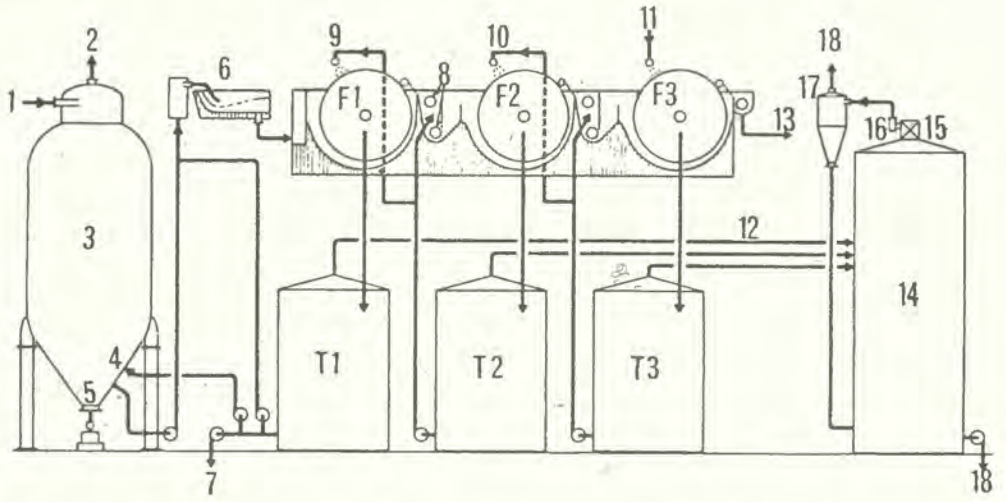


Figure 2.2. Wash curves at batch diffuser washing (5)

Figure 2.2 shows two examples of how a technical liquor extraction can proceed. Curve 2 shows washing with water only, while curve 3 shows the more common method of first displacing with a weak liquor and finally with water. The real washing procedure thus differs considerably from the ideal one. It is characteristic of washing curves that they flatten out, which means that a large amount of wash liquor will have to be added in order to get the pulp completely clean. It also means that the extracted liquor will be diluted.

To obtain the desired washing result the pulp is normally washed in several consecutive stages.

The stages are arranged in series with the liquor flow counter current to the pulp flow. In this way the pulp is washed several times, each time with a cleaner liquor. On the last stage the washing is performed with clean water or liquor condensate. Figure 2.3 shows an example of a three filter wash plant.



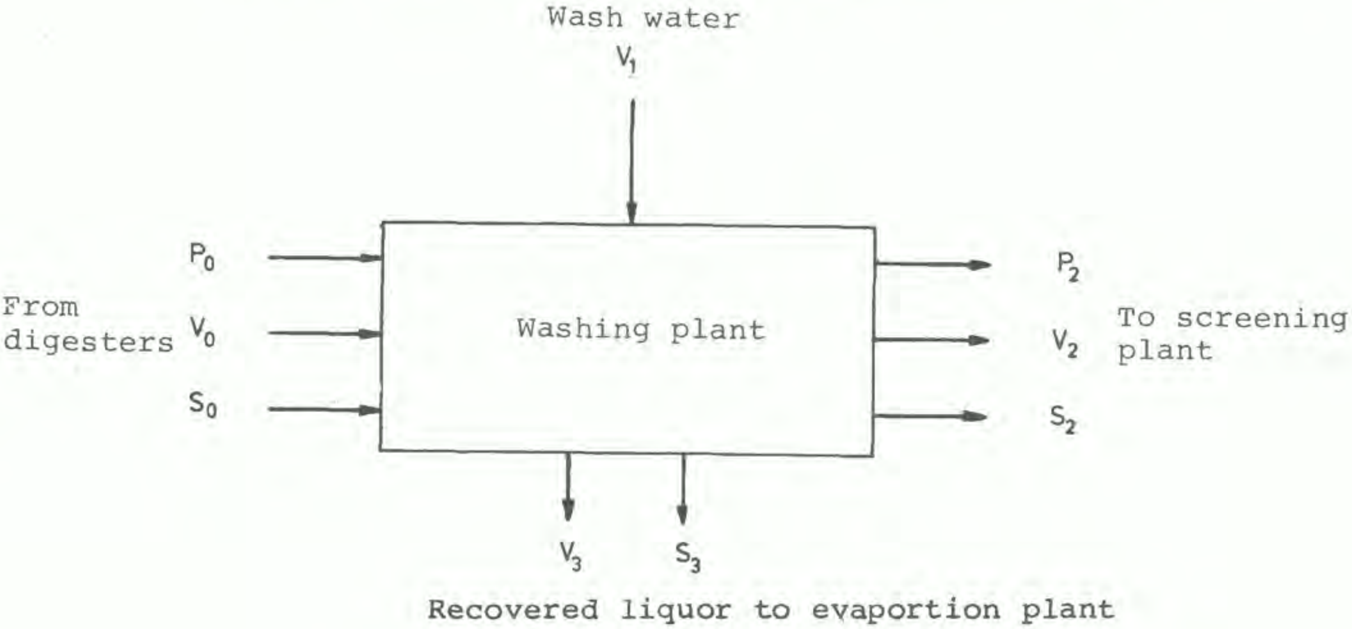
1. Blow pipe from digester
2. To blow condensor
3. Blow tank
4. Dilution with weak liquor
5. Agitator
6. Knotter
7. Weak liquor to evaporation and digester plants
8. Intermediate breaker
9. Filtrate from T 2
10. Filtrate from T 3
11. Warm water
12. Foam pipe
13. Washed pulp
14. Foam tank
15. Foam separator
16. Fan
17. Cyclone
18. Liquor to evaporation plant

T 1 Weak liquor tank
T 2-3 Wash liquor tanks
F 1-3 Filters

Figure 2.3. Wash system with three one-zone filters (5)

2.3 Washing definitions and efficiency factors

A schematic flow sheet for a washing plant is given in Figure 2.4. The commonly used terms in washing are defined in Figure 2.5 using the symbols in the previous figure.



P = pulp kg
V = water kg
S = solids content kg
L = liquor kg

Figure 2.4. Schematic flow sheet for a washing plant (2)

Term	Definition	Remark
Original liquor	$L_0 = V_0 + S_0$	
Liquor lost	$L_2 = V_2 + S_2$	with outgoing pulp
Recovered liquor	$L_3 = V_3 + S_3$	to evaporation plant
Liquor weight ratio	$W = L_3/L_3$	
Washing yield	$Y = S_3/S_0$	
Dry content	$DS = S_3/S_0$	of recovered liquor
Liquor weight ratio	$W = \frac{V_3+S_3}{V_0+S_0}$	
Concentration ratio	$C = Y/W$	

Figure 2.5. Terms and definitions in washing

The dry content of the original liquor is usually in the 20 to 25 % range and that of the spent liquor to evaporation 12 to 19 %. Many equipment and operational parameters have a significant influence on the dry content (and also other washing efficiency measures) and therefore large differences between mills are common.

The dilution factor (DF), which is a very useful term in the operation of a washing plant, is a way of expressing the relation between the wash water flow and the pulp flow. It is usually calculated as ton of dilution liquid per ton of B.D. pulp.

The dilution (D) is that amount of the water added at the washing which dilutes the extracted liquor.

$$D = P_0\left(\frac{1-C_0}{C_0}\right)\left(\frac{V_3+S_3}{V_0+S_0} - \frac{S_3}{S_0}\right)$$

or $D = L_0\ (W-Y)$

where C_0 is the pulp consistency $= \dfrac{P_0}{P_0+V_0+S_0}$

The expression above can also be converted to:

$$D = V_1-(V_2-V_0\,\frac{S_2}{S_0})$$

If the dilution (D) is expressed per ton of washed pulp it is called the Dilution Factor (DF). It is usually 2-3 ton/ton 90 % pulp. The washing result as a function of the dilution factor for various equipment combinations is shown in Figure 2.6.

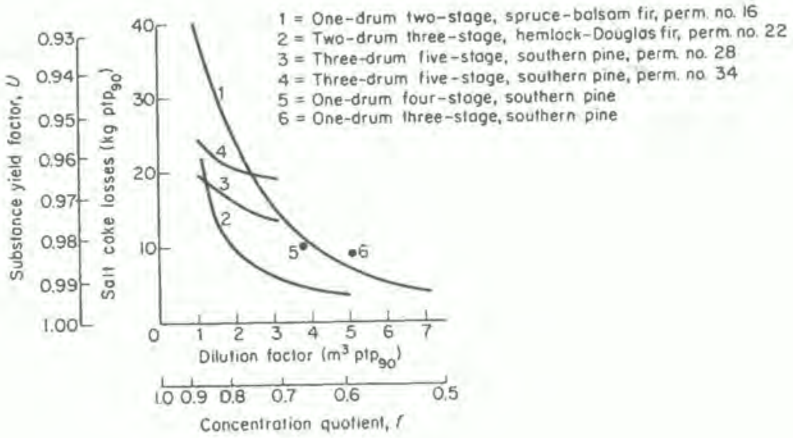


Figure 2.6. Dilution curves for brown stock filter washing with various numbers of drums and stages, and with pulps of various types (Harper-Paul, Klein et al, Waters-Bergström, West et al) (4)

The washing loss is a measure of the efficiency of the washing as well as of the environmental load from the washing plant. In a sulphate washing plant the losses correspond to 2-5 % of the original liquor solids content. In the most modern mills values of 1-2 % can be obtained. The washing loss is often expressed as kg Na_2SO_4/t pulp.

The rest loss is that amount of dry substance which is more firmly bound to, and enclosed in, the fibre walls and which is difficult to wash out. It is also called the "non-washable" substance. Because of sorption fenomenae influenced by pH, Kappa number and wood species the amount of sodium adsorbed varies considerably. The rest loss is often defined by a standardized laboratory washing procedure.

The total loss (S_2) is the total of rest loss and washing loss.

The washing efficiency of a single washing apparatus is often expressed as the "displacement ratio" or the extent of displacement actually obtained to that which theoretically could have been obtained. If the vat liquor strength of a filter (C_0 % solids content) in the sheet is reduced to the strength of the wash liquor (C_3 % solids) the difference (C_0-C_3) is the maximum reduction possible. However, this is never achieved and the resulting strength of the liquor left in the sheet (C_2 % solids) is always higher. The resulting reduction is C_0-C_2 and the "displacement ratio"

$$\text{DR (displacement ratio)} = \frac{C_0-C_2}{C_0-C_3}$$

DR attains values between 0 and 1 (Figure 2.7). The closer to 1 the more efficient the washing. Typical DR-values for the filters in a three stage wash plant may be 0.80-0.55-0,60 respectively at a dilution factor of 2-2.5. The DR-value is improved by higher dilution factor. Air mixed into the pulp reduces the DR. The displacement ratio is also influenced by pulp characteristics and the specific filter loading.

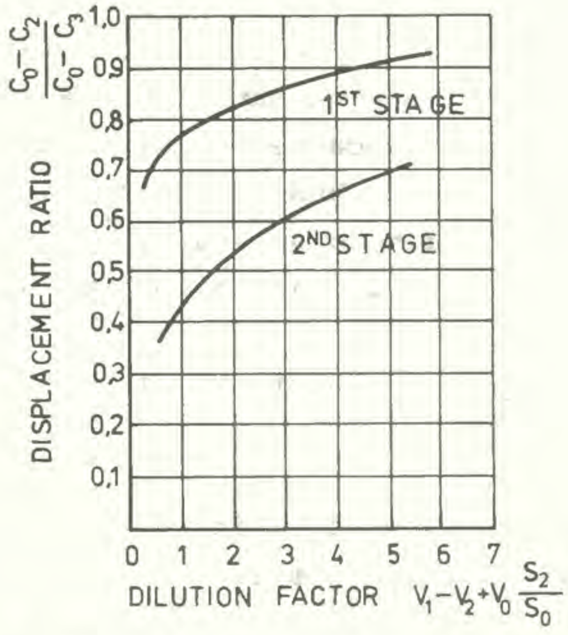


Figure 2.7. Example of displacement ratio curves for first and second stage of a brown stock filter washing plant

2.4 Washing equipment

Batch diffusers

In the batch diffuser the washing is performed by displacement and diffusion. The displacing liquid often used in the first stage is diluted black liquor from a diffuser containing fully washed pulp; the washing is then continued with clean hot water. To cool the pulp before discharging, the washing is sometimes concluded with cold water (Figure 2.8).

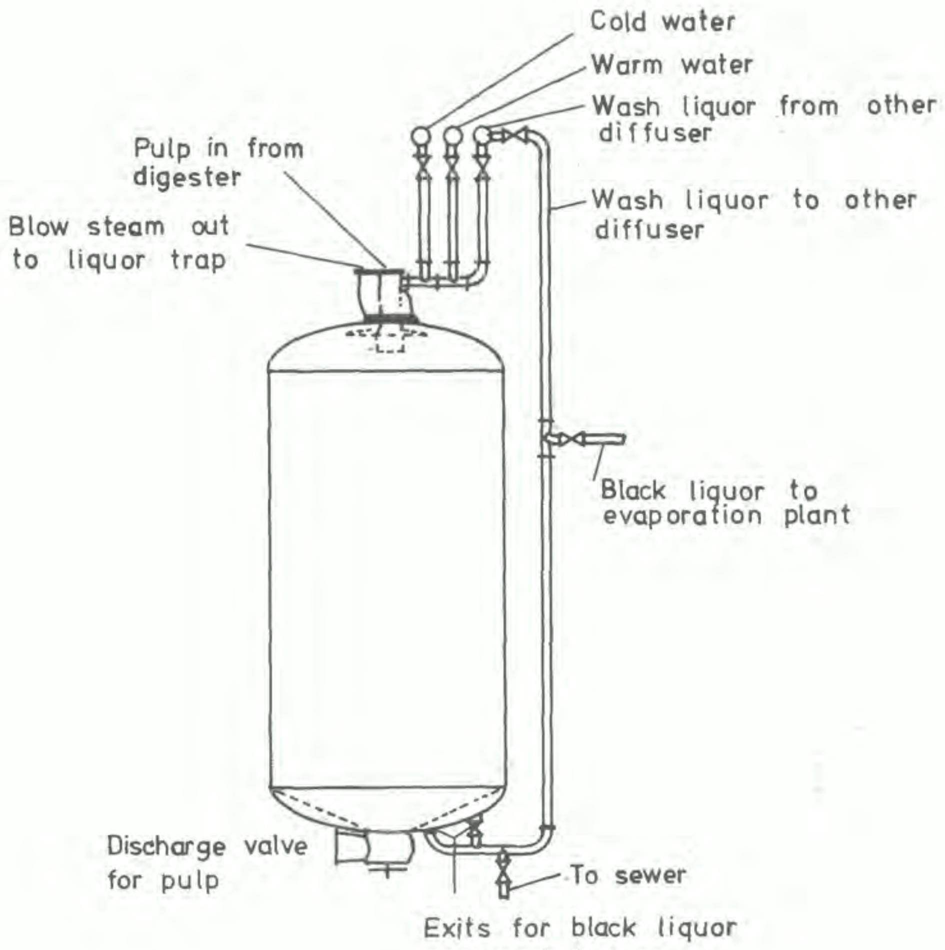
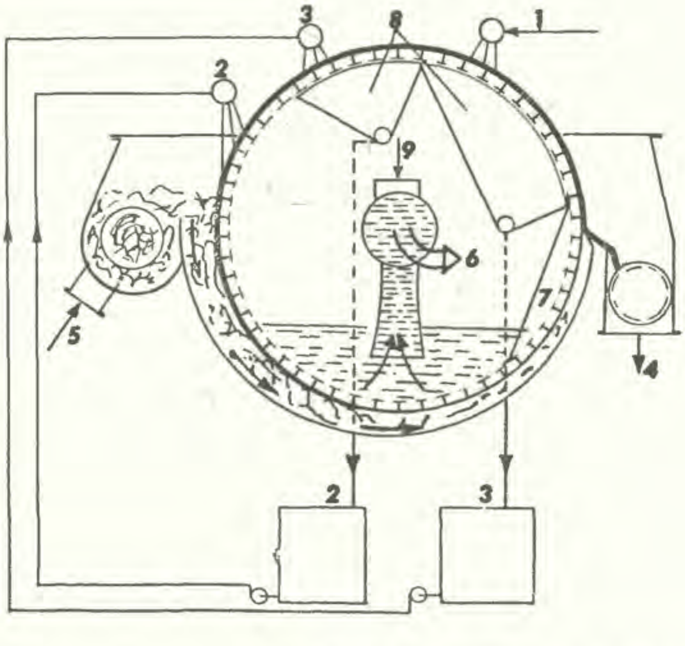


Figure 2.8. Batch diffuser for washing of sulphate pulp (5)

While the batch diffusers are certainly capable of efficient washing when dimensions in relation to output are correct, they have a number of disadvantages. The long washing time (10-20 h) makes them space-consuming and inflexible as regards capacity. The washing operation is unstable and an uneven result due to an irregular displacement zone is fairly common. Excessive amounts of water will then be needed. Such conditions make it difficult always to maintain the high washing efficiency required of modern equipment - for instance to conform with environmental standards. Batch diffusers cannot be recommended for new installations.



1. Warm water
2. Wash liquor
3. Weak wash liquor
4. Washed pulp
5. Pulp-liquor mixture
6. Thin liquor to evaporation
7. Discharge zone, not under vacuum
8. Zone compartments
9. Connection to vacuum pump

Figure 2.9. Zone wash filter (Kamyr)

Filter washers

The mechanism in filter washing is dilution, dewatering and displacement on a number of wash filters connected in series (Figure 2.9). The stock is diluted to a consistency of about 1 per cent before each filter and is dewatered on the rotating drum where a pulp sheet is formed. On the sheet a wash solution is applied by means of showers, thereby displacing most of the liquor present, The pulp is then removed from the filter drum - normally at a consistency of between 10 and 15 per cent. The wash liquor, usually clean hot water or condensate, is added to the last filter of the series, the filtrate from which serves as the wash liquor for the previous filter.

Large buffer volumes of filtrate are necessary to prevent overflows at unbalance in the system. Air drawn through the pulp sheet on the filter causes foaming of the displaced black liquor, and a free volume in the filtrate tanks is therefore required. It may also be necessary to install systems for reducing foaming and recovering the liquor.

The large liquor volumes result in a sluggish system with a long time lag. There is considerable risk of filter vats and liquor tanks overflowing, but this can be controlled by diking this area and using an electrical interlocking system. These disadvantages are common to all types of filter washers.

Open filter washers also present a problem of occupational hygiene through the emission of large amounts of moist air containing obnoxious sulphur compounds. To remedy this the filters are furnished with hoods and ventilators. The polluted air can be passed into a destruction furnace. The pressure filters have air tight hoods, since they work at an elevated pressure. Thus a solution to the work space environmental problem is incorporated into the design.

Presses

In a conventional press wash the washing is done by repeated dilutions and dewaterings. A wash press also has a washing zone incorporated where washing by displacement is done (Figure 2.10). Presses can be used with advantage in the final stage in a washing plant when it is desired to separate a closed system in the washing and screening sections from another system in the next department. By pressing the consistency is increased to about 40-45 percent, so that only a small amount of liquid will remain in the pulp.

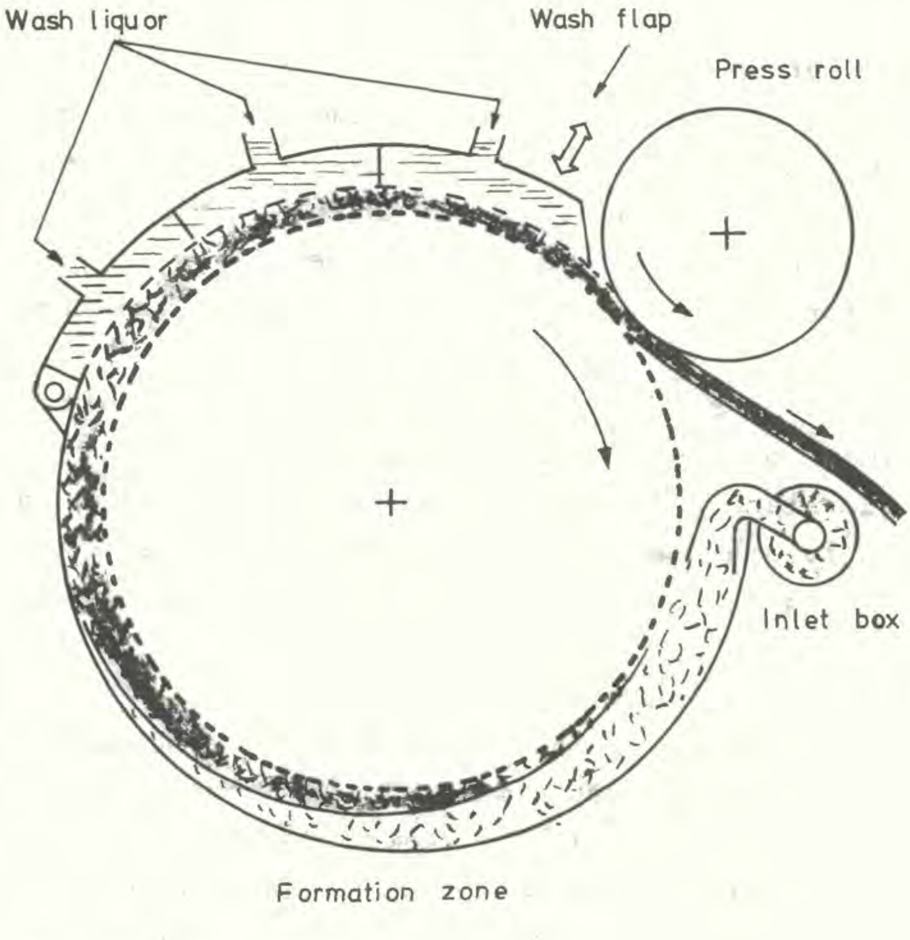


Figure 2.10. Wash press

In traditional presses of the screw, disc or cylinder types there is no displacement washing. The washing efficiency of the press is thus dependent on the mixing efficiency at the dilution before it. Thorough mixing is difficult and requires energy to achieve. Moreover, press maintenance is a considerable cost item. Presses are vulnerable to hard, foreign matter coming into the press nip and must be protected by efficient scrap removal.

Hi-heat washing in continuous digesters

In a hi-heat zone the pulp is washed at near cooking temperature for 2 to 5 hours (Figure 2.11). The washing efficiency is equivalent to 1-3 washing filters. Washing in the digester also facilitates the subsequent washing procedure since no air is entrained and foaming is thus minimized. For new plants a washing zone of fairly long time - preferably 4 hours - is recommended. For pulps with a high Kappa number which are refined after the cook and thus difficult to wash, it may be advisable to prolong the hi-heat washing even further.

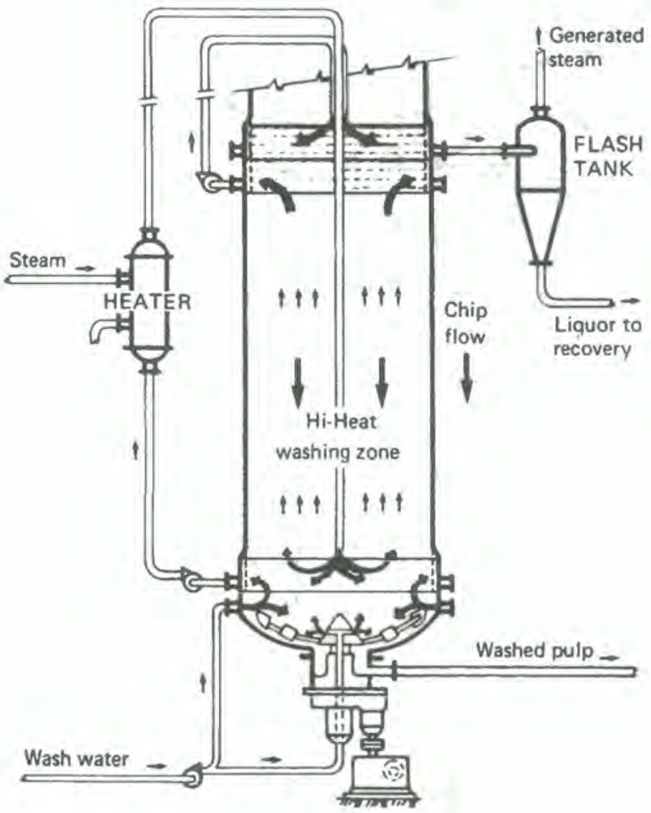


Figure 2.11. Washing zone in a continuous digester (Kamyr)

Continuous diffusers

The continuous diffuser or radial washer is increasingly used for supplementing hi-heat washing in continuous digesters. This combination ensures a completely closed system and avoids the emission of malodorous gases and admixture of air, with the foaming and other problems associated with filter washing.

The pulp is fed into a funnel-shaped container, which is furnished with a system of concentric rings for supply and withdrawal of washing liquor and filtrate. The ring system moves upwards with the pulp and periodically returns to its initial position. The washing is thus effected by displacement at a constant pulp consistency of 8-10 per cent (Figure 2.12).

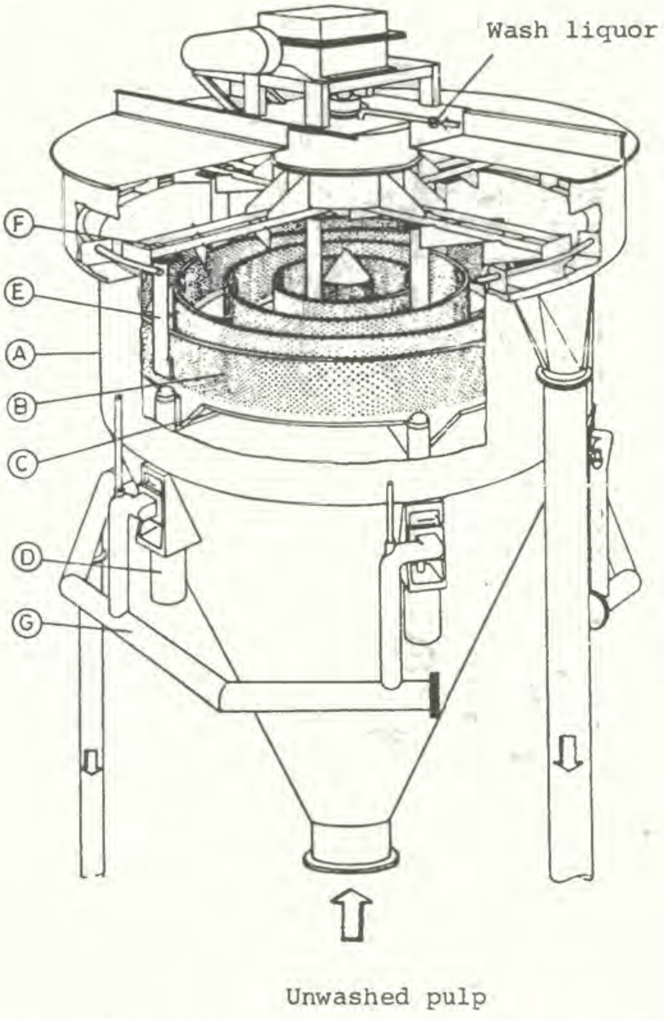


Figure 2.12. Continuous diffuser (radial washer) Kamyr

Continuous diffusers have also been installed at positions other than immediately after a continuous digester, for instance after batch digesters and oxygen bleaching plants. Where the consistency of the incoming pulp is lower than 7-10 % the diffuser should be preceded by a thickener.

2.5 Washing of various types of pulps

Chemical softwood and hardwood pulps are normally washed in filter wash plants, in the case of batch digesters, and in hi-heat washing in the bottom part of a continuous digester which is then followed by one or two stage washing in radial washers or on filter washers. 4-5 hour washing in the bottom part of a continuous digester corresponds in washing efficiency to about three washing filters in series.

The wash press is sometimes used as the final washing stage in a washing system. When high pulp dryness (30-40 %) is required, at the entrance to an oxygen bleach reactor it may also be advantageous to install the wash press. The washing effect obtained on a wash press corresponds approximately to two washing filters in series.

High yield pulps do not require such careful washing as the chemical pulps in order to obtain a satisfactory washing result from an environmental point of view. This is due to the lower amount of cooking chemicals and dissolved wood components. For a 75-80 % yield pulp 92 % recovery gives the same discharge per tonne as 98 % recovery for a chemical pulp.

High yield sulphate or soda pulps are defibrated in disc refiners after the cook and afterwards they are washed in presses, radial washers or in wash filter plants consisting of three filters or sometimes even two filters. High yield pulps are sometimes so free (7-10°SR) even after defibration that running them over a wash filter plant may cause difficulties. Therefore screw presses are more common for dewatering of high yield pulps. A three stage press installation can give over 95 % chemical recovery at a dilution factor as low as 1,2. A careful mixing of the wash liquor after each stage is essential for a satisfactory washing result.

Normal values for wash filter loadings (and dewatering properties of the pulp) are given in Table 2.1.

Table 2.1. Wash filter loadings and dewatering properties of various sulphate and soda pulps

Pulp type	Wash filter loading t_{100}/m^2d	Freeness* °SR
Softwood	5-7	12-13
Hardwood		
birch	4-6	15-16
eucalyptus globulus	6-9	-
Bagasse	2-4	20-25
Bamboo	4	14-16
Esparto	-	16
Reed	-	18-19
Rice straw	1.5-2	40
Wheat straw	0.5-2	

* Assuming chemical pulp yields and no refining

Bamboo pulps are usually cooked in batch digesters and washed on filter wash plants (3-4 stages) but continuous digesters some with hi-heat washing, are also in operation. Mills using bamboo as raw material normally also use other raw materials such as hardwood. Sometimes the hardwood and bamboo chips are mixed before going into the digester.

For wash filters the filter loading is usually around 4 BD tons per m^2 filter surface and 24 h. Higher loadings, up to 5-6 BDT/24 h, m^2, have also been reported. Bamboo pulps are rich in silica which causes rapid clogging of the filter wires especially in the first filter. Frequent washing of the filters is therefore essential to maintain low washing losses.

Normal washing losses at dilution factor = 2 is for chemical pulps:

3-filter plants	25-35 kg Na_2SO_4/t_{90}
4-filter plants	15-20 kg Na_2SO_4/t_{90}

Bagasse is often pulped in continuous tube type digesters without any washing stage incorporated. In older mills the cooking is performed in batch type digesters. The washing in both cases normally is performed on 2-3 drum filters in series. Many mills do not recover the cooking chemicals and there is subsequently no need to keep the dilution factor down. Common values of the dilution factor is 4-10 tons per ton pulp and clean wash water is often added on all filters. In comparison normal dilution factor for softwood pulp wash plants is 1.5-3.5 ton/t_{90}.

The drainage of bagasse pulps is slow and wash filter loadings of 2-4 ton per ton and 24 h are common. The bagasse spent liquor contains high amounts of silica which reduces the capacity of the wash plant. Typical washing losses are in the range 18-45 kg Na_2SO_4/t_{90}. The lowest values are from new installations.

The filter size should be chosen to compensate for the clogging of the filters and to avoid reduction of the pulp dryness off the filters. A minimum of 12 % should be acceptable in a new plant. The dryness of the pulp leaving the filter is essential in order to keep the losses down. The wash water temperature should also be kept as high as the filter design permits, usually 65-70°C.

It is doubtful whether radial washers can be used due to the slow washing characteristics of bagasse pulp. However, wash presses and dewatering presses probably can be successfully employed.

Straw pulping is in small mills often performed using batch ball type digesters. Washing equipment is normally one or two drum wash filters but 3-drum filter wash plants are becoming more and more popular. The dewatering of straw pulp is quite slow which sometimes causes running problems on wash filters.

In order to get a good pick-up of pulp in the filter vat and a satisfactory pulp dryness on the filter the fitting of a good vacuum in the filters is recommended. It is usual to incorporate not more than one washing stage per filter. However, because of the variety of straw species used and variations in the cooking conditions, a considerably lower surface load may sometimes have to be accepted.

In the sulphate and soda pulping of straw most of the silica is dissolved from the pulp. Clogging of the wash filter cloths and formation of silicarich deposits below the filter wire is a serious problem in the washing of straw pulps. Frequent stops for washing and changing filter wires are routine in straw pulp mills.

2.6 Discharge control in washing plants

Most of the black liquor solids remaining in the pulp after washing is removed during screening or other open process stages and goes to the sewer.

In all operations where the objective is to obtain the best possible washing result and environmental protection with a minimum of wash water consumption, it is essential to maintain close control of the washing plant. The following is a schematic check list for the operation of a filter wash plant. It is also in parts applicable to other types of washing plants. (3)

I Maintain a constant ratio between the amount of wash liquor and pulp to be washed and a constant sheet consistency, i.e. an optimum dilution factor at all times which requires:

  A. Constant tonnage rate; elimination of small swings in tonnage rate as well as intermittent shutdowns. (The wash room should never become the buffer between the digesters and screen room.)

  B. Controlled flow of wash liquid and an equal wash liquor distribution across the pulp sheet.

  C. Balanced liquor tank levels and flows.

II Obtain the maximum amount of mixing between the liquor in the sheet from the previous stage and the dilution liquor added at the intermediate repulper which requires:

  A. Good agitation with complete disintegration of the sheet entering the repulper.

  B. The lowest workable vat consistency.

1) Consistent with a drum speed which does not overload the foam system.

2) By elimination of air in the entering sheet, thereby obtaining the maximum drainage rate.

3) By avoiding entrained air in the dilution liquor by maintaining proper tank levels.

4) By maintaining 50 % submergence of the filter drum.

III Good sheet formation which is a function of the vat consistency and agitation. Uneven formation gives low displacement ratio.

IV Prevent the build-up of soap in the system by assuring its constant removal.

Also from a process point of view it is important to maintain a constant washing loss with the pulp from the last washing filter to the next department, especially if that department is a bleach plant or a paper mill, which are sensitive to variations of black liquor content in the pulp. It is well known that the bleach chemical consumption will increase on occasions when there has been disturbance in the washing plant. A good indication of the washing result can be obtained by constantly recording the conductivity of the liquor leaving the pulp mat on the last washing filter.

The washing plant contributes to the air pollution of a sulphate pulp mill emitting odorous gases corresponding to 1-3 kg/h of totally reduced sulphur for a filter washing plant of a 300 t/d mill. From radial washers or other closed type washers there are no odorous compounds discharged.

Open type washing apparatuses are covered by ventilated hoods in order to protect the operating personnel from the obnoxious gases. The hoods are ventilated by suction fans discharging to the atmosphere outside the building or, in most modern plants, to some type of gas collection system. The gas collection system conveys the gases to incineration, usually in one of the boilers at the mill. Such systems are further described in a later chapter.

2.7 Cost estimates for washing plants

Examples of cost estimates for complete washing plants for straw, bagasse and tropical hardwoods are given in Table 2.2. The total investment for presses is 80-85 % of that for filters. The washing loss for presses can be expected to compare with that for filters.

When the total specific costs are calculated (Table 2.3) the difference between filters and presses becomes 2.0 to 5.3 USD per tonne. The capital costs have been estimated assuming 10 years and 10 % depreciation. The cost item "maintenance" is very difficult to estimate and depends entirely on the preventive maintenance procedures at the mill.

Table 2.2. Investment cost estimate (1979 price level) for 3-stage washing plants (in million USD)

Item	Washing filters 3-stages			Screw presses 3-stages		
	Wheat straw	Bagasse	Trop hardwood	Wheat straw	Bagasse	Trop hardwood
	50 t_{90}/d	150 t/d	300 t/d	50 t_{90}/t	150 t_{90}/d	300 t/d
Main equipment (filter drums (316) filter troughs (ms), repulpers, transport screws, hoods, tanks (ms), pumps installation, instruments, (screw presses if applicable)	1,3	2,2	3,0	1,2	2,0	2,5
Installation	0,3	0,4	0,5			
Building and foundations	0,3	0,4	0,6	0,18	0,3	0,4
Piping and valves incl erection	0,25	0,4	0,6	0,2	0,35	0,5
Electrical (incl motors, cables, mccs, transformers and installation)	0,11	0,22	0,4	0,14	0,35	0,65
Engineering, administration	0,4	0,4	0,4	0,4	0,4	0,4
Various 8 % of above	0,27	0,32	0,44	0,17	0,27	0,36
Insurance and interest costs during the erection 6 % of above	0,17	0,26	0,36	0,14	0,22	0,29
Total installed cost	3,04	4,60	6,30	2,43	3,89	5,1
(Estimated power cons. kWh/t_{90}	60	50	45	110	100	90

(316) = steel quality AISI 316

(ms) = mild steel

Table 2.3. Specific costs (USD/t) for filters and presses for washing straw, bagasse and hardwood pulp

	Filters, 3-stages			Presses, 3-stages		
	Straw	Bagasse	Hwd	Straw	Bagasse	Hwd
Capital costs	28	14	10	22	12	8
Energy[a)] el power	1.80	1.50	1.35	3.30	3.00	2.70
steam	+2.50	+2.50	+2.50	-	-	-
Maintenance[b)]	5.20	2.65	1.80	6.95	3.70	2.45
	37.50	20.65	15.65	32.25	18.70	13.15

a) 3 US cents/kWh

b) Assumed to be 3 % of capital for filters and 5 % for presses

A rough comparison of washing efficiencies and costs for a number of washing alternatives is given in Table 2.4. It must be emphasized that the values are only indicative and should only be used for preliminary estimates. For more up-to-date and detailed data well known suppliers or consultants should be contacted for a more thorough analysis.

Table 2.4. Comparison of washing efficiency and energy requirement for different washing alternatives

	Stages	Washing efficiency %	Dilution factor DF	Energy kWh/t_{90}
Filters	3	96-97	2.5	40-50
	2	98	2.5	50-60
Presses	3	96-97	1.5	75-100
Radial washers	2	97-98	2.5	10-20
Hi-heat	4[a)]	95-96	2.5	5-15

a) 4h washing zone

2.8 Washing plant calculations

In the following some examples of wash plant calculations useful for environmental as well as economical considerations are given. For basic data see Figure 2.4 and 2.5.

A. Calculation of the dilution factor

The case: Estimate the dilution factor (DF) from the following data:

Pulp consistency in the blow tank (C_0): 12 %

Original liquor consistency ($\frac{S_0}{V_0+S_0}$): 21 %

Thin liquor consistency ($\frac{S_2}{V_3+S_3}$)2: 15 %

Total washing loss ($\frac{S_2}{S_0}$): 3 %

Assumption: The dilution D ton

Calculation: $$D = P_0\left(\frac{1-C_0}{C_0}\right)\left(\frac{V_3+S_3}{V_0+S_0} - \frac{S_3}{S_0}\right)$$

$$\frac{S_3}{S_0} = 0,97$$

We chose P_0 = 1,0 tonne as a base for the calculation

$$D = 1.0 \; \frac{1 - 0.12}{0.12} \; \left(\frac{0.21 \times 0.97}{0.25} - 0.97\right)$$

$$D = 2.85$$

The dilution factor (DF) is 2.85 t/t_{100} in this case.

B. Economy of washing plant improvements

The diagram in Figure 2.13 shows the influence of the dilution factor on the washing result. Such a figure can be made up for a specific filter wash plant to be used for economic calculations.

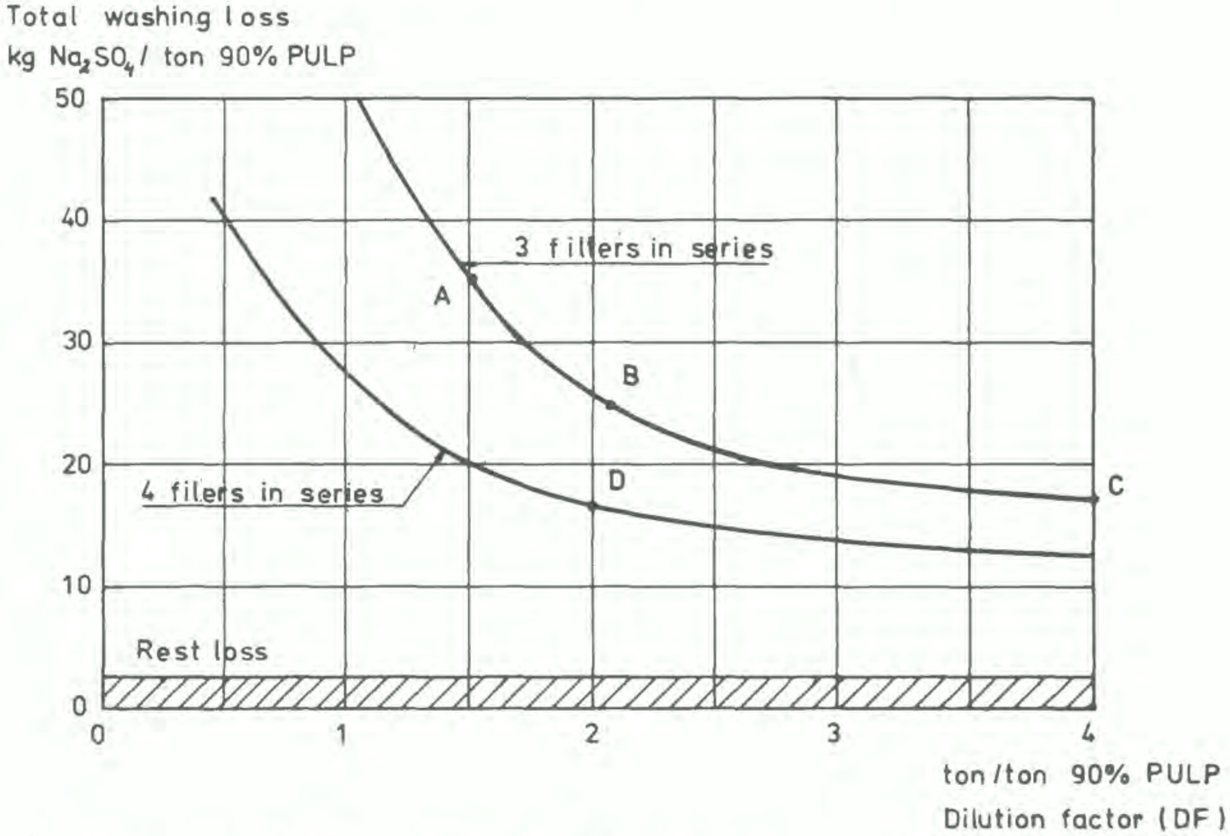


Figure 2.13. The relationship between total washing loss and dilution factor for a filter wash plant (1)

The relationship shown is only an example and cannot be used for practical calculations.

B.1. The case. In a three filter wash plant installation the normal operation point is A. The sodium losses will be reduced from 35 kg/t_{90} to 25 kg/t corresponding to 97 % washing efficiency (point B).

What will the cost be? Pulp yield is 47 %. Marginal low pressure steam cost is USD 10 per ton. Price of Na_2SO_4 is USD 100 per ton. There is surplus capacity in the 5-stage evaporation plant.

Assumptions: The washing efficiency is equal for sodium and for organic substance. 1 ton of organic substance liberated in the cook corresponds to 4 ton of low pressure steam generated in the recovery boiler.

Calculations: Saving of Na_2SO_4 will be 10 kg/t_{90} equal to 1.00 USD/t_{90}.

Saving of organic substance

$$\left(\frac{0.9}{0.47} - 0,9\right) \times \frac{10 \times 0.03}{25} \times 4 \times 10 = 0.48 \text{ USD}$$

Steam for evaporating 0.6 tonne water/t_{90} in a 5-stage plant requires about 135 Mcal/tonne evaporated water.

$$\frac{135 \times 0.6}{9200} \times 140 = 1.23 \text{ USD}$$

Cost of evaporating steam = 1.23 USD/t_{90}.

Total cost: 1.23 - 1.00 - 0.48 = - 0.25 USD.

Consequently there will be a saving of 0.25 USD/t_{90} pulp.

B2. The case: In the same mill producing 30 000 t_{90}/year of pulp the washing efficiency must be increased to 98 %. What will the cost be assuming that there is no more capacity in the evaporating plant and boiler plant. Estimated cost of evaporating capacity is USD 22/kg H_2O, h. The extra cost for boiler capacity is about USD 80/kg steam, h. 10 % interest and 10 years depreciation period is presumed (annuity = 16.27 %).

Assumption: A washing loss of 2 % means about 17 kg of Na_2SO_4 lost with the pulp. The diagram shows that the diluting factor must be increased to approximately 4.0 (point C).

Calculations: Saving of Na_2SO_4 8 kg/t_{90} equal to 8 x 0.10 = USD 0.80/t_{90}.

Saving of organic substance

$$\left(\frac{0.9}{0.47} - 0.9\right) \times \frac{8 \times 0.3}{25} \times 4 \times 10 = \text{USD } 0.39$$

Cost of additional steam to evaporate 4 - 2.1 = 1.9 t/t_{90}:

$$\frac{135 \times 1.9}{9200} \times 140 = \text{USD } 3.90\text{/tonne of water}$$

Investment cost to increase evaporating capacity is about USD 22/kg water/h. Maximum pulp production is about 4.2 t_{90}/h.

Cost estimation: 1900 x 4.2 x 22 = USD 135 000 or USD 28 600 per year which is equal to USD 0.93/t_{90}.

Investment cost to increase steam boiler capacity is about $\frac{1900}{5-1} \times 4.2 \times 80$ = USD 159 600 or equal to USD 26 000 per year or USD 0.87/t_{90}.

Total cost: 3.90 + 0.93 + 0.87 - 0.80 - 0.39 = $\underline{\underline{4.51/t_{90}}}$.

B.3. The case: There is also the possibility of installing an additional washing filter. In such a case no investment is required in the evaporation plant or the boiler. The dilution factor is estimated to be 2.0. The total investment cost for an extra filter has been calculated to USD 1000000 equal to USD 162700/year or 5.42 USD/t_{90}.

Calculations:

Saving of Na_2SO_4 = USD 0.80 (same as before)

Saving of organic substance = USD 0.39 (same as before)

Saving of low pressure steam in the evaporation plant:

$$\frac{2.1 - 2.0}{4} \times 10 = \text{USD } 0.25/t_{90}$$

Cost of the additional filter installation:

$$\frac{10\ 000\ 000}{5} = \text{USD } 162\ 700/\text{year equal to USD } 5.42/t_{90}$$

$$\text{Total cost: } 5.42 - 0.80 - 0.25 = \text{USD } \underline{\underline{3.98/t_{90}}}.$$

In the solution B.3 the goal to reduce the environmental load from the washing plant is achieved with USD 0.53/t_{90} more economically than in the solution B.2. Furthermore when the investment is paid off the mill will produce each ton of pulp USD 4.15 less in solution B.3 than in B.2. (Solution B3 may, however, consume 15 kWh/t_{90} more than B.2 which will reduce the difference somewhat.)

Literature reference list, chapter 2

(1) Jönsson S-E:
Filter washing (in Swedish)
Sw Paper Journal 64 (1961):15, 565-68

(2) Kommonen F.:
Pulp washing evaluation for design and operation
Paperi ja Puh 1968, No 6, 347-357

(3) Perkins J.K., Welsch H.S., Mappus J.H.:
Brown stock washing efficiency
Tappi Vol 37 (1954), No 3, 83-89

(4) Rydholm S.:
Pulp and paper processes
Interscience Publishers, N.Y. 1965

(5) Sveriges Skogsindustriförbund, S-285 00 Markaryd
Yrkeshandbok No Y 206 (Tvättning av massa - in Swedish)

3. SCREENING

3.1 Closure of screening systems

From a conventional, open screening system relatively large volume of white water is discharged. The effluent contains residual black liquor solids, fibres and screening rejects. To reduce the total costs for environmental control it is in most cases advantageous to decrease the effluent volume or to completely close the white water system.

Simplified process schemes showing the main features of open versus closed screening are given in Figure 3.1. In a closed screening system the screen room decker is converted to a washing filter. The filtrate is used to dilute the incoming unscreened pulp and the excess is used in the washing plant proper. The reject system with suitable reject upgrading systems should also be closed.

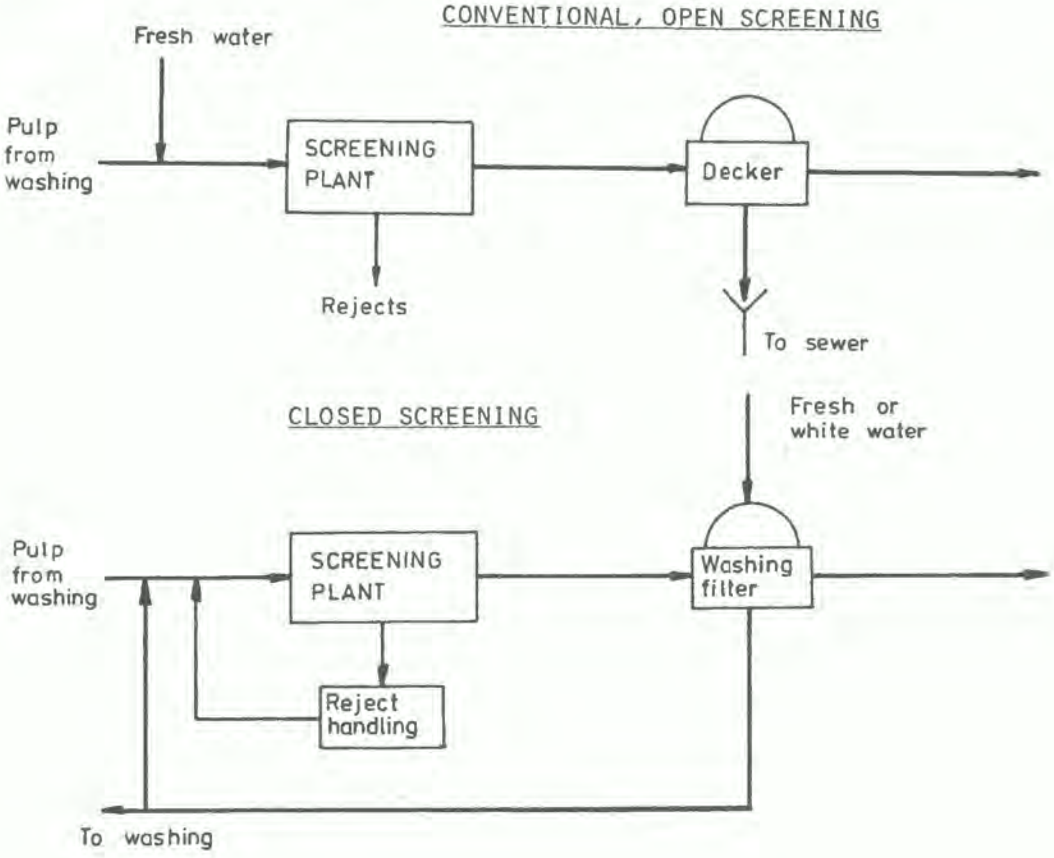


Figure 3.1. Simplified process schemes for conventional and closed screening systems

By this closure - and conversion of the decker to a filter - a reduction in pollution load can be achieved (Table 3.1). The figures in the table refer to the conditions in a line for softwood sulphate pulp with an initial washing loss of about 20 kg Ns_2SO_4/t. The "effluent" from the closed screening is the material brought with the screened pulp to the next open process stage.

Table 3.1. Example of discharges from open and closed screening systems

		Open	Closed
Effluent volume	m^3/t	30-100	0
BOD_7	kg/t	10	5
Colour	kg/t	30-50	10-20
Suspended solids	kg/t	5-10	0

There are three major factors to be born in mind before closing the water system:

- the best screening result is normally obtained at a low consistency (i.e. using large water volumes)
- handling of rejects is simplest in an open system
- an open screening system is an efficient way of washing the pulp.

In the following pages various strategies for rejects handling in a closed screening system will be discussed, together with methods of achieving washing efficiency. The operation of a closed screening system will be compared to the results that can be expected from external measures to attain a certain discharge level.

3.2 Reject handling systems

A closed reject system is one of the most important features of a closed screen room. The rejects from a screening plant usually are of two types: coarse reject, consisting of knots and uncooked chips and fine reject consisting of sand, bark, fibre bundles etc. The fine reject, particularly the sand, is removed from the system.

The liquid losses from the system must be minimized. Therefore if a reject is taken out from the screening plant it must be dewatered and preferably pressed. The resulting white water should be recirculated.

Reject handling systems can be classified in one of the following three groups (1):

A. Recooking
B. Refining and rescreening of reject
C. In-line refining

Recooking

The recycling of the coarse reject to the digesters is an alternative that has gained more and more acceptance. It has the advantage of a low power consumption and a low investment cost compared to the refining of the reject. It compares favourably with other alternatives from a dirt speck point of view which is vital when bleached pulp is produced. The bleach chemical consumption of the recooked fibres is about the same as for one stage cooked fibres.

The drawback is that the yield of the recooked fibres will be lower than for ordinary fibres. For a pine sulphate pulp 35-40 % yield can be expected instead of 45-50 %.

The rejects for recooking should be dewatered in order to reduce liquor losses from the screening plant and in order to save steam in digesters and evaporation plant. An example of a screening plant arranged for recooking of the coarse rejects is shown in Figure 3.2. The consistency of the reject from the flat screen to the digester plant is 15-25 %. The effluent from the screening filter (thickener) is recirculated to the washing plant (radial wash) and for dilution in the screening plant.

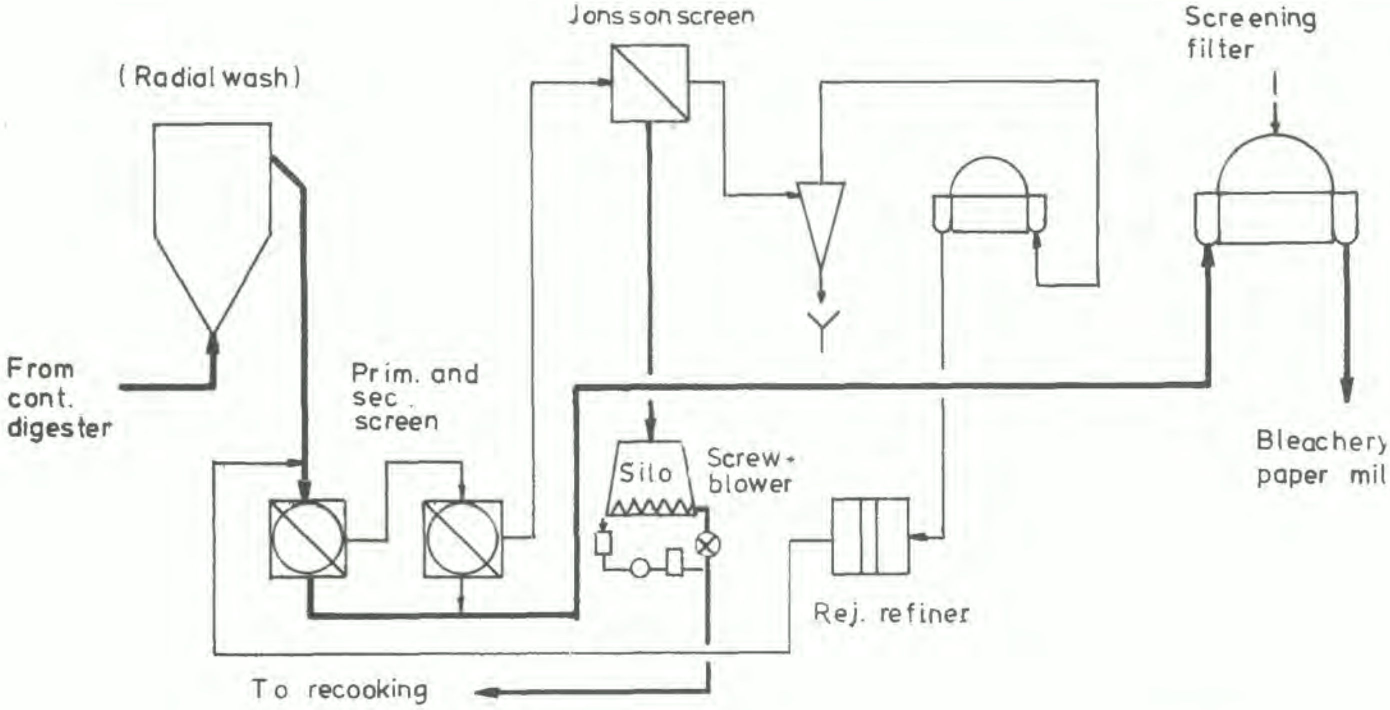


Figure 3.2. Flow sheet of screening plant arranged for recycling of reject to the digesters

Refining and screening of the reject

The closed screening plant can also be designed for treatment of the coarse reject in a refiner, thus desintegrating the knots to single fibres of fibre bundles (Figure 3.3 and 3.4). This type of reject treatment is rather expensive to operate due to high power demand.

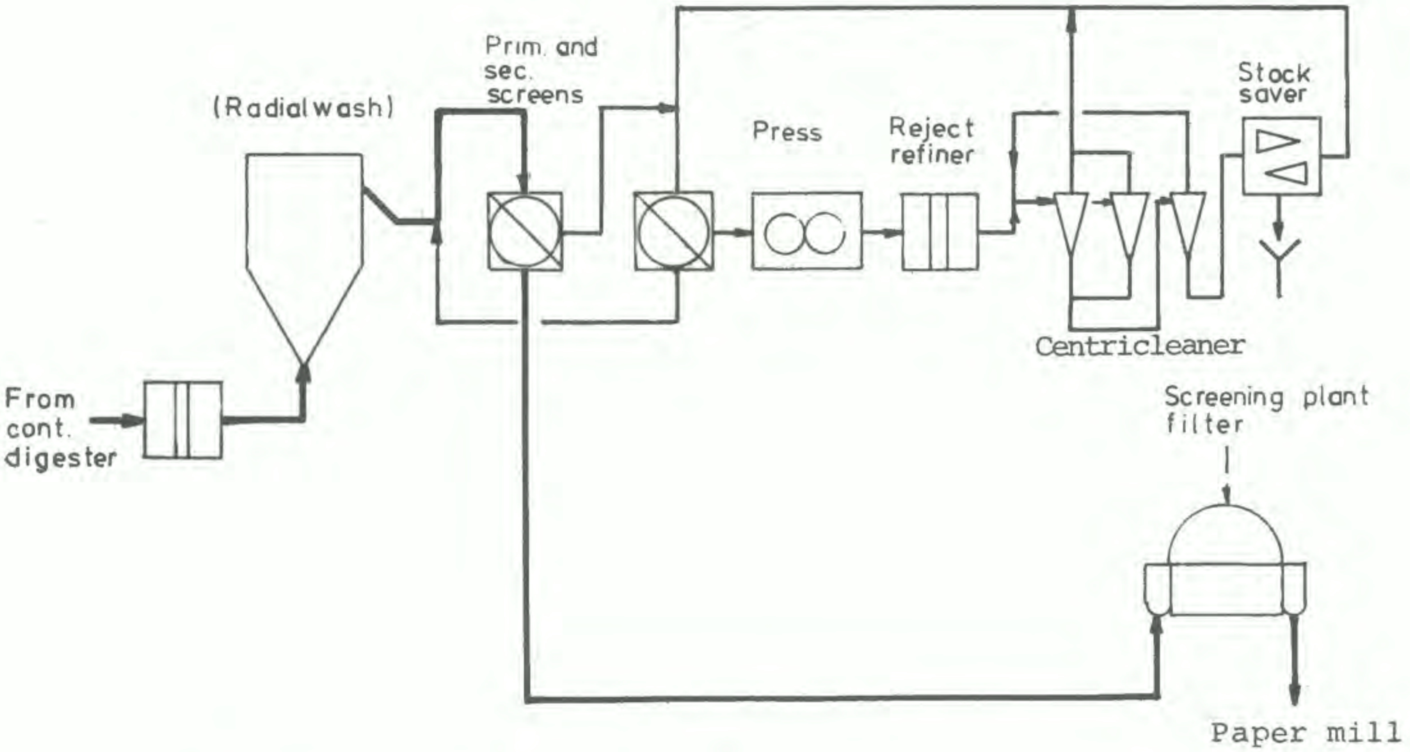


Figure 3.3. Flow sheet of a screening plant with refining + screening of reject

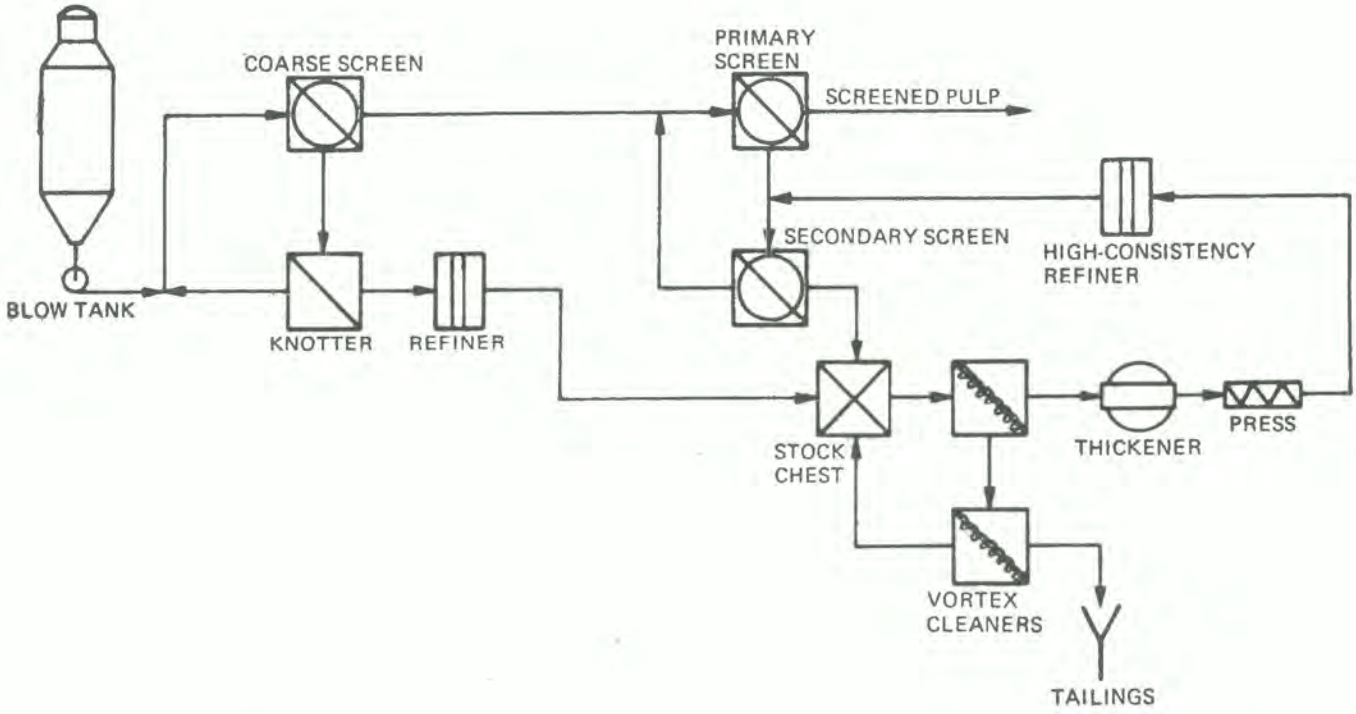


Figure 3.4. Flow sheet for a closed screening department with closed rejects treatment

In order to obtain a satisfactory fibre separation in the refiner the fibre concentration should be high; 10 % or preferably 30 %. This means that a disk refiner is the best type of refiner in that position. If a low consistency refining at 1-3 % is applied, the pulp freeness is greatly reduced and the power consumption will be higher. A press (or a flat screen) are suitable machines for raising the pulp consistency.

The system shown in Figure 3.3 is rather simple. It is not normally recommended if the pulp is going to be bleached afterwards because of the risk of specks and dust (bark particles etc.) in the bleached pulp. The consumption of bleaching chemicals of the refined reject is also, of course, considerably higher, up to twice the consumption of normal unbleached fibres. The system is more suitable for an integrated mill producing unbleached paper or paperboard.

A more elaborate system for rejects refining is shown in Figure 3.4. This system can be expected to reduce the risk of dirt particles in the final bleached product as compared to the previous one.

In-line refining without a screening plant

This system can nowadays be considered an established technology for the manufacture of unbleached sulphate pulp in an integrated mill. The schematic flow sheet is shown in Figure 3.5, which indicates the simple design of the system. The pulp consistency can be kept high (5-10 %) in the whole line and the white water flows will be small. The last refiner in the system operates at 20-40 % consistency in order to obtain as efficient as possible a shive reduction. The refiner can be of disk refiner type or a Frotapulper. The Frotapulper gives a limited freeness loss for a certain shive reduction.

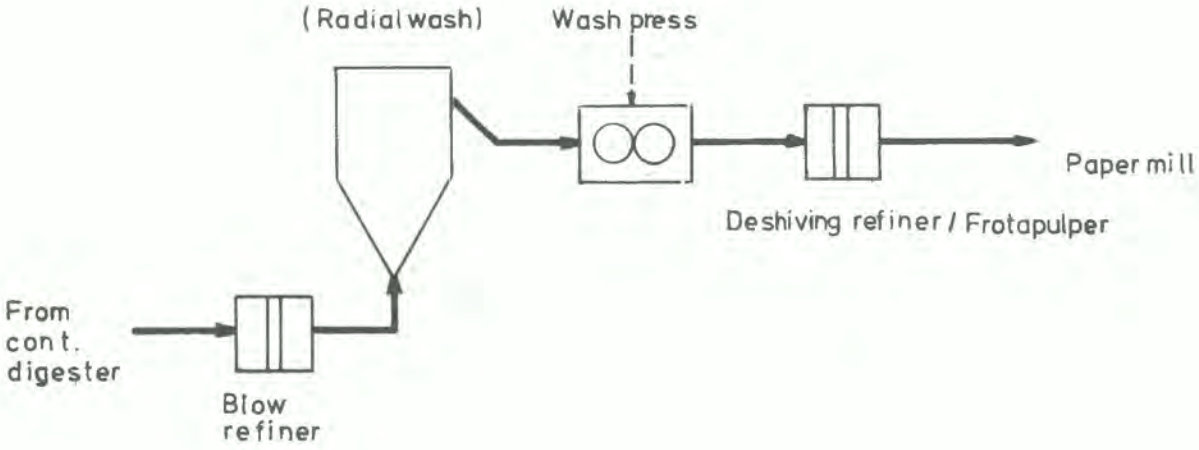


Figure 3.5. Pulp line with in-line refining replacing the screening plant

This type of reject treatment system has been applied in sack paper fabrication lines. However, the shive content of the paper fabricated can be expected to be higher than if a conventional screening system had been used. An extra screening stage, if required, could be installed further on in the mill, maybe just before the paper machine.

In this system it is difficult to operate sand removal equipment because of the high pulp consistency which requires that the raw material is free from sand and scrap material before going to the digester.

Comparison of costs

Costs for arranging the shive and knots removal in the production of unbleached sulphate softwood pulp according to the three principles are given in Figure 3.6. In all cases allowances have been made for the marginal production increase obtained when no rejects leave the process line. The investment cost is calculated assuming a new process line and does not include washing equipment.

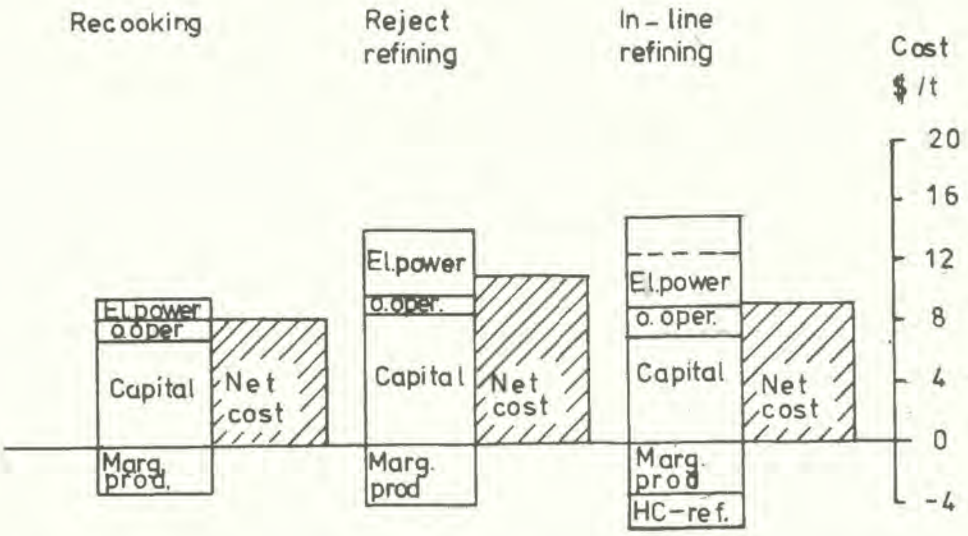


Figure 3.6. Cost comparison of 3 alternatives for arranging the shive removal of unbleached sulphate pulp. 300 t_{90}/day pulp production. 1979 price level.

The lowest investment cost (5.25 M USD) is obtained for the alternative with recooking which also shows the lowest specific cost. In-line refining turns out to give almost the same specific costs, however.

The same comparison for a bleached production is given in Figure 3.7. It is important to point out that the full

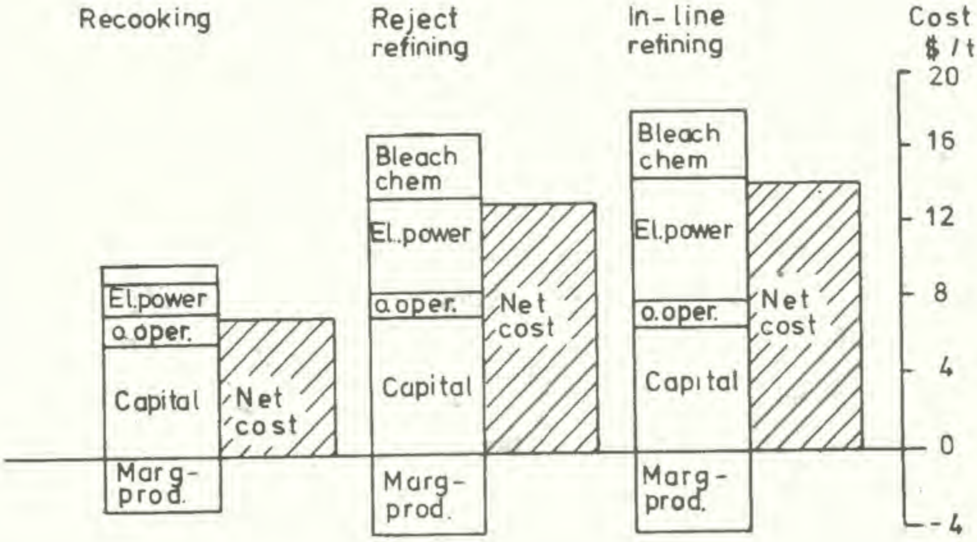


Figure 3.7. Cost comparison of 3 alternatives for arranging the shive removal of bleached sulphate pulp. 300 t_{90}/day pulp production. 1979 price level.

scale mill experience with in-line refining is quite limited and that severe foaming at the reject refiner is often experienced in closed screening and reject refining. For the in-line and reject refining alternatives an extra cost for bleaching chemicals is added due to the increased lignin content of the pulp entering the bleach plant. This results in a cost increase as compared to the treatment of unbleached pulp. Re-cooking, however, shows the least increase and a good cost performance.

3.3 Integrated washing and screening

In a mill with closed screening the washing and screening departments are combined to form a closed unit. The screening department thickener is the last washing stage, and the white water from the screening process is used in an earlier washing stage. The screening department will thus be completely closed, and under normal conditions there is no discharge of process water.

Because of the efficient leaching in an open screening system the carry-over of black liquor solids from the washing plant to the following sections is usually low. To obtain as well washed a pulp from an integrated washing and closed screening system as from a conventional washing plant followed by an open screening department, it would thus be necessary to add washing stages. The screening department decker can often be supplemented so as to operate as one of the added washing stages.

In Table 3.2 the effect of various combinations of washing equipment and screening systems on the carry over to the bleaching is demonstrated. It should be noted that the spent liquor dry substance contributes both to the effluent load and to the chemicals consumption in the bleach plant.

Table 3.2. Carry-over of black liquor solids to the bleach plant for open and closed screening system. Same dilution factor in each case

Brown stock washing	Screening	Washing after screening	To bleach plant kg Na_2SO_4/t
3F[a)]	60 m^3/t[b)]	-	9.5
3F	30 "	-	14.0
4F	30 "	-	9.5
3F	Closed	F	14.0
3F	"	2F	9.5
4F		F	9.5

a) denotes 3 filters in series

b) denotes an open screening system with 60 m^3/t effluent volume

3.4 Operation of closed screening systems

One important consequence of closing the washing and screening systems is that the temperature in the screening department is higher than is usual in open screening systems. The high temperature (which may reach 60-80°C) puts special demands on the design of the apparatus. The screens must be airtight or, in the reject handling system, furnished with hoods and ventilators. To control the temperature it may be necessary to install heat exchangers.

A typical operating problem in a closed screening system is the formation of foam. The washing ahead of the screening must therefore be highly efficient (to prevent build-up of dissolved solids in the white water system) and air entrainment must be prevented. The screens should be of the closed type and screw conveyors and open tanks should be avoided. The reject handling system is usually critical for air entrainment.

The general experience (relating to softwoods) is that the total loss of Na_2SO_4 after washing in combination with closed screening is not more than 20 kg/t_{90}. Where the raw material is rich in resin the alkali loss with the pulp from the last filter should not exceed 15 kg of Na_2SO_4.

When closing a screening plant it is usual to reduce the number of possible points in the system where white water or fibres could leak out. It is recommended that only one large white water storage tank be used in the screening plant from which any surplus white water in the system will be discharged. The only point in the system where clean water is added to the system should be on the screening decker.

Finally it should be pointed out that closing the white water system in one part of a mill influences all other mill departments. Closed screening requires better control of raw material pretreatment and cooking, i.e. homogenous chips, reasonable reject quantities, digester control etc.

3.5 Internal compared to external measures

When considering closed screening a comparison should always be made with the benefits of external treatment of the discharges.

Closed screening has the following advantages:

- Lower fibre losses - since they are, as a rule, related to the discharge volume.
- Inorganic material is saved. Thus the need for make up chemicals will be reduced.

- Organic material (heat value) will be saved.

- Lower fresh water treatment and pumping costs.

- Lower waste water volumes. Thus lower investment costs for external (primary and secondary) treatment facilities.

- Less power consumption or less chemicals for BOD removal at the external treatment plant.

The following disadvantages of closed screening can be expected.

- Investment costs for the installation of closed screening. In an existing mill the cost depends entirely on existing equipment and buildings. At a new mill there will be none, or a very small extra cost in comparison to an open screening plant. The price of closed screens is about the same as that of open screens.

- Possible foaming problems.

Each individual mill has to put a price on each of the factors mentioned in order to evaluate closed screening economically. For new mills it is normally advantageous to install closed screening both from an environmental and an economical point of view. For an existing mill no generalized recommendation can be given.

Case study

An example will show the cost differences between closed screening and external treatment for a new pulp mill.

The case: Is closed screening more economical than open screening and a larger external treatment plant?

Assumptions: Bleached kraft mill using annual plants (bagasse, straw, bamboo, etc.) as raw material. Production 100 t/d. Three stage filter wash plant followed by open or closed screening plant with a final dewatering filter (thickener). 96,5 % recovery (28 kg Na_2SO_4 loss) with open screening or 98 % (16 kg Na_2SO_4 loss) with closed screening. Reject handling equal in both cases. The open screening plant will use 100 m^3/t_{90} fresh water. El power: 0.83 USD/kWh.

Fibre savings (because of reduced effluent volume, accidental discharges etc): Normally in the order of 5-10 kg/t_{90} pulp, say 5 kg/t_{90}. Pulp value say 200 USD/t_{90}.

Annual saving: $0.005 \times \frac{200}{0,9} \times 35,000 = \underline{\underline{39,000 \text{ USD}}}$

Na_2SO_4 make up saving: 28-16 = 12 kg/t_{90}. Price 100 USD/t.

Annual saving: $12 \times 0.100 \times 35,000 = \underline{\underline{42,000 \text{ USD.}}}$

Organic material savings: About 900 kg/t_{90} of organic material is recovered. The corresponding amount of l.p. steam generated is about 4.5 t/t_{90}. The value of steam is governed by the price of oil. Say 10 USD/tonne steam.

Annual saving: $\frac{98-96.5}{100} \times 4.5 \times 10 \times 35,000 = \underline{\underline{23,600 \text{ USD.}}}$

Fresh water handling: Pumping cost from river to water treatment plant (say 40 m pumping pressurs) + raw water treatment (cleaning cost), probably about 2 cents/m^3. 70 % pump efficiency.

Pumping of 100 m^3/t_{90}: $\frac{100 \times 0.735}{3600 \times 0.07 \times 0.7} \times 40 \times 0.03 \times$

$\times$ 35 000 = 16,300 USD/y.

Water cleaning: 100 x 0.02 x 35,000 = 70,000 USD/y.

Annual saving: 16,300 + 70,000 = 86,300 USD.

(The investment cost saving for smaller water treatment equipment is disregarded here.)

Effluent treatment plant: The sedimentation plant can be made somewhat smaller and the secondary treatment plant (5 days retention time) can be made about 5 x 100 x 100 = = 50,000 m^3 smaller. The corresponding investment saving should be at least 300,000 USD or about 49,000 USD/year.

BOD removal cost: The BOD_5 consumption of 14 kg/t_{90} organic substance from the screening plant is about 6 kg/t_{90}. About 1 kWh is required to remove 1 kg of BOD_5 with aerators. Aerator capacity of 25 kW + electrical installation may cost 20,000 USD.

Annual power saving: 6 x 1 x 0.03 x 35,000 = 6,300 USD.

Capital cost of aerators 20,000 x 0.163 = 3,260 USD.

Total annual saving: 6,300 + 3,260 = 9,560 USD.

(Possible costs for chemical precipitation and smaller sludge handling costs are disregarded here.)

Bleaching chemicals: Additional cost corresponding to the remaining inorganic content after the open screening plant is estimated at 4 kg/t_{90} of Na_2SO_4:

Cl_2: (16-4) x 1.0 x 0.170 x 35,000 = 71,400 USD/year.

NaOH. (16-4) x 0.2 x 0.170 x 35,000 = 14,300 USD/year.

Total annual cost. 71,400 + 14,300 = 85,700 USD

Extra investment cost for closed screening may include such items as a larger than usual dewatering filter after the screening plant (to serve as washing filter), larger chests for foam space allowance and possibly some heat exchanger for cooling. The extra cost may be in the area of 150,000 USD at the very most or 150,000 x 0.163 = 24,500 USD/year. If, however, another extra washing filter is considered necessary, the corresponding costs and savings must be taken into account.

The advantages of a cleaner environment are difficult to evaluate in terms of money.

Answer:

In this example, with the factors taken into consideration, the saving in favour of a closed screening plant is 139,260 USD/year (39,000 + 42,000 + 23,600 + 86,300 + 49,000 + + 9,560 - 85,700 - 24,500) or equal to about 3.98 USD/t_{90}.

Literature reference list, chapter 3

(1) Warnqvist B.
Closed screening - report from a SSVL project.
Swedish Paper Journal 80(1977):13, 402-404, 421.

4. BLEACHING

4.1 Discharge to water from bleaching

In the bleaching operation the pulp is treated successively with chlorine - containing chemicals and alkali to degrade and dissolve the residual dark coloured lignin. The bleach plant effluents contain high amounts of organic material some of which is chlorinated.

As has been demonstrated previously a number of in-plant technologies are available to reduce the discharge to water from the cooking-washing-screening sections of the mill. Likewise the pollution due to condensates and accidental spills can be reduced efficiently. When these measures have been carried out the bleach plant effluent is the dominating source of pollution (Table 4.1).

Table 4.1. The discharges (in kg/t) to water from different mill departments. Softwood sulphate pulping

Source of discharge	BOD_7	Colour
Cooking-washing-screening	4	10
Condensates	2	-
Bleaching	16	175
Accidental spills	3	15
	25	200

There are basically three ways to reduce the bleach plant discharge:

a) partial or complete recycling to the recovery system to destroy (burn) the organic material in the effluent

b) external treatment of the effluent to remove organic material

c) use of bleaching chemicals which give rise to less polluting material

Formerly the chlorine content of the effluent and the chloride build-up in the recovery system drastically limited the possibilities of recycling bleach effluents. Today there are several systems available for removing chlorides from sulphate process recovery systems (5) and one mill (6) recycles the entire bleach plant effluent. The effluent from oxygen bleaching and from alkali refining or extraction stages (when starting the bleaching sequence) can be recycled with little or no chloride in-put.

A number of external treatment methods have been suggested and tried (5). To our knowledge the only full scale installation working is ion-exchange treatment of the E_1-effluent (1). The external treatment methods will be covered in a separate volume.

Chlorinated organic compounds in the bleach effluents are being investigated for possible environmental effects. Extended use of bleaching agents which do not primarily cause chlorination e.g. chlorine dioxides, peroxides and oxygen could substantially reduce any problems due to such compounds.

4.2 Bleaching chemistry

Bleaching is performed in a number of stages with chlorine, hypochlorite and chlorine dioxide, the object of which is to degrade the lignin in the pulp. Between these stages the pulp is treated with alkali to dissolve the lignin degradation products.

Up to 80-90 % of the lignin degradation products formed in the chlorination of sulphite pulps are water soluble and are therefore removed in the subsequent washing stage. The degradation products formed in the chlorination of sulphate and soda pulps are water soluble to a much lesser extent. To remove as much as possible of the lignin residues the pulp is treated with alkali.

The results of the alkaline extraction depend on temperature, duration of the treatment, amount of alkali added, pulp consistency and the quality of the pulp and its previous treatment. A high temperature results in a more rapid reaction, which is thus completed in a shorter time. Too high a temperature (about 60°C) results in dissolution of hemicelluloses, with consequent increase in the amount of dissolved organic substance (BOD_7) in the effluent. The dissolved lignin compounds consist to a large extent of multivalent acids. Their solubility increases steadily with the alkalinity up to pH 9-10, and then only slightly. Normally the pH during the alkaline extraction should be kept within the range of 10 to 11.

In the bleaching of dissolving pulp - for example viscose pulp - a high cellulose content is aimed at. The dissolution of hemicellulose that occurs in the alkaline extraction is utilized, and this stage is therefore carried out at 95-125°C, and with a large amount of alkali, of the order of 10 per cent, calculated on the weight of pulp. In such an alkali refining the dissolution of easily biodegradable material and the BOD/COD value of the effluent can be very high.

In hypochlorite bleaching the degradation and the dissolution of the reaction products is predominant. The lignins are broken down to acidic compounds which, with alkali, form water soluble salts. In solution these are further oxidized (partly to carbon dioxide) some of the hypochlorite thus being consumed by products already dissolved.

The final bleaching of a fully bleached pulp is usually carried out with chlorine dioxide in two stages with an intermediate alkaline extraction stage. The bleaching is usually performed in acid solution. A technical grade chlorine dioxide solution normally contains some chlorine, and the pH of the aqueous solution, 4-4,5, is suitable for acid chlorine dioxide bleaching. The chlorine dioxide stage is usually interrupted by adding sulphur dioxide or alkali.

In oxygen bleaching the oxygen attacks both the lignin and the cellulose molecules. The reaction of the lignin can be described as a combined effect of oxygen and hydrogen peroxide. The effluent from the oxygen stage thus contains appreciable amounts of degraded carbohydrates and lignin fragments. The BOD of the effluent is relatively high and to gain any environmental benefits it is necessary to arrange for an effective wash after the stage and recycle of the effluent.

4.3 Prolonged delignification in the cook

In the manufacture of sulphate and soda pulp the spent liquor from the washing plant is passed through a recovery process whereas (with the exception of an oxygen bleaching stage) all waste liquors from subsequent stages are discharged to the mill effluent system. An obvious way of reducing pollution from the bleach plants is a prolonged delignification in the cooking process. On the other hand a prolonged delignification results in a decreased pulp viscosity and yield which is prohibitive from a pulp quality point of view. For this reason the standard cooking procedure sets a lower delignification limit at a Kappa number of 30-35 for softwood and 20-25 for hardwood pulp.

To prolong the delignification in the cook without unduly reducing the pulp quality, the following points should be observed:

- The incoming fibrous raw material should be as even as possible with respect to size distribution, moisture content and composition.

- The impregnation with the cooking liquor should be effective.

- The conditions in the digester must be controlled to minimize the lignin content variations within the digester.

- The cooking conditions (alkali charge, time - temperature relationships etc) must be closely controlled to yield a constant cooking result (lignin content).

- The cooking conditions must be chosen to favour a high viscosity of the pulp. In the first place the sulphidity should be kept at a high level.

- The bleaching must be done in such a way that the pulp viscosity and yield is preserved. This can be achieved with e.g. chlorine dioxide in the chlorination stage, close control of conditions in the hypo stages and overall bleach plant control.

Prolonged delignification in the cook is primarily of interest when producing softwood sulphate pulp. By applying the measures indicated above for unbleached pulp the Kappa number level can be lowered to 28-30. Bleach plant control gives a further reduction to Kappa numbers 25-27 (Figure 4.1).

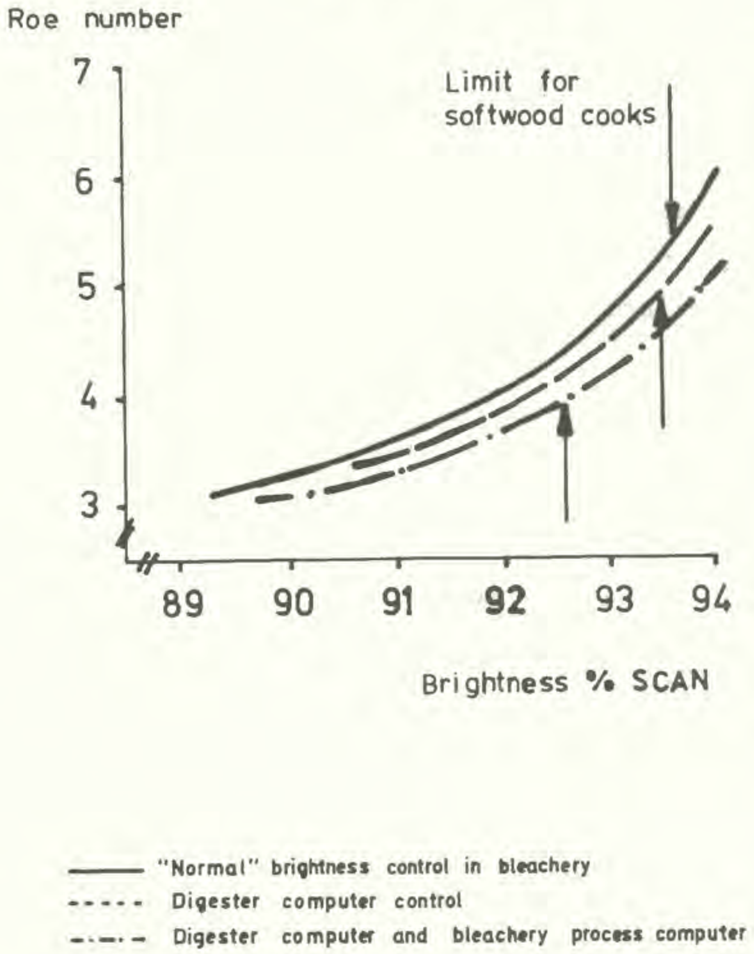


Figure 4.1. Roe number as a function of brightness for the sequence OCEDED with different computer alternatives as a parameter

The discharge from the bleach plant is reduced in proportion to the reduction in Kappa number (Table 4.2). Prolonged delignification gives a marked reduction in the colour of the effluent and the amount of organically bound chlorine is reduced by 50 %. A low Kappa number of the unbleached pulp makes it economically possible to increase the amount of chlorine dioxide in the chlorination. By going from 25 to close to 100 % a further reduction of colour and of chlorinated organic compounds is obtained.

Table 4.2. Bleach plant discharges when applying prolonged delignification in softwood pulping

Bleaching sequence	Kappa number	BOD_7 kg/t_{90}	Colour kg/t_{90}	Org chlorine kg/t_{90}
C_DEHDED[a)]	35	16	175	13
C_DEDED[b]	25	12	100	6
DEDED	25	11	60	2

a) 10 % chlorine dioxide (of active chlorine) in the C-stage

b) 25 % chlorine dioxide (of active chlorine) in the C-stage

The mill experience with prolonged delignification is very limited. To our knowledge no mill is running according to this strategy today. Important factors which have to be evaluated in each individual case are the increased demands for control and stable running conditions, the decrease in pulp yield and the increased risk for lower pulp quality. On the positive side of the balance is the improved effluent quality and the lower demand for bleaching chemicals.

4.4 Oxygen bleaching

4.4.1 Process description

It has long been known that pulps can be delignified with oxygen at an alkaline pH. This process is, however, accompanied by a breakdown of the carbohydrates. The breakdown can be inhibited by the presence of magnesium ions. It was early recognized that oxygen bleaching offers the possibility of reducing the detrimental effects of bleaching plants on the environment; the bleaching solution and the substances dissolved in it can be recycled to the recovery system and burnt more easily than is the case for the liquors from bleaching with conventional chlorine agents. One condition is, of course, that the bleaching sequence is begun with the oxygen stage, so that the spent liquor from this stage does not contain chlorides. Another prerequisite for economic handling of the spent liquor from oxygen bleaching is that the oxygen stage is placed ahead of the final brown stock washing stage so that the oxygen stage liquor and the black liquor can be recovered, evaporated and burnt together. Most of the chemicals added in the oxygen stage are then reclaimed in the mill's chemical recovery system.

The environmental effects will depend on how far the oxygen delignification can be carried. For reasons of quality only about half of the remaining lignin can be removed by this method, since the delignification is less selective at lower lignin contents. In order to produce bleached - and also some semi-bleached - pulp grades it is therefore essential to combine oxygen bleaching with traditional bleaching methods.

Today, oxygen bleaching is performed at a consistency of 25-30 per cent in a reactor, to which gaseous oxygen is fed. Ahead of the reactor, alkali is added, equivalent to 2-4 per cent of NaOH (calculated on the dry pulp), with a small amount of a magnesium inhibitor. The heating to the reaction temperature of 80-100°C is performed outside or within the reactor, with live steam. The heat of reaction raises the temperature in the reactor by a further 5-10°C.

The necessary amount of alkali can most simply be added in the form of sodium hydroxide, but part, if not all, of this might have to be replaced by another alkali - for instance oxidized white liquor. This may be required because of the need to control the sodium balance of a modern mill with a high degree of closure.

A schematic diagram for the equipment is given in Figure 4.2. After dilution to about 4 per cent consistency, unbleached pulp is taken from a high consistency tower and led to a mixing tank, where the consistency is adjusted to about 3.5 per cent. Here, magnesium sulphate - equivalent to about 0.05 per cent of magnesium - is also added. The stock is then pumped to a press for dewatering to about 30 per cent consistency. From there it is carried in a screw conveyor to a low-pressure mixer where alkali is added. Here the temperature is also raised to 80-100°C with live steam.

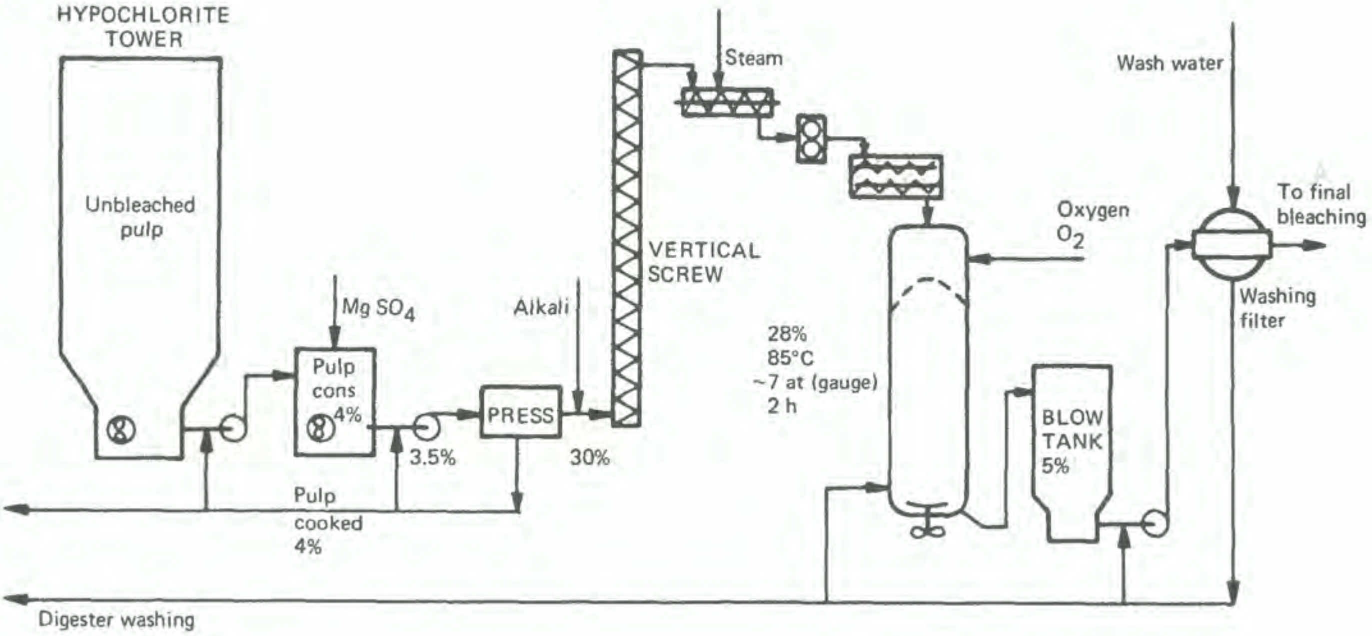


Figure 4.2. Oxygen bleaching, Gruvön, plant layout

By means of a screw or a reinforced thick stock pump the stock is fed into the reactor where it is shredded in a fluffing device. The reactor has a reaction zone where the retention time is 1-2 hours, and a dilution zone where the stock is diluted to 4-5 per cent with water from the subsequent washing stage. The pulp is blown from reactor pressure to a blow tank, where it is further diluted before pumping to one or two washing stages. Excess filtrate from here is used for dilution ahead of the oxygen stage and also as wash water in the preceding filters.

The pulp then undergoes final bleaching with conventional bleaching agents. Today, in bleaching softwood sulphate pulps to a brightness level of 92 per cent (SCAN) five more bleaching stages are considered necessary besides the oxygen bleaching, for instance C/D EDED.

Processes are presently being developed for oxygen bleaching at about 10 % consistency by Kamyr-KMW, MoDo, Rauma Repola and Sund. This type of bleaching is expected to give lower total investment costs than bleaching at 25-30 % consistency.

4.4.2 Effect of process parameters on pulp quality

Several process modifications related to the oxygen bleaching of pine pulp were studied at a pilot plant reactor of 150 t/d at the Husum pulp mill in Sweden during 1972-1973. The flow sheet of the pilot plant is shown in Figure 4.3.

The experiments included such studies as:

- the effect of system closure on pulp viscosity

- the use of other alkali sources than NaOH for the regulation of pH in the oxygen stage

- washing efficiencies after the oxygen bleaching stage

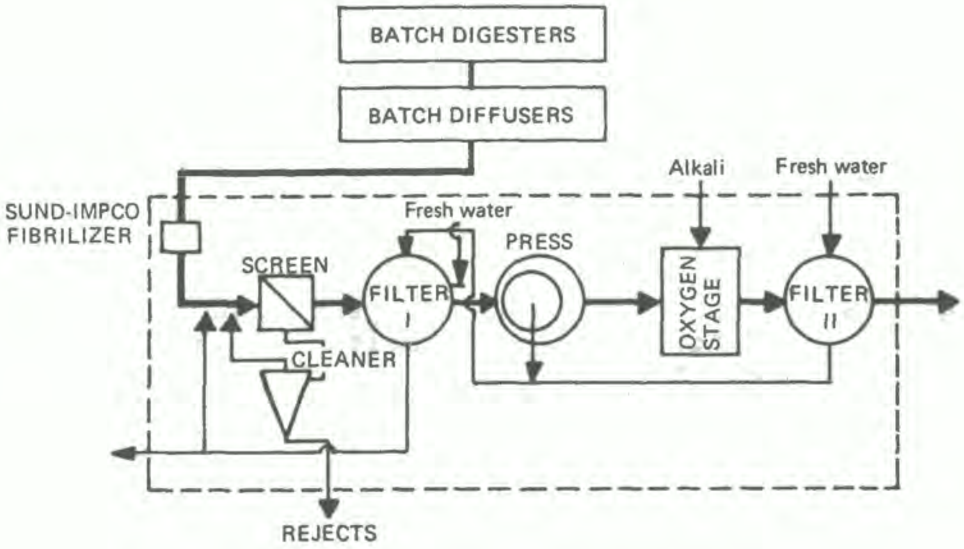


Figure 4.3. Oxygen bleaching of pine kraft pulp. Flow sheet of the Husum pilot plant

Some of the conclusions that could be drawn from the experiments were as follows (4):

1. The return of spent liquor from the filter stage after the oxygen reactor had no detrimental effect on the pulp viscosity. When the system was run without closure and no waste liquor from the oxygen stage was recirculated the dissolved solids content of the incoming pulp was 4 kg/t of pulp whereas it was 12 kg/t of pulp when the spent liquor was recirculated (Figure 4.4).

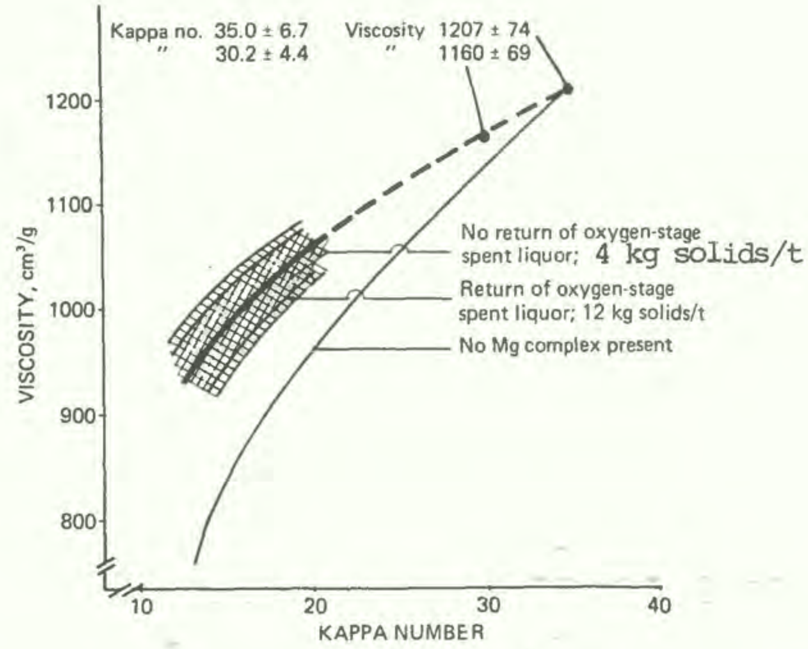
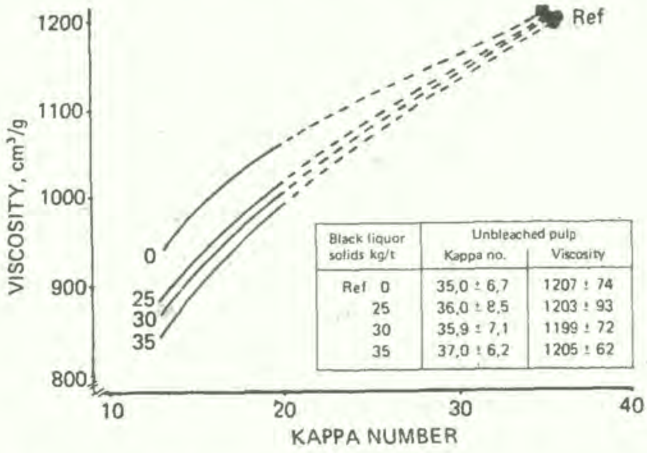


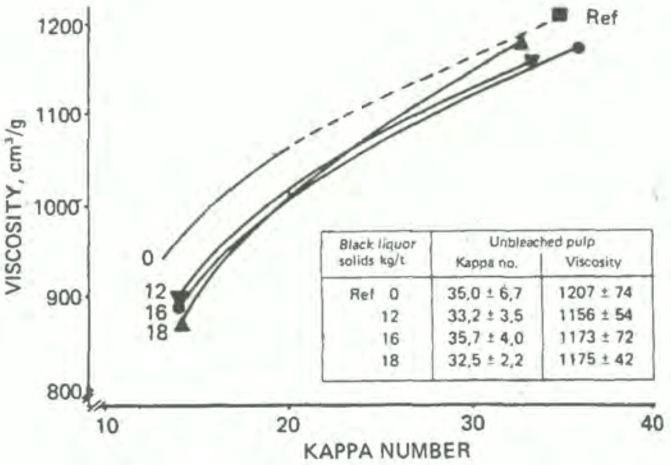
Figure 4.4. Effect of returned spent liquor from oxygen stage on pulp viscosity; oxygen bleaching in pilot plant

2. Black liquor was added to the pulp entering the oxygen reactor in order to simulate a low washing efficiency before the bleaching stage. The addition of black liquor was studied both with open and closed waste liquor systems. In both cases the black liquor had a detrimental effect on the pulp viscosity (<u>Figures 4.5</u> and <u>4.6</u>).



Black liquor solids kg/t	Unbleached pulp	
	Kappa no.	Viscosity
Ref 0	35,0 ± 6,7	1207 ± 74
25	36,0 ± 8,5	1203 ± 93
30	35,9 ± 7,1	1199 ± 72
35	37,0 ± 6,2	1205 ± 62

Figure 4.5. Effect of black liquor on pulp viscosity in oxygen bleaching



Black liquor solids kg/t	Unbleached pulp	
	Kappa no.	Viscosity
Ref 0	35,0 ± 6,7	1207 ± 74
12	33,2 ± 3,5	1156 ± 54
16	35,7 ± 4,0	1173 ± 72
18	32,5 ± 2,2	1175 ± 42

Figure 4.6. Effect of black liquor on pulp viscosity in oxygen bleaching (process control of the cook, closed system)

The consumption of oxygen also increases somewhat with increasing amounts of unoxidized black liquor to the reactor (Figure 4.7).

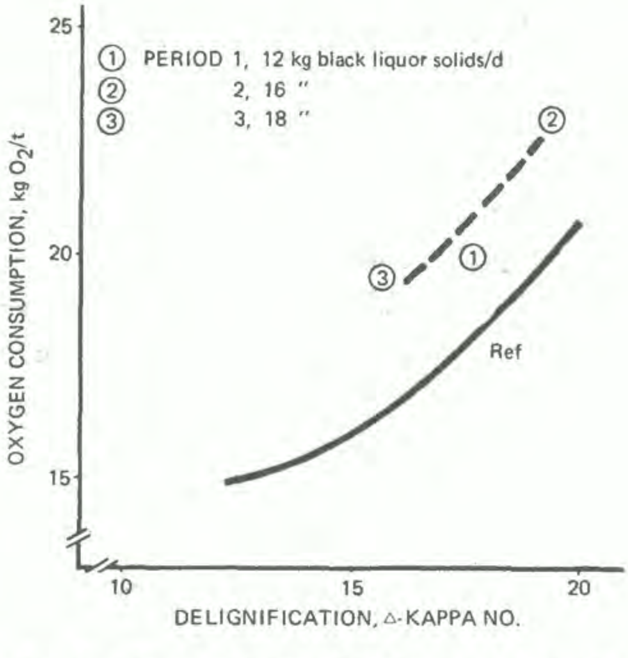


Figure 4.7. Oxygen consumption versus degree of delignification. Closed screening system

3. When bleaching pine sulphate pulp the delignification can be carried out to a final Kappa number of 13-20 corresponding to a reduction of 40-60 % starting with kappa 32-35. If a 50 % reduction is achieved, finishing at kappa 17, the solids dissolved in the oxygen stage correspond to approximately:

BOD_5	8-9	kg/t of pulp
COD	40	kg/t of pulp
Colour (Pt)	45	kg/t of pulp

To these values must be added the contents contained in the incoming pulp to the oxygen reactor in order to get the total quantities in the oxygen waste liquor.

4. The efficiency of the washing stage following the reactor should be at least 80 % in order to take advantage of the oxygen stage for environmental protection. This efficiency can be achieved with two filter washers or one filter followed by a press.

5. The use of unoxidized white liquor or green liquor instead of sodium hydroxide as the source of alkali in the oxygen stage lowered the pulp viscosity somewhat (Figures 4.8 and 4.9). Also the oxygen consumption will increase by 3-4 kg/t pulp if white or green liquor is used as the alkali source.

   However, oxidized - that is sulphide free - white liquor does not have the viscosity lowering effect on the pulp. It is equal to sodium hydroxide.

   There are also indications that a low sulphidity (15 %) unoxidized white liquor could be used without detrimental effect to the pulp viscosity.

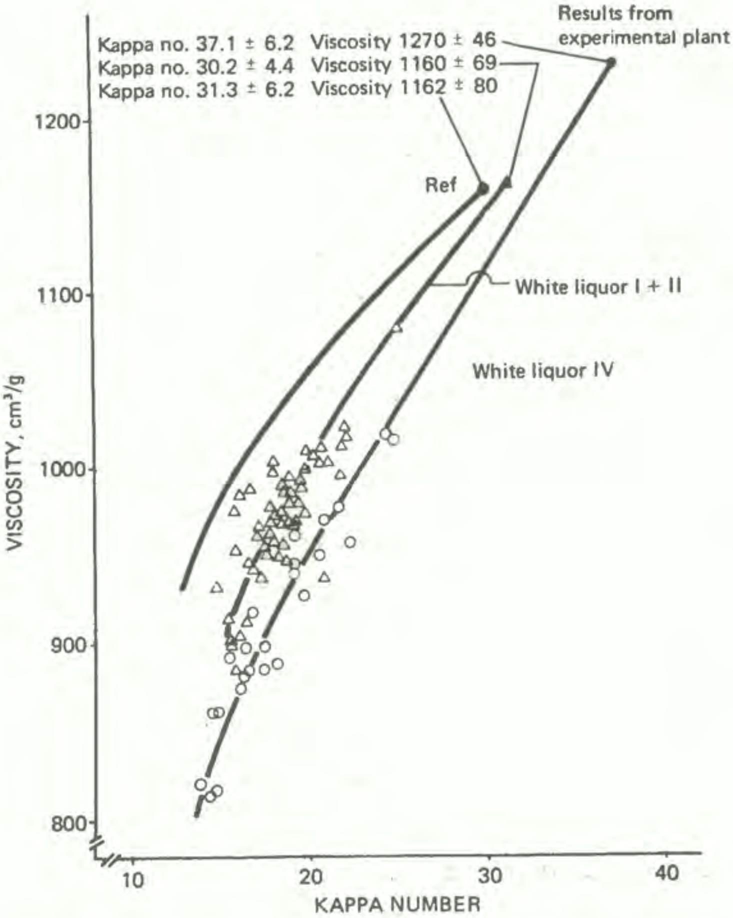


Figure 4.8. Viscosity versus Kappa number in oxygen bleaching of well washed pulp

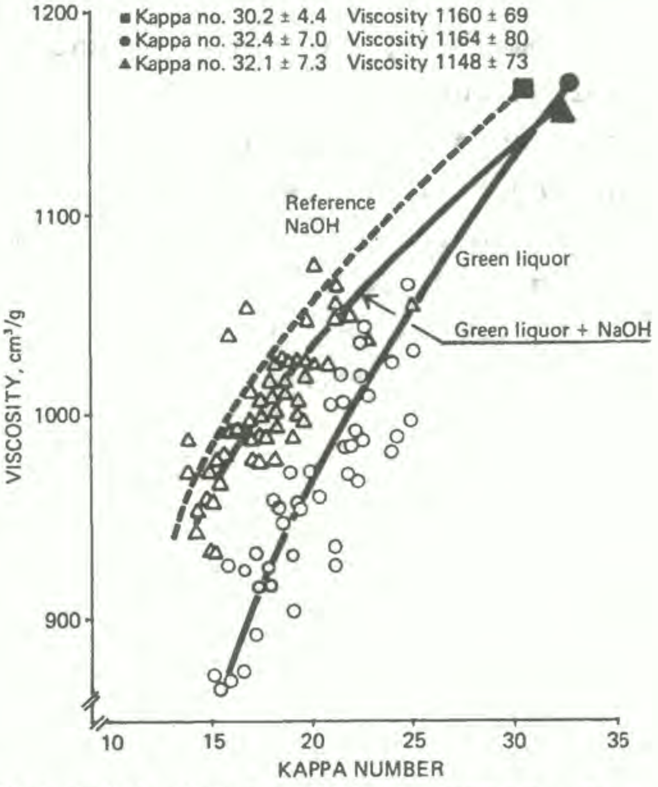


Figure 4.9. Viscosity versus Kappa number. Oxygen bleached pulp. Green liquor in oxygen stage

4.4.3 Insertion of the oxygen stage in the washing system

The study was related to the manufacture of fully bleached softwood sulphate pulp of market grade using the bleaching sequency OC/DEDED. It was assumed that unoxidized black liquor solids entering the oxygen stage reactor should normally not exceed about 20 kg/t of 90 per cent unbleached pulp, and that the recovery of solids dissolved in the oxygen stage should normally not be less than 80 per cent.

The limit of 20 kg/t of unoxidized black liquor solids corresponds to the present standard for pulp washing systems in kraft mills i.e. a washing loss of 10-20 kg of Na_2SO_4/t of pulp. This can be achieved in a 3-4 hour continuous Hi-Heat system and one washing stage outside the digester or a four-stage filter-washing system. In either case a moderate dilution factor is assumed.

With such washing systems supplemented with the press of the oxygen stage it is possible to reduce the washing loss to 12-15 kg/t of unbleached 90 per cent pulp with a dilution factor of about 2.

Table 4.3 gives some examples of the amount of unoxidized black liquor solids entering the oxygen reactor for three dilution factors and different washing efficiencies. In the case of low washing efficiencies the amount can be more than doubled to reach 20-25 kg (cases 112-113 and 712). This can be compensated for by increasing the dilution factor (the volume of wash water) to the last washing stage by about 1 t/t of 90 per cent pulp.

Table 4:3. The influence of the washing system on the amount of unoxidized black liquor going to the oxygen bleach system

Washing system b)							Unoxidized black liquor solids to oxygen reactor kg/t a) Dilution factor, t/t a)		
							1.3	2.0	2.7
		H		SF	P	O_2			
DR		97		60		-	16.4	12.3	9.6
DR		97		50		-	-	14.3	11.9
DR		95		60		-	-	21.2	17.0
		H	R	SF	P	O_2			
DR		97	85	60		-	-	5.3	
	F	F	F	SF	P	O_2			
DR	85	60	60	60		-	-	5.7	
DR	70	60	60	50		-	-	14.6	9.5
		F	F	SF	P	O_2			
DR		85	60	60		-	18.8	11.8	8.0
DR		70	60	50		-	-	(abt 26)	(abt 7)

a) 90 per cent unbleached pulp

b) DR Filter efficiency (depends on dilution ratio)
F Filter
H Hi-Heat washing
O Oxygen
P Press
R Cont diffuser (radial washing)
SF Dewatering filter
T Drum filter

In a batch cooking process followed by a well dimensioned filter washer system, three filter stages before the oxygen stage may be adequate (case 621). Whether the screening system is placed before or after the oxygen stage, it must be closed. In the examples given above the screening section with the associated filters were placed before the oxygen stage in order to protect the presses from knots, etc.

From the standpoint of pollution control, investment costs and the quality of the bleached pulp it is desirable to place the oxygen stage as near the digester as possible. Account should be taken of the sensitivity of the washing system to variations and disturbances in operating conditions. Because of the closure of the system, and the flow of liquor counter-current to the pulp, much of the spent liquor from the oxygen stage and black liquor solids that have already passed through the oxygen reactor will be returned to the washing stage ahead of the reactor. At the reactor inlet the total amount of solids dissolved in the pulp's liquid phase will be about 45-55 kg/t of 90 per cent unbleached pulp.

4.4.4 Pulp quality and discharges in the final bleaching of softwood sulphate pulp

To benefit fully from the environmental potential of oxygen bleaching the delignification in the oxygen stage must be carried out as far as possible without jeopardizing the required pulp quality and yield. It is also necessary to have an efficient pulp washing system after the oxygen stage; the greater the degree of delignification permitted in the oxygen stage the more efficient should this washing system be.

Advanced delignification is facilitated by an even lignin content (reflected in the Kappa number) of the unbleached pulp. If there are large and rapid fluctuations in Kappa number the lignin content of the oxygen-bleached pulp has to be raised. The amount of unoxidized black liquor entering the oxygen reactor will also affect the discharge of BOD, COD and colour (Figures 4.10, 4.11 and 4.12).

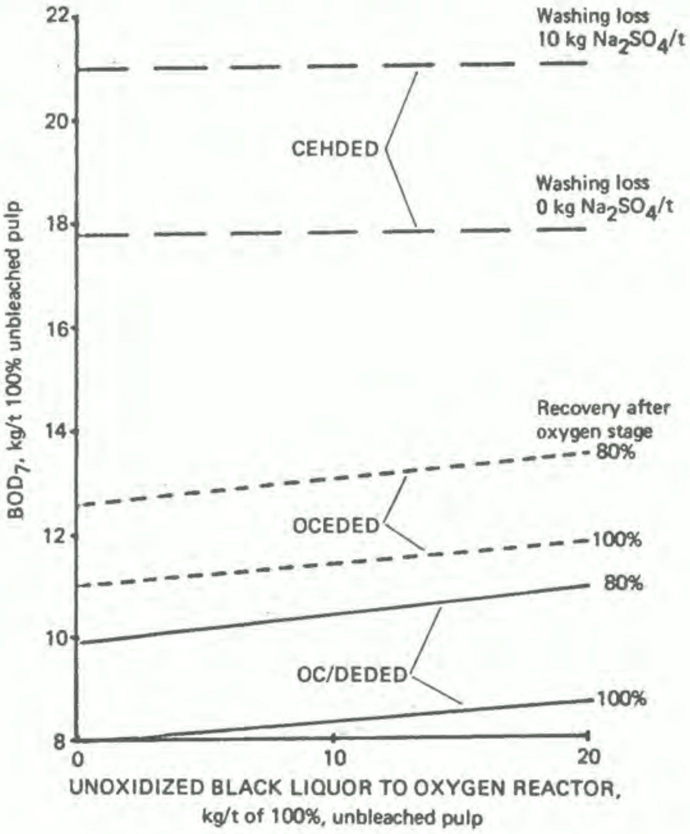


Figure 4.10. BOD$_7$ from bleaching plant versus amount of unoxidized black liquor to oxygen reactor (closed screening department)

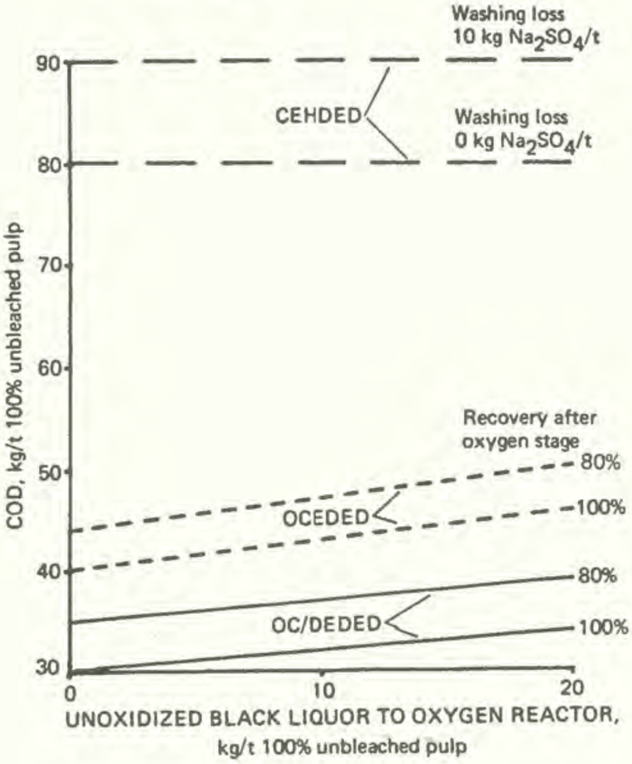


Figure 4.11. COD from bleaching plant versus amount of unoxidized black liquor to oxygen reactor (closed screening department)

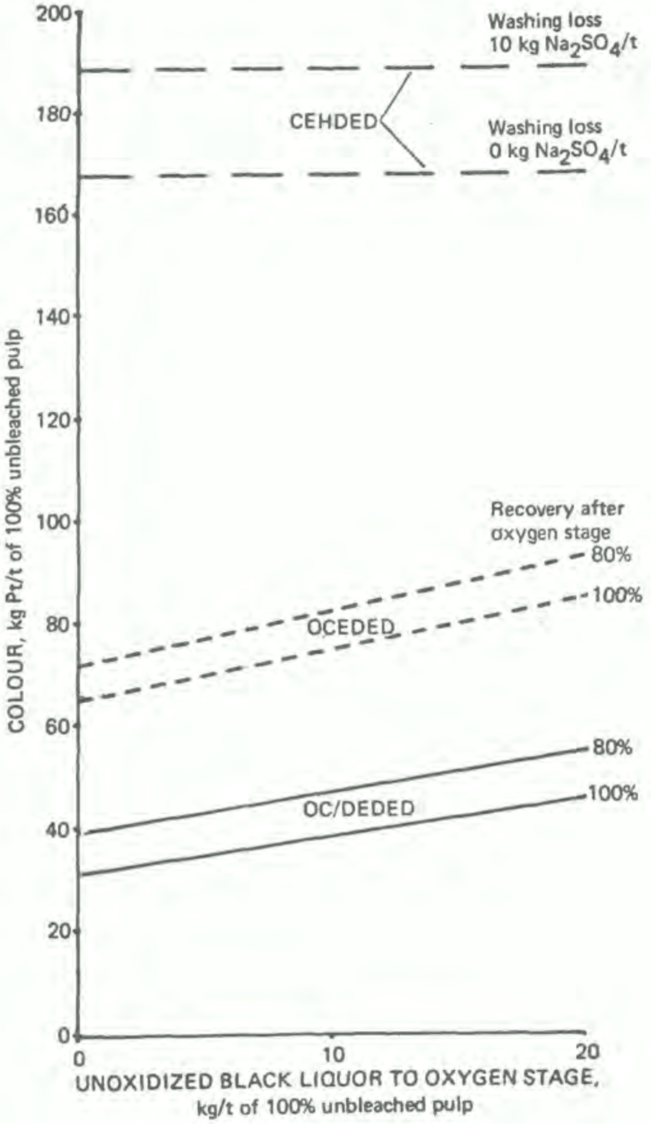


Figure 4.12. Colour discharged from bleaching plant versus amount of unoxidized black liquor to oxygen reactor (closed screening department)

Other factors having a bearing on the pollutant profile are:

- Control of chemical charge in the chlorination stage and the subsequent alkali stage
- The extent to which further delignification occurs in these stages

- The conditions for the final bleaching (chemicals, temperature, etc.)

- The design of the filtrate system and the degree of closure

- The required final brightness

In Table 4.4 the discharges of environmental pollutants are compared for conventional bleaching and oxygen bleaching of softwood sulphate market pulp (brightness 92 + per cent SCAN). In case 1 it is assumed that the screening system is closed and that a washing loss corresponding to about 9 kg of Na_2SO_4/t of pulp is carried on to the C-stage. Of the bleachery discharge about 3 kg/t of BOD_7, 9 kg/t of COD and 20 kg/t of colour (Pt) derive from the washing loss. In case 2 it is assumed that about 18 kg/t of unoxidized black liquor solids accompanies the pulp to the oxygen reactor and that there is roughly 80 per cent recovery after the oxygen stage. The Kappa number of the unbleached pulp is about the same in the two cases.

Table 4.4. Comparison of discharges of pollutants for conventional and oxygen bleaching of kraft pulp for marketing, brightness 92 + % (SCAN)

	Discharge, kg/t*		
	BOD_7	COD	Colour (Pt)
1. CEHDED	19	81	170
2 OC/DEDED	9.8	35	50

* Unbleached 90 % pulp

With the above assumptions, the reduction in the discharges after changing over from the CEHDED to the OC/DEDED and OCEDED sequences are given in Table 4.5. The addition of chlorine dioxide in the chlorination stage clearly reduces the discharges of BOD, COD and colour.

Table 4.5. Percentage reduction in pollutant levels on changing from the sequence CEHDED to OC/DEDED and OCEDED

	Percentage reduction on changing to OCEDED	 OC/DEDED
BOD	35	45-50
COD	40-45	55-60
Colour (Pt)	50	70

The degree of delignification in the oxygen stage affects the strength of the fully bleached pulp. When oxygen bleaching was performed to a lower Kappa number than 14 and laboratory bleaching with the sequence CEDED was continued to a brightness of 92 + there was a marked reduction in the tear factor of the pulp (Figure 4.13).

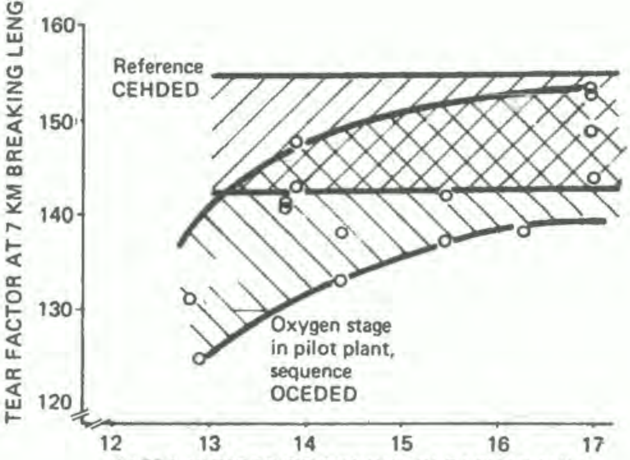


Figure 4.13. Tear factor at 7 km breaking length versus Kappa number after oxygen stage

Within the Kappa number interval 14-17 (60-50 % delignification) each Kappa number unit corresponds to about 3 units of tear factor and 10-15 cm^3/g of viscosity.

Transfer to the chlorination stage (OCEDED) of an oxygen-stage waste liquor corresponding to a washing loss of 9-16 kg of Na_2SO_4/t of pulp lowered the viscosity of the fully bleached pulp by 15-25 cm^3/g. It did not result in a significant impairment of the strength properties. When chlorine dioxide was added in the chlorination stage (C/D) the transfer of oxygen-stage spent liquor had no effect on the viscosity. Transfer of black liquor to the chlorination stage in conventional bleaching lowered the viscosity by about 30 cm^3/g with a washing loss of 20 kg of Na_2SO_4/t of pulp.

The design of the chlorination stage has important implications for the viscosity and strength of the fully bleached pulp. Addition of chlorine dioxide in the chlorination stage gave a significantly higher viscosity and tear factor than was obtained with normal chlorination.

In the example given in Table 4.6 the Kappa number after oxygen stage was 15 (pulp from the pilot plant), corresponding to 55 per cent delignification. The advantage of adding chlorine dioxide is also illustrated in the plot of viscosity of the fully bleached pulp against that of oxygen bleached pulp (Figure 4.14). The drop in viscosity after the oxygen stage with the sequence O C/DEDED is lower than that with the sequence O CEDED.

Table 4.6. Effect on the viscosity of adding chlorine dioxide in the chlorination stage

	Brightness % SCAN	Viscosity cm^3/g	Tear factor (7 km breaking length
OCEDED	93	760	135
OC/DEDED	93	864	151

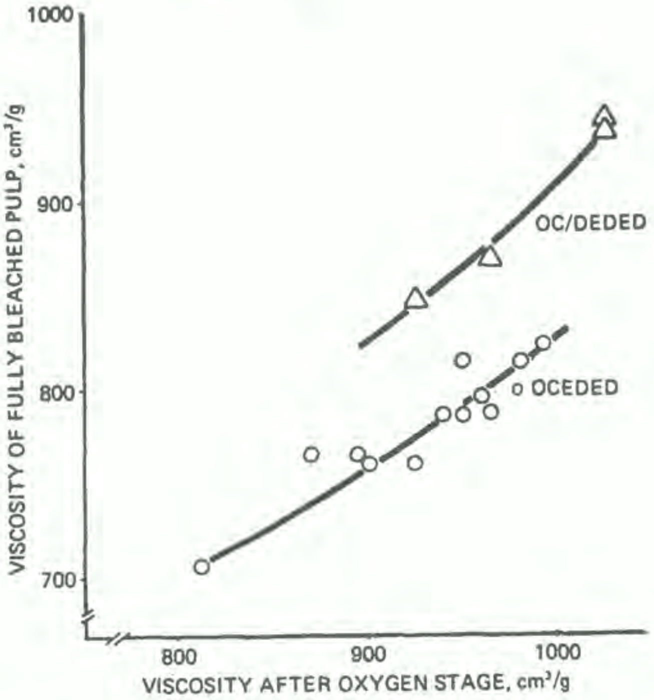


Figure 4.14. Viscosity of bleached pulp versus viscosity after oxygen stage

The tear factor at a breaking length of 7 km plotted against viscosity of the fully bleached pulp is shown in Figure 4.15. The viscosity of the conventionally bleached pulps is between 900 and 970 cm^3/g and the tear factor is in the interval 143-155. The same tear factor was obtained for oxygen-bleached pulps with a final viscosity of 825-95 cm^3/g.

The degree of delignification in the oxygen stage has a relatively important bearing on the discharge of COD but has relatively little effect on that of BOD (Figure 4.16). In the example in Table 4.7 a comparison is made of the discharges with the CEDED sequence for two well-washed oxygen-bleached pulps delignified to 50 and 60 % respectively, in the oxygen stage (Figure 4.17). By way of comparison, conventional bleaching of well-washed pulps with an average Kappa number of 33 gave the following values:

BOD_7	18 kg/t of pulp
COD	76 kg/t of pulp
Colour	160 kg/t of pulp

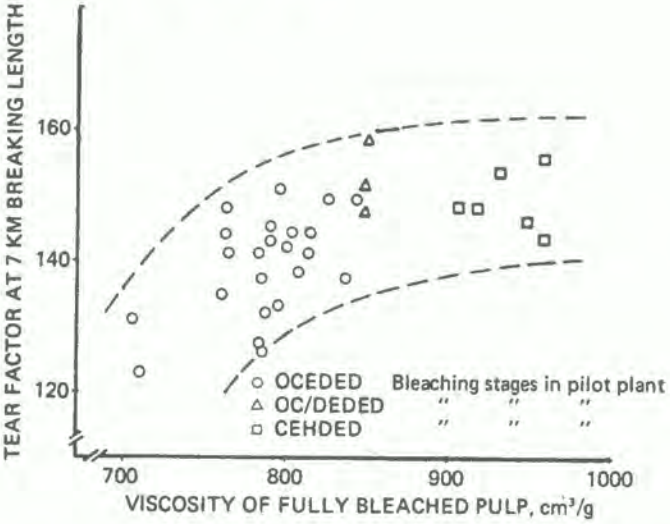


Figure 4.15. Tear factor at 7 km breaking length versus viscosity of fully bleached pulp

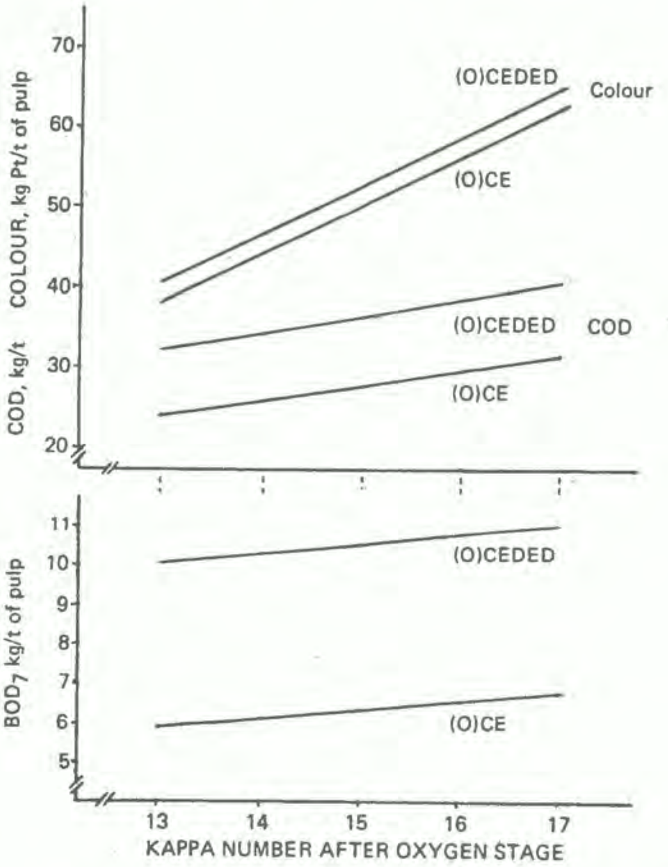


Figure 4.16. Colour, COD and BOD_7 from CE and CEDED bleaching of oxygen bleached pulp versus Kappa number after oxygen stage

Table 4.7. Discharge of pollutants with two oxygen-bleached pulps delignified to 50 and 60 % in the oxygen stage

	Discharge, kg/t*		
	BOD_7	COD	Colour (Pt)
Kappa number after O-stage			
13 60 % delignification	10	32	41
17 50 % delignification	11	41	65

* Unbleached 90 % pulp

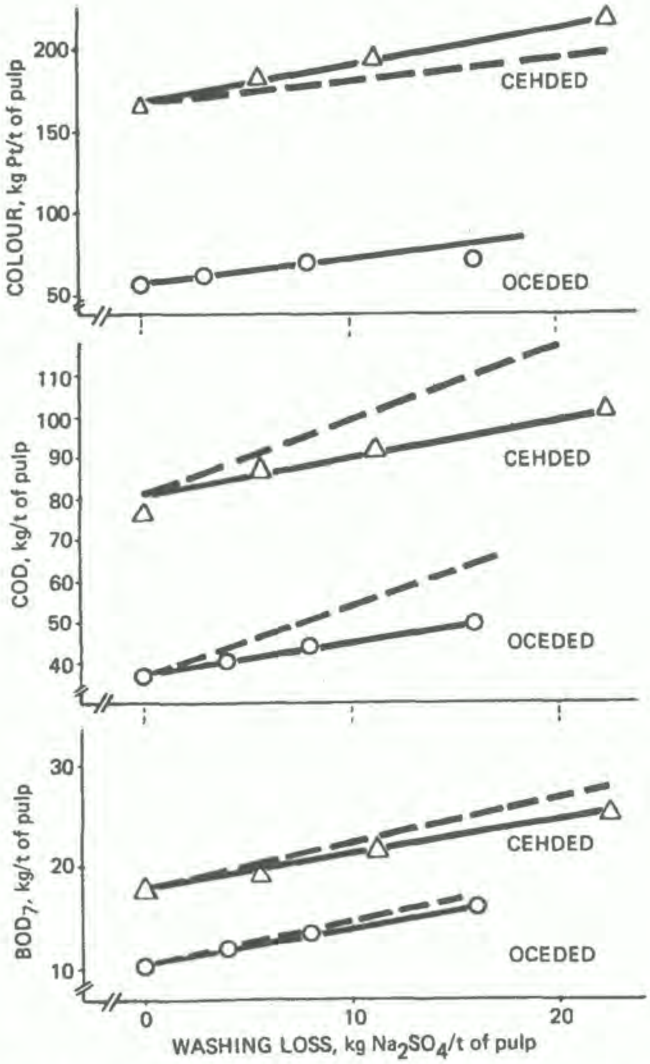


Figure 4.17. Colour, COD and BOD_7 from OCEDED and CEHDED sequences versus washing loss in oxygen stage returned to stage C

In both conventional bleaching and bleaching with an oxygen sequence 60-65 % of the total and 75-80 % of the total COD are accounted for by stages C and E. The discharge of colour from these stages constitutes 90-95 % of the total discharge/t.

Transfer of oxygen-stage spent liquor to the chlorination sage (OCEDED) increases the pollutant level in the bleaching effluent to an extent that is dependent on the volume recycled (Figure 4.17). The broken lines represent the pollutant levels that would theoretically be obtained if the transferred liquor was not altered in the chlorination stage. It is also seen that such a transfer in conventional bleaching (CEHDED) has a similar effect on the pollutant profile. The BOD_7 and COD of the transferred spent and black liquors are reduced by about 20 and 50 % respectively in the chlorination stage. The amount of colour of the spent liquor is unaffected, but that of the black liquor is increased by about 60 %. This is probably due to a reaction between the black liquor lignin and the chlorine whereby the lignin becomes more intensely coloured. The dependence of the discharges on the washing loss fed to stage C is shown in Table 4.8.

Table 4.8. Effect of recirculation of "washing loss" to stage C on the pollutant levels

	OCEDED[a]			CEHDED		
	BOD_7	COD	Colour (Pt)	BOD_7	COD	Colour (Pt)
	kg					
Washing loss to stage C						
0 kg Na_2SO_4/t	10.2	37	56	17.6	81	166
5 kg Na_2SO_4/t	12.0	41	63	19.3	85	177
12 kg Na_2SO_4/t	15.5	49	78	22.8	94	199

a) 55 % delignification in the oxygen stage

Table 4.9 shows the pollutant levels obtained when an oxygen bleached pulp, Kappa number 15 (55 % delignification), is bleached to the same lignin content with CE and C/DE stages.

Table 4.9. Pollutant levels with CE and C/DE bleaching to the same lignin content

		Discharge, kg/t[a)]		
		BOD_7	COD	Colour (Pt)
		kg/t		
Oxygen-stage spent liquor in C and C/D				
0 kg Na_2SO_4/t	(O)CE	6.3	28	55
0 kg -"-	(O)C/DE	4.5	25	45
9 kg Na_2SO_4/t	(O)CE	7.6	34	63
9 kg -"-	(O)C/DE	5.8	30	53

a) Discharges from the oxygen stage are not included

4.4.5 Chemical consumption in softwood sulphate pulp bleaching

The quantities of bleaching chemicals required in the bleaching stages after the oxygen stage are dependent on the Kappa number of the oxygen-bleached pulp. A high number increases the chlorine requirement (sequence OCEDED), but a larger chemical charge is also required in the first D stage. In the Kappa number interval studied (13-17 after the oxygen stage) the chlorine consumption increases in proportion to the Kappa number by a little more than 2 kg/t of pulp and per unit of Kappa number. The quantity of chlorine dioxide used increases by approximately 0.5 kg of active chlorine/t of pulp and per unit of Kappa number. The cost of bleaching chemicals after the oxygen stage thus falls when the degree of delignification in the oxygen stage is increased. This is, however, accompanied by an increase in the amounts of alkali and oxygen consumed in the oxygen stage by about 1 kg of NaOH and 1 kg of oxygen per tonne of pulp and per unit of Kappa number.

The transfer of oxygen-stage spent and black liquor to the chlorination stage in bleaching with the sequences OCEDED and CEHDED respectively raises the chlorine consumption in stage C by about 0.7 and 1.5 kg per tonne of pulp and per kilogram of washing loss (Na_2SO_4), respectively. In addition, there is a marginal increase in the chlorine dioxide consumption in stage D_1 (sequence OCEDED) and in the hypochlorite consumption in stage H (sequence CEHDED).

Table 4.10 shows the quantities of chemicals used in oxygen bleaching and conventional bleaching of softwood sulphate pulp, with a washing loss of 10 kg of Na_2SO_4/t of pulp before stage C (Kappa number 33, degree of delignification 55 %, final brightness 92+).

Table 4.10. Quantities of chemicals consumed in oxygen and conventional bleaching of pine sulphate pulp

Washing loss to stage C[a)] (kg of Na_2SO_4/t)	OCEDED		CEHDED	
	0	10	0	10
Bleaching agents (kg/t):				
Chlorine	29	36	69	84
Chlorine dioxide	24	25	23	23
Hypochlorite	-	-	10	11
Sodium hydroxide	45	45	41	41
Oxygen	21	21	-	-
Magnesium	0.5	0.5	-	-

a) The ratio of sodium to the chemical consuming agents is different for black liquor and oxygen-stage spent liquor. Na_2SO_4 as the basis of comparison is therefore only a rough measure

The transfer of oxygen-stage spent liquor and black liquor corresponds to a cost increase of USD 0.15 and 0.29/kg for this washing loss (Na_2SO_4). The consumption of sodium hydroxide in the oxygen stage has been calculated at 20 kg/t of pulp. This alkali can, of course, be replaced with oxidized white liquor.

With oxygen bleaching and C/D chlorination about 55 % delignification can be permitted in the oxygen stage if the fully bleached product is to be equivalent to that obtained with conventional bleaching. With normal chlorination - the sequence CEDED -50 % delignification is hardly recommendable. The cost of the chemicals for these alternative oxygen bleaching processes will be largely the same, at USD 23.00-23.50/t of pulp while for the conventional procedure it will be USD 29.25/t.

The cost estimates are based on the consumptions and chemical prices given in Table 4.11. It should be noted that the use of sodium hydroxide is assumed in the oxygen stage; if oxidized white liquor is used instead, the numbers will be lower.

Table 4.11. Consumption and price of chemicals assumed in the computation of the relative costs for the bleaching sequences OCEDED, OC/DEDED and CEHDED

	Chemical consumption, kg/t			Price of chemicals USD/kg
	OCEDED[a]	OC/DEDED[a]	CEHDED	
Bleaching chemicals				
Chlorine active Cl	34	25	69	0.165[b]
Chlorine dioxide active Cl	25	28	23	0.32[b]
Hypochlorite active Cl	-	-	10	0.32[b]
Sodium hydroxide	43	45	41	0.17
Oxygen	10	21	-	0.14
Magnesium	0.5	0.5	-	0.50

a) For the oxygen sequences 50 % (OCEDED) and 55 % (OC/DEDED) delignification in the O-stage has been assumed

b) Per kg of active chlorine

The price of oxygen is for delivered liquid oxygen. A very large mill 500-1000 t_{90}/24 hours might install its own oxygen plant and could possibly reduce the oxygen costs.

4.4.6 Oxygen bleaching of hardwood sulphate pulp

Oxygen bleaching is applied also to hardwood pulps on a commercial basis. The environmental benefit of oxygen bleaching is not as high for such pulps, however, as it is possible to reduce the Kappa number already in the cooking process to a low level (18-22).

In the Husum pilot plant a number of oxygen bleaching sequences for producing fully bleached hardwood sulphate pulps were evaluated. The results showed that to avoid impaired yield and viscosity the delignification should be stopped at about 50 % (as for softwood pulps). To achieve this delignification 10-15 kg/t of oxygen and sodium hydroxide is consumed.

All pulps were bleached to 90-91 % SCAN brightness and the total bleached yield was 94-95.5 %. The resulting discharges (with at least 80 % recovery of the O-stage liquor) are given in Table 4.12.

Table 4.12. Bleach effluent parameters (in kg/t) for various bleaching sequences for birch sulphate pulp

	CEDED	OCEDED	OC/DPD	ODPD
Kappa number[a]	18.5	10.9	10.9	7.8
BOD_7	10.1	8.1	6.0	3.4
COD	42	28	29	12
Colour	68	26	9.6	3.4

a) Of unbleached or oxygen bleached pulp

Oxygen bleaching alone reduces the colour of the effluent. If it is combined with high amounts of chlorine dioxide or peroxide in the final bleaching the overall pollution load from the bleach plant is markedly diminished. The chemical consumption for the bleaching sequences are given in Table 4.13.

Table 4.13. Chemicals consumed in the bleaching of birch sulphate pulp

	Chemical consumption[a]			
	CEHDED	OCEDED	OC/DPD	ODPD
Chlorine	37.3	22.3	18.8	-
Chlorine dioxide (active Cl)	15.5	25.3	20.6	31.1
Hypochlorite (active Cl)	9.7	-	-	-
Hydrogen peroxide	-	-	7.3	13.6
Sodium hydroxide	28.3	35.8	27.2	54.2
Oxygen estimated	-	10-15	10-15	10-15

a) kg active chemical per tonne 90 % bleached pulp

The Cellulose d'Aquitaine mill in Saint Gaudens, France, has practised oxygen bleaching of mixed hardwood (predominantly oak and beech) sulphate pulp since 1973. The total discharges from the mill before and after installation of the oxygen bleaching system are given in Table 4.14. The most drastic decrease is shown by the colour value which has diminished by 50 %.

The bleach chemical consumption is given in Table 4.15 where also the chemical costs have been calculated. With the prices assumed the chemical cost for the oxygen sequence is 2.35 USD lower than for the conventional.

Table 4.14. Total mill effluent parameters (in kg/t_{90}) for conventional and oxygen bleaching of hardwood sulphate pulp

	CEDED	OCEDED
BOD_5	29	21
COD	81	70
Colour[a)]	81	40

a) Measured at 387.5 nm and pH 7

Table 4.15. Chemical costs in oxygen and conventional bleaching of hardwood sulphate pulp in Cellulose d'Aquitaine (3)

	CEDED		OCEDED	
	kg/t	USD/t	kg/t	USD/t
Chlorine	54	9.18	36	6.12
Sodium hydroxide	31	5.27	38[a)]	6.46
Hypochlorite (as Cl_2)	5	1.60	-	-
Chlorine dioxide	19	6.08	12	3.84
Oxygen	-	-	24	3.36
Chemical costs		22.13		19.78

a) 15 kg/t NaOH is charged in the oxygen stage

4.4.7 Effect of oxygen bleaching on the mill's alkali balance and recovery system

In the oxygen stage an alkali charge equivalent to about 20 kg of sodium hydroxide per tonne of 90 % unbleached pulp is required to achieve 50 % delignification of softwood sulphate pulp with an initial Kappa number of 30-35. With an 80 % transfer of the inorganic part of oxygen-stage spent liquor to the recovery system and if pure sodium hydroxide is used as the alkali source in the oxygen stage, the liquor system receives sodium equivalent to 16 kg of NaOH or 30 kg of Na_2SO_4 per tonne of pulp.

In the production of fully bleached pine pulp about 25 kg of active chlorine in the form of chlorine dioxide is required for bleaching to a final brightness of 92 % (SCAN), with the sequence O/C/DEDED. The production of this quantity by the conventional Mathieson method gives a spent acid that, if led into the liquor system, will raise the sodium level by 10 kg of sodium sulphate per tonne of pulp.

The total quantity of sodium entering the liquor system from the oxygen bleaching process and the residual acid is thus enough to balance the total sodium losses in a well run mill with the most up-to-date equipment in the washing and screening departments and good control of the temporary and accidental discharges. In modern mills an appreciable excess would be obtained.

Against this background efforts have been made to find alternative alkali sources for the oxygen bleaching process. As has been shown above, the results as regards pulp quality and chemical consumption are practically the same if pure sodium hydroxide is replaced by oxidized white liquor or a mixture of unoxidized white liquor and sodium hydroxide (at least 50 % of hydroxide). One possible disadvantage of using oxidized white liquor is the greater tendency for scaling in the evaporating plant owing to the higher sulphate and carbonate contents of the oxygen spent liquor.

By adjusting the proportions of sodium hydroxide, white liquor and oxidized white liquor it is thus possible in practice to obtain a situation where the alkali requirement for oxygen bleaching is in balance with the mill's sodium cycle.

4.4.8 Cost estimates for oxygen bleaching system

Investment and operating costs for two oxygen bleaching systems have been calculated for the mill sizes 100 and 300 t/d. The bleaching sequence assumed was O C/D EDED and for comparison the cost for a conventional C/DEHDED plant has also been calculated. The Kappa number of the unbleached pulp was assumed to be 30-35 and the delignification in the oxygen system is about 50 %.

The amount of unoxidized black liquor solids entering the oxygen reactor does not exceed 20 kg/t of 90 % unbleached pulp, and the recovery of oxygen-stage spent liquor is not less than 80 %. In the conventional bleaching plant the washing plant gives a loss not exceeding 10 kg of Na_2SO_4/t.

In the investment calculations the same evaporator plant capacity is assumed in the two cases; this would probably require a somewhat larger washing plant after the oxygen stage. It has thus been assumed that hypochlorite might be added in the oxygen sequence in certain cases. It has also been assumed that even if a new mill is built with a conventional bleaching plant the screening department will be of the closed type. The chemical recovery system is dimensioned for returning the oxygen-stage spent liquor and using oxidized white liquor as the alkali source in the oxygen stage.

In Table 4.16 the difference in investment cost between conventional and oxygen bleaching plants is given. For 100 t/d the oxygen plants are 1.8 to 3.6 M USD more expensive depending on the washing equipment. The corresponding figures are 5.3-6.3 M USD for a 300 t/d plant.

The operating costs for the two mill sizes are given in Tables 4.17 and 4.18. Oxygen bleaching is 4-5 USD/t cheaper in operating costs compared to the conventional sequence.

When, however, the capital costs are added (Table 4.19) oxygen bleaching turns out to be more expensive. For the 100 t/d mill the difference is 9 USD/t and for the 300 t/d line 3 USD/t.

Even though all costs have been calculated for softwood sulphate pulp approximately the same figures can be expected for hardwood sulphate pulp.

Table 4.16. Investment costs for softwood sulphate pulp bleaching plants

Alternative[a]	Costs M of USD	
	100 t/d	300 t/d
1. Hypochlorite stage of conventional bleaching plant	1,9	3,2
Washing (H+F+SF) for F	0,9	1,7
Total (for comparison)	2,8	4,9
2. Oxygen stage P+O	3,4	6,0
Washing before oxygen stage (H+SF)	-	-
Washing after oxygen stage (F+F)	1,8	3,4
Supplementary investments	0,4	0,8
Total (for comparison)	5,6	10,2
Difference 2-1	2,8	5,3
3. Oxygen stage P+O	3,4	6,0
Washing before oxygen stage (H+SF)	-	-
Washing after oxygen stage (F+P)	2,6	4,4
Supplementary investments	0,4	0,8
Total (for comparison)	6,4	11,2
Difference 3-1	3,6	6,3
Additional cost for one F washing stage	0,9	1,7

a) For key to abbreviations see Table 4.3

Table. 4.17 Operating costs. Comparison between oxygen bleaching and conventional bleaching for production of 100 t/d of 90 % bleached pine pulp

Item		Oxygen bleaching			Conventional bleaching		
		Quantity	USD/t	Mill USD/yr	Quantity	USD/t	Mill USD/yr
Materials and energy			20.82	0.729		27.53	0.964
Raw wood		d)					
Bleaching chemicals:							
Chlorine	17 c/kg	23	3.91		60	10.20	
Sodium hydroxide	17 c/kg	23	3.91		37	6.29	
Chlorine dioxide	32 c/kg	25	8.00		24	7.68	
Sodium hypochlorite	32 c/kg	-	-		9	2.88	
Oxygen	14 c/kg	19	2.66		-		
Magnesium compounds, Mg	9 c/kg	0.5	0.05		-		
Na_2SO_4 (washing loss)	6 c/kg	2			8	0.48	
Na_2SO_4 (oxidized white liquor)	6 c/kg	7	0.54		-		
Heat energy USD 9.80/Gcal a)		d)	-		d)	-	
Electrical energy 2.5 c/kWh		70 c)	1.75		-	-	
Labour and maintenance			0.151	0.106			
Production staff		d)	-		d)	-	
Maintenance: Machines 4 % of 2.6 M				0.104	-		
Buildings 1 % of 0.2 M				0.002	-		
TOTAL				0.835			0.964
Difference				-0.129			

a), b), c) and d). See Table 4.18

Table. 4.18 Operating costs. Comparison between oxygen bleaching and conventional bleaching for production of 300 t/d of 90 % bleached pine pulp

Item	Oxygen bleaching			Conventional bleaching		
	Quantity	USD/t	Mill USD/yr	Quantity	USD/t	Mill USD/yr
Materials and energy		20.32	2.134		27.53	2.892
Raw wood	d)			d)		
Chemicals		19.07				
Heat energy USD 9.80/Gcal	d)	-		d)	-	
Electrical energy USD 2.5 c/kWh	50	1.25		-	-	
Labour and maintenance			0.200			-
Production staff	d)			d)		
Maintenance: Machines 4 % of 4.9 M			0.196	-		-
Buildings 1 % of 0.4 M			0.004	-		-
TOTAL			2.334			2.892
Difference			-0.558			

a) 1 Joule = 0.239×10^{-9} Gcal i.e. USD 9.80/Gcal = = USD 2.34/GJ

b) The oxygen price of USD 140/t may be considered to apply to purchased liquor oxygen. Mills may be able to procude their own oxygen cheaper

c) Energy requirements for oxidation of white liquor to be added

d) Same for both alternatives

Table 4.19. Summary of operating and capital costs for pine pulp mills with 100 and 300 t/d output. New plants (M USD/yr)

	100 t/d		300 t/d	
	Oxygen bleaching	Convent. bleaching	Oxygen bleaching	Convent. bleaching
Materials and energy (see Tables 4.18 and 4.19)	0.729	0.964	2.134	2.892
Labour and maintenance	0.106	-	0.200	-
Total	0.835	0.936	2.334	2.892
Difference	-0.129		-0.558	
Capital costs	0.456		0.864	
Total amount/cost	1.291	0.964	3.198	2.892
Difference	0.327		+0.306	
Difference per t_{90} pulp	9.34		2.91	
If the BOD_7-reduction is estimated to 9.0 kg/t_{90} pulp, the anti-pollution cost will be	1.0 USD/kg BOD_7		0.32 USD/kg BOD_7	
If the COD-reduction is estimated to 90 - - 41 = 49, the anti-pollution cost will be	0.19 USD/kg COD		0.06 USD/kg COD	

4.5 System closure in bleach plants

4.5.1 Background

A first step towards recycling of bleach plant effluents to the recovery system, or to separate systems for destruction or treatment, is closure of the bleach plant water system to reduce the effluent volume. System closure also reduces the demand for energy to heat the pulp suspension. From a pollution point of view closure results in a reduction of the liquid load on an external treatment stage. It will also presumably lead to a marginal reduction in the BOD and colour levels. A decrease in the fibre discharge can be expected.

Water or waste water is used in a bleaching plant for the following purposes:

- To convey unbleached pulp to the bleaching plant
- Dilution to a suitable consistency for chlorination usually 3-4 %
- To convey the pulp from the bleaching towers to subsequent washing filters and for dilution (to 1 %)
- Washing of filters (7-10 m^3/t of pulp)
- Wire sprays and sealing water
- Supply of bleaching liquid and heat energy (steam)
- To convey bleached pulp from the bleaching plant

If diffuser washing is used no water is needed for wire sprays or dilution between the bleaching towers and the subsequent washing stages.

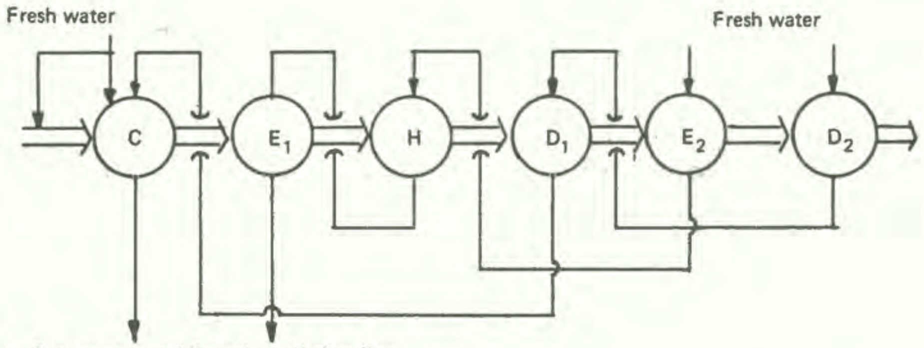
4.5.2 Principles for system closure

Three main principles for closing the bleachery water system exist (Figure 4.18).

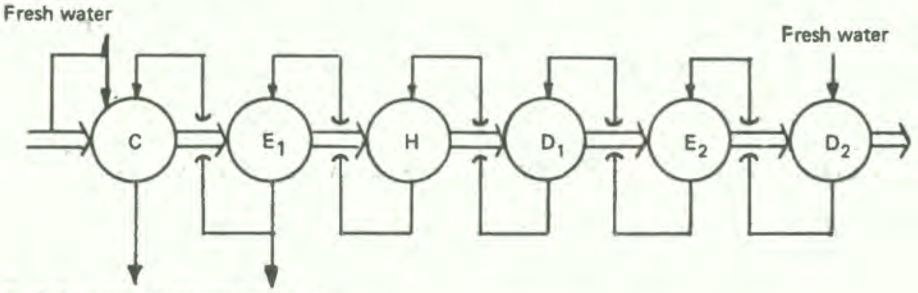
A. Separate recirculation of acidic and alkaline filtrates.

B. Strictly counter-current recirculation of filtrate

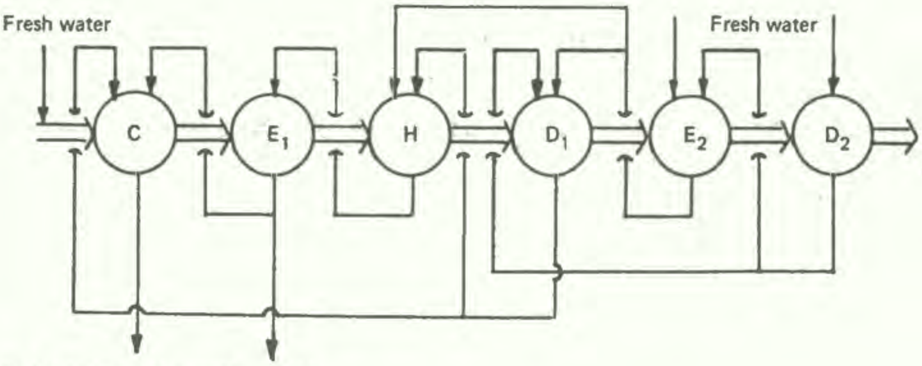
C. Mixed counter-current washing, consisting of a combination of A and B.



A. Return to an acidic and an alkaline line



B. Return strictly counter-current



C. Mixed counter-current washing

Figure 4.18. Three main principles for closing bleach plant water system of kraft mill

Four alternative systems for closing the water systems will be dealt with below from the aspects of the processes and operation.

Alt. 1. Separate recirculation of acidic and alkaline filtrates (A). Open chlorination stage.

Alt. 2. As in 1. Closed chlorination stage.

Alt. 3. Recirculation strictly counter-current (B). Open chlorination stage.

Alt. 4. Recirculation strictly counter-current (B). Closed chlorination stage.

The calculations in the four alternatives are given in Table 4.20 for the sequence CEHDED and as a comparison also for sequence CEHD.

Table 4.20. Calculated volumes of effluent for the four alternative systems of closure (m^3 per 90 % bleached pulp)

Sequence	Alternative system of closure			
	1	2	3	4
CEHDED	38	20	31	13
CEHD	37	19	30	12

In alternative 2 there is a risk of foaming on the chlorination stage filter, with consequent reduction in capacity and difficulty in regulating the temperature in the hypochlorite stage.

Alternative 4 might well incur complications at least as serious as those in alternative 2.

4.5.3 Closure of the chlorination stage

To be able to reduce the volumes discharged from conventional bleach plants the water system must be closed and the washing liquid conducted counter-current. Because the chlorination normally is performed at a lower consistency than in other stages it is particularly important to examine the possibility of using water from the chlorination stage for diluting the pulp before chlorination.

It can be expected that as the degree of closure of the effluent systems is increased there would be changes in the pulp quality and chemical consumption and also in operation factors. The main operational disturbances that might occur are foaming on the chlorination filter with a resulting decrease in capacity, and more severe corrosion problems.

When the degree of closure in the chlorination stage is increased, the alkali charge in the subsequent stage must be increased in order to keep the Kappa number constant (Figure 4.19). At Kappa number 6.5 the increase is 15 kg of NaOH/t of pulp for a washing efficiency of 95 % when closing from open to complete closure. A complete closure implies that the dilution of the pulp after the high-consistency tower is achieved with filtrate from the chlorination stage only.

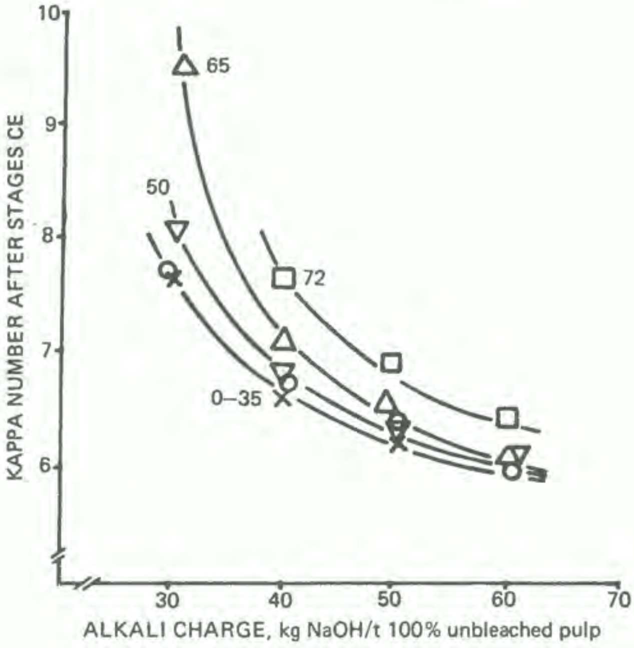


Figure 4.19. Kappa number of pulp versus alkali charge in stage E. Parameter: Theoretical degree of closure, C theor.

An increase in the degree of closure of the chlorination stage results in a slight decrease in the discharge of colour in the chlorination effluent. The colour of the filtrate of the extraction stage is not affected, nor is the BOD level. However, closure raises the costs for bleaching chemicals; the increase being dependent on the washing efficiency of the chlorination filter; in this example it is of the order of USD 3/t of pulp but this cost can be reduced with more efficient washing.

4.5.4 The economy of system closure

In the foregoing the alternative principles for closure of the system for the whole bleaching plant have been discussed, and also the specific case of closure in the chlorination stage.

Closure of the chlorination stage does not result in any change in the pulp properties. It can, however, lead to operational disturbances which may raise the costs for the alkali in stage E_1. Return of hypochlorite filtrate has some environmental advantages, for example, a lower discharge of colour in the E_1 filtrate and the cost of chemicals in stage E_1 is decreased by about 2 USD/t of pulp.

The values in Table 4.21 illustrate the changes in costs that may result from the alternative closure methods CEHDED 1 and 4. The reference is a fictive bleaching plant with a water consumption of 100 m^3/t in which hot water washing is effected with a volume equivalent to four washing stages. The values for alternative 4 have been placed in parentheses because the applicability of this alternative is doubtful.

The increase in the chemical costs in these examples is offset by savings in the form of reduced fibre losses and hot water needs. The net profit for the various alternatives varies between USD 2 and 5/t.

The overall economic assessment must also take into account the required investments, although this is not easy in the case of modification of an existing bleaching plant. In a new plant the extra investment entailed by a moderate closure of the water system is also difficult to judge on a

Table 4.21. Estimated changes in material and energy costs for closing system in a bleaching plant with the sequence CEHDED

		Ref	Separate acidic and alcaline		Counter current	
			1. Open C	2. Closed C	3. Open C	4. Closed C
I INCREASE IN COSTS						
Bleaching chemicals (Bleached 90 % pulp)	USD/tonne	0	1,5	3,1	2,0	(3,6)
II DECREASES IN COSTS						
A. Fibres						
Volume of effluent	m^3/tonne	100	38	22	30	14
Difference from ref	m^3/tonne	0	62	78	70	86
Recovered fibres	kg/tonne	0	1,5	1,9	1,7	2,1
Saving fibres	USD/tonne	0	-0,6	-0,8	-0,7	(-0,8)
B. Heat						
Hot water requirement	m^3/tonne	30	15	15	7,5	7,5
Difference from ref	m^3/tonne	0	15	15	22,5	22,5
Saving heat	USD/tonne	0	-4,5	-4,5	-6,8	(-6,8)
Total change in costs	USD/tonne	0	-3,5	-2,2	-5,5	(-4,0)

Assumed conditions: Effluent volume of the reference bleaching plant: 100 m^3/tonne pulp

Fibre content of effluent: 25 mg/l

Value of recovered fibres: USD 0,40/kg

Hot water consumption in the reference bleaching plant: 30 m^3/tonne (corresponding to 7,5 m^3/tonne for each of 4 washing stages)

Costs for hot water. USD 0,30/m^3

general basis, but it is normally small (pipes, pumps, instruments and equipment for process control). If a high degree of closure is chosen better construction materials have to be selected. This leads to drastically increased costs.

The theoretical savings made possible by re-use of water must be weighed against the disadvantages for the interference with production and the risk of impairment of pulp quality. It is obvious that alternative 1 is the least problematic in this respect and perhaps offers a saving of 3.50 USD/t. It is, however, impossible to perform a reliable appraisal of the alternatives without mill scale studies on a practical basis.

4.6 Recycling of chlorine containing effluents to the recovery system

Chlorine is normally introduced in the recovery system with the spent acid, chlorine containing make-up chemicals, salt-water transported logs etc. Losses of chloride occur with losses of black and white liquor, washing losses and with flue gas dust. In this way about 1 kg Cl per tonne pulp can be removed from the recovery system. Recycling of bleach plant effluents can be expected to result in chloride inputs in excess of 1 kg Cl per tonne. In that case a special system for chloride removal has to be installed to prevent build up of high chloride levels in the recovery system.

A number of systems are presently being developed. The systems are based on the following principal ways of removing chlorine selectively from the mill's chemical system:

1. From the precipitor catch or flue gases of the recovery boiler

2. From white liquor or green liquor

3. From the flue gas of the lime kiln

The first method is based on the fact that sodium chloride is enriched in the precipitator catch in comparison to the content in the smelt from the recovery boiler. The NaCl is removed by leaching the precipitator dust with a solution of sodium sulphate and chloride. However, only about 75 kg dust/t_{90} is carried over to the precipitator, part of which is NaCl (Figure 4.20).

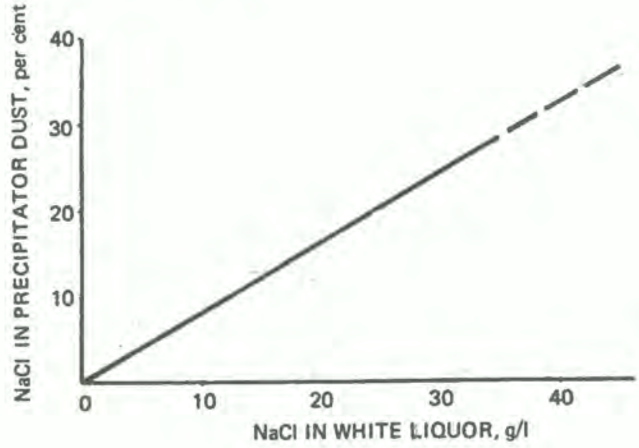


Figure 4.20. Amount of sodium chloride in precipitator dust versus amount in white liquor

Part (25-40 %) of this NaCl is already in the recovery boiler transformed to hydrogen chloride. This can be removed by scrubbing the flue gases with water or by emitting them directly to the atmosphere.

The second principle involves one method for the evaporation of white liquor which was developed by W.H. Rapson and D. Reeve (2) and is called the Salt Recovery Process (SPR). The first millscale system is installed at the Great Lakes

Paper Co, Thunder Bay, Ontario, Canada. Another method includes the cooling down of the green liquor to +5 to +10°C at which temperature 55-70 % of the carbonate is precipated. The green liquor is then causticized and concentrated through evaporation.

The third principle - absorption of hydrogen chloride from the lime kiln flue gas - assumes the adsorption of the chlorine containing organic compounds on lime mud before it enters the lime kiln.

Of all the above mentioned methods the highest chloride bleed out capacity is shown by principle 2. The SRP system is the best developed according to this principle and will be described in more detail below.

The method has been described in a number of articles. A flow sheet for the system is presented in Figures 4.21 and 4.22. The brown-stock washing is performed with the bleachery effluent, and the smelt from the recovery furnace is dissolved in the same effluent. The white liquor is causticized and then evaporated, the sodium chloride and carbonate crystallizing out. The concentrated white liquor including the sodium hydroxide and sulphide then goes to the digester. This procedure would require transfer of the whole of the bleachery effluent to the brown-stock washing system, but with present-day techniques this is impracticable if only because of the large volumes involved.

The solids are leached with water and most of the sodium carbonate and some of the chloride are dissolved. The solution is returned to the causticizing system. Solid sodium chloride from the leaching process remains.

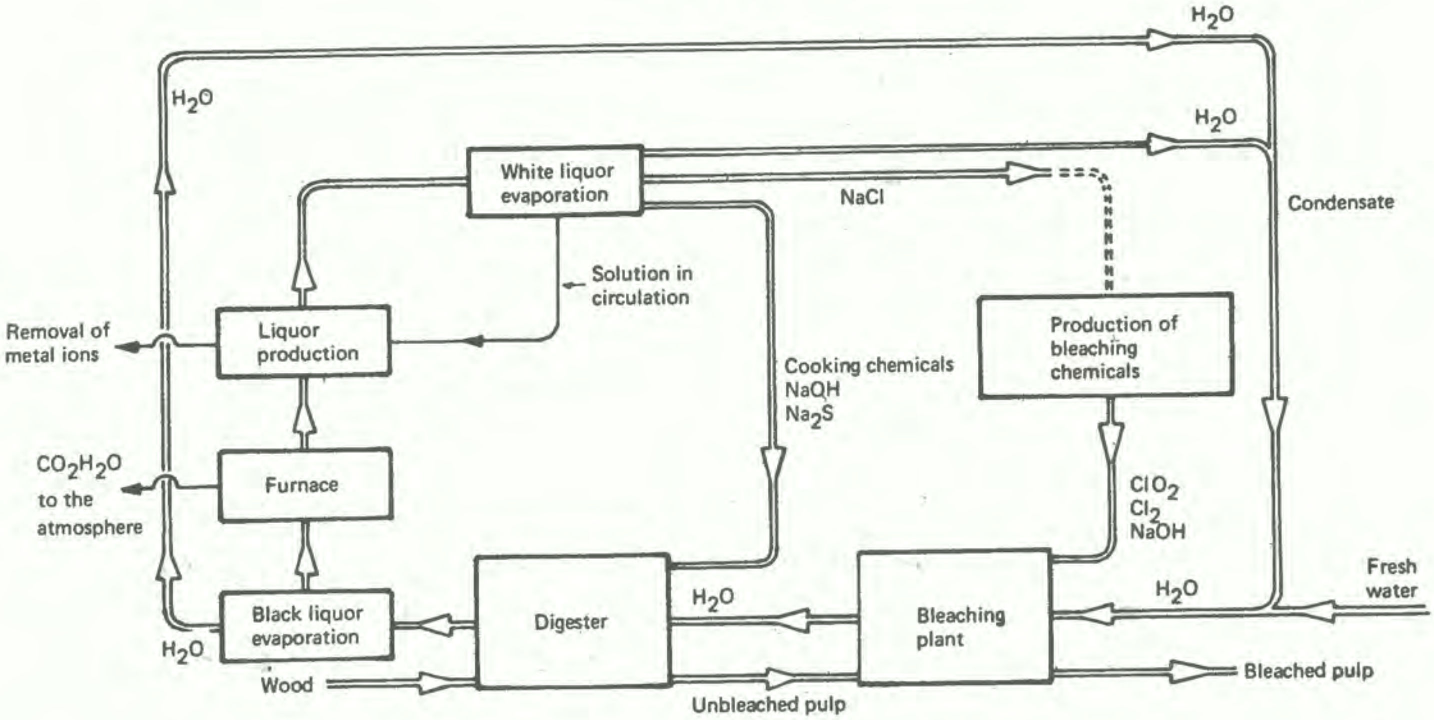


Figure 4.21. The closed mill concept

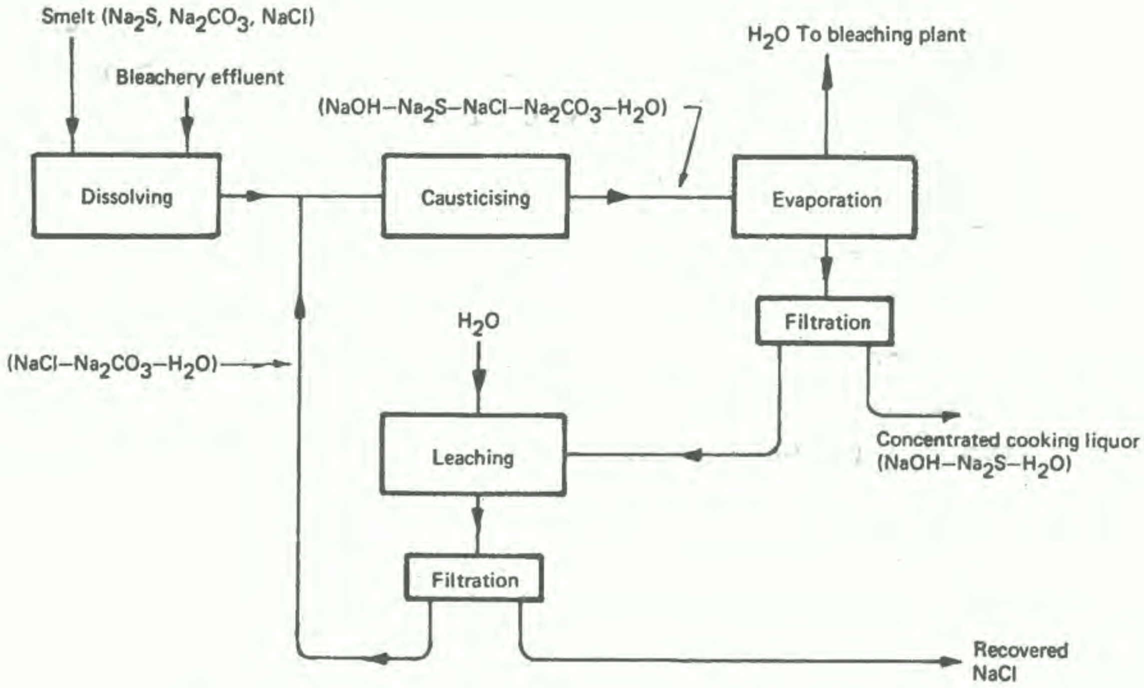


Figure 4.22. Sodium chloride recovery by evaporation of white liquor

The amount of chloride that can be expelled with this system has been calculated at about 50 kg of NaCl/t of pulp. This is only one third of the amount leaving a traditional bleaching plant. To reduce the chloride level Rapson proposes that the chlorine in the first bleaching stage be largely replaced with chlorine dioxide.

For this system to be introduced it would be necessary to close the bleaching plant and thus to modify the prebleaching. The investment cost for the sodium chloride recovery unit (white liquor evaporation, crystallizer, filter) is estimated at USD 1.25 million and for the increase in the evaporator capacity, at USD 0.6 million, calculated for a 300 t/d mill. Assuming a 10 % interest rate and a 10 year depreciation period the cost would be about USD 3.00/t of pulp.

In addition there are the expenses for closing the bleaching department and for the increase in the amount of chlorine dioxide. On the credit side there is the reduction in the cost of process water treatment and the elimination of costs for external treatment of the effluent.

Literature reference list, chapter 4

(1) Andersson L.G., Broddevall B., Lindberg S. and Phillips, J.:
Tappi 57 (1974) 4, 102

(2) Reeve D. and Rapson W.H:
Pulp and Paper Mag of Canada 75 (1970) 13, 48

(3) SSVL: Oxygen bleaching of sulphate pulp (in Swedish), Stockholm 1977

(4) The SSVL Environmental Care Project. Brolins Offset, Stockholm 1974

(5) SSVL: Klorid i återvinningssystem (in Swedish), Stockholm 1977

(6) Anonymus: Great Lakes Paper launches first closed cycle kraft pulp mill. PTJ 1977, March 15, 29-34

5. SPENT LIQUOR EVAPORATION

5.1 Evaporation principles

The standard method of concentrating the spent black liquor is by heating it to such a temperature that the water is evaporated. The function of evaporators is to concentrate the black liquor obtained from the pulp washing system to such a dry solids content that, when sprayed into a recovery furnace, it will ignite and continue to burn the organic matter it contains.

The black liquor from the washing plant has a concentration of 10-20 % dry solids and the evaporation is carried out up to a dry solids content of 55-65 %.

Two different methods, indirect evaporation and direct evaporation, are used. The first one is based on indirect evaporation of the liquor with steam in a multiple-effect evaporator from thin to thick liquor. In the other one the final part of the evaporation is carried out by direct contact evaporation with flue gases from the recovery furnace.

5.1.1 Indirect evaporation

A multiple-effect evaporation plant is a series of evaporators arranged so that the vapour generated from one evaporator body becomes the steam supply to the next evaporator in the series. The main advantage of the multiple-effect system is the efficiency with which it utilizes the steam. A five-effect evaporator station will remove between 4 and 4.5 tonnes of water per tonne of steam.

A typical system used in Scandinavian sulphate mills (with softwood as raw material) is shown in Figure 5.1. It is based on the use of five Kestner long-tube vertical evaporators. The units are numbered according to the direction of the steam, No 1 being where live steam is supplied. The steam from one stage is used as a source of heat in the next stage. The steam from the last stage is run to a surface condenser, where the liquor steam heat is used to produce hot water. To help in keeping the vacuum a vacuum pump or a steam ejector is connected after the surface condenser. The liquor is usually passed through the evaporators in the order 3-4-5-1-2.

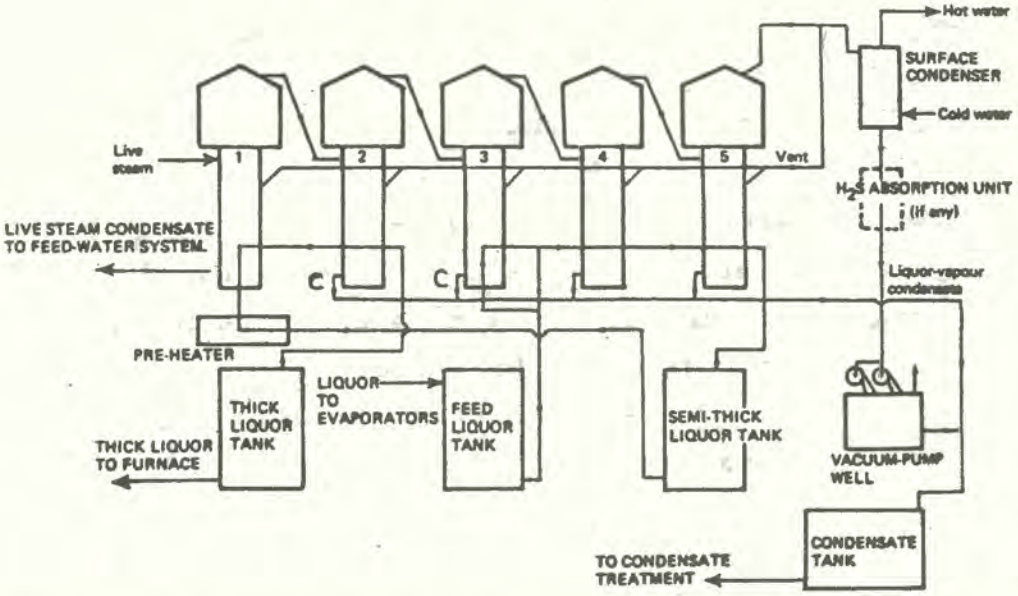


Figure 5.1. Black liquor evaporation in Scandinavian kraft mills (the condensate segregation not shown)

The condensate of the live steam from stage 1 is clean and can be used directly as boiler feed water, but steam condensates from the other stages and the condensate from the surface condenser are contaminated with methanol and sulphur compounds. The methanol raises the oxygen consumption of the condensate and the sulphur compounds impart an offensive smell. The condensate also may contain small amounts of black liquor.

A description of a 5-effect evaporation plant for liquor from non-wood pulping is given in Appendix 2.

Heat-transfer in an indirect evaporation effect is expressed by the fundamental equation:

$$Q = K \cdot A \cdot t$$

where Q = the rate of heat transfer (kW/h)

K = the overall coefficient of heat transfer (kW/m^2 h K)

A = the area of heating surface (m^2)

t = the total temperature drops across the heating surface (i.e, the temperature difference between the saturated steam and the liquor) (°K)

The higher the viscosity and the lower the rate of circulation, the lower is the rate of heat transfer in the evaporator.

The long-tube raising-film evaporator, type Kestner (Figure 5.2), is the predominant evaporator type for black liquor. It operates on the principle of evaporating from a film of liquor passing over the heating surface. The fundamental principle involved is the elimination, as far as practicable, of the hydrostatic head on the heating surface. In actual practice this is never completely accomplished, because some pressure drop is required to circulate the liquor and vapour but most of the rise in boiling point due to the hydrostatic head which occurs in other types of evaporators is eliminated. Consequently the lower average boiling point in each effect results in a higher working temperature drop, and higher evaporative capacity per square meter of heating surface is obtained than in submerged-tube-type evaporators. Another important factor promoting the higher capacity is the high vapour velocity caused by the enormous increase in vapour volume as the liquor starts boiling in the tubes. The tubes are typically 30-50 mm in diameter and 7-9 m long.

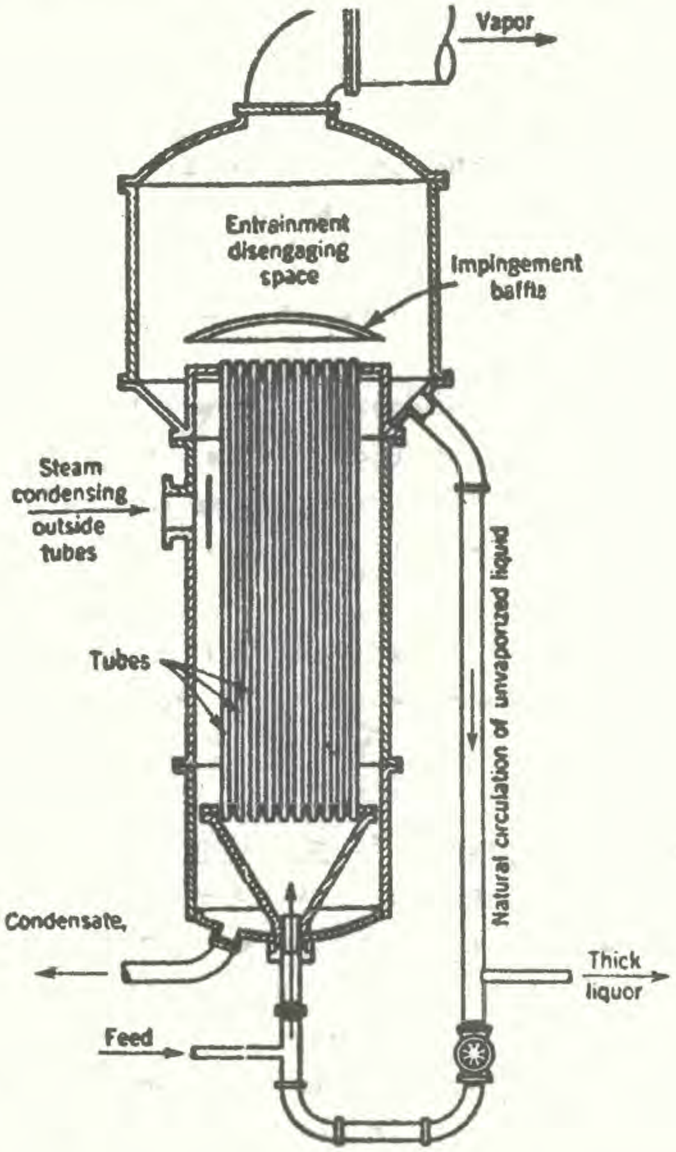


Figure 5.2. Cut-away view of long-tube evaporator body

The price for a 5-effect evaporation plant for 50 tonnes/h evaporated water is 2-2.5 million USD excluding building and instrumentation costs.

Forced circulation (Figure 5.3) is used especially when the scaling problems are severe, e.g. at black liquor concentration of 45-65 % dry solids. In such an apparatus the liquor is circulated through a vertical tube evaporator by a pump.

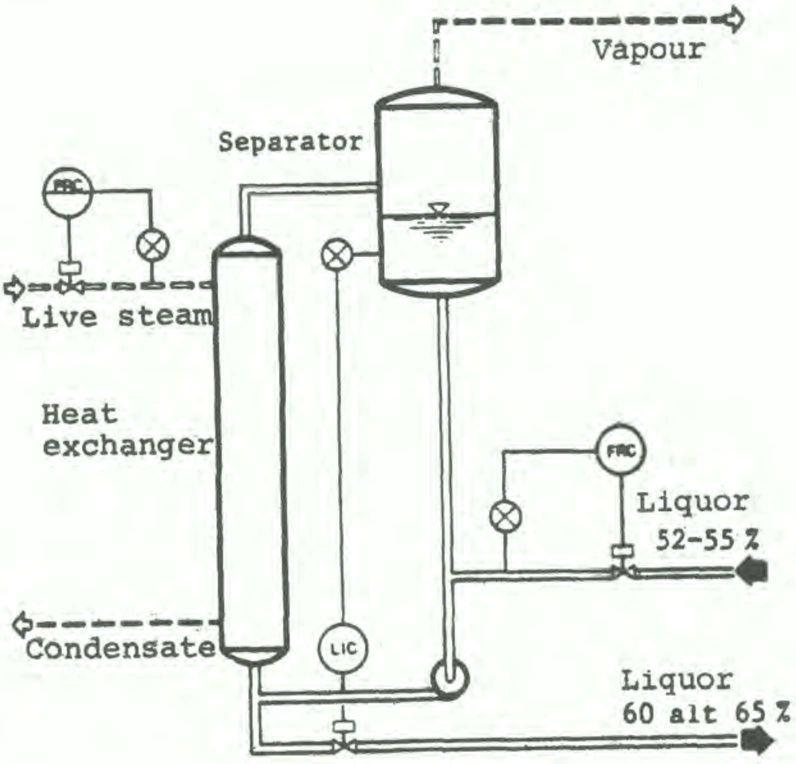


Figure 5.3. Forced circulation evaporator (Rosenblad)

Appendix 1 gives a technical description of an evaporation plant of the raising film type.

In falling-film evaporators (Figure 5.4) the liquid enters at the top, flows downward inside the heated tubes as a film, and leaves from the bottom. The bodies are large, 2 to 10 m in diameter. Vapour evolved from the liquor is usually carried downward with the liquor, and leaves from the bottom of the unit. In appearance these evaporators resemble long vertical tubular exchangers with a liquid-vapour separator at the bottom and a distributor for the liquor at the top.

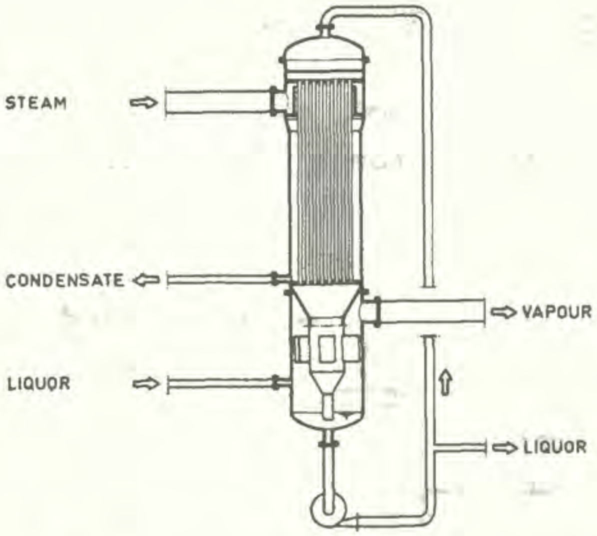


Figure 5.4. Falling-film type evaporator

In the short-tube evaporator (Figure 5.5) the tubes are "short", 1.2-2.5 m, and fairly wide, 5 to 100 mm in diameter. In the short-tube vertical evaporator the steam condenses outside the tubes. The tube bundle contains a

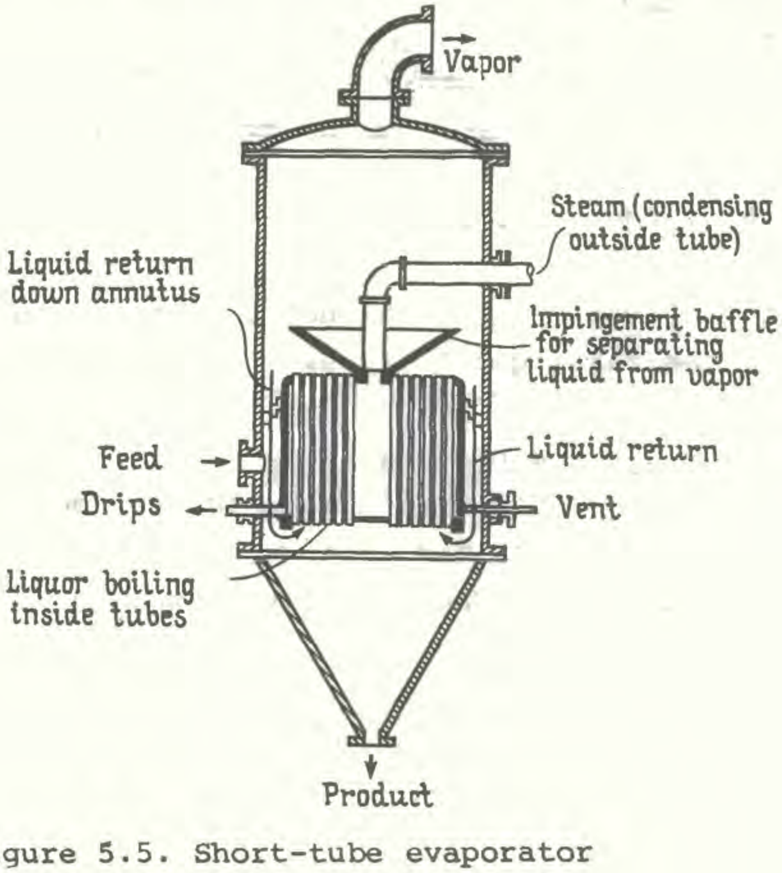


Figure 5.5. Short-tube evaporator

large central downcomer, the cross-sectional area of which is 25 to 40 % of the total cross-sectional area of the body. Most of the boiling takes place in the smaller tubes, so that the liquid rises through these tubes and returns through the downcomer. Drops of liquid fall through the vapour in the tall space above the tubes, with their removal from the vapour often assisted by baffle plates over the vapour outlet. Thick liquor is withdrawn from the bottom of the shell. In this evaporator the driving force for flow of liquid through the tube is the difference in density between the liquid in the downcomer and the mixture of liquid and vapour in the tubes.

In the Lockman multiflash evaporator the effects are built one above the other and the evaporator has the form of a distillation column and thus requires only a small floor space (18). It is used mostly for pre evaporation of sulphite and sulphate pulp liquors and is especially suited for increasing the evaporation capacity of already existing evaporation plants. It is easy to operate and the capacity can be doubled, simply by adding more effects at the top of the evaporator column.

5.1.2 Direct evaporation

The first part of the liquor evaporation up to 40-55 % dry solids is done in a multiple-effect evaporator and then direct-contact evaporation is used to further concentrate the black liquor. Flue gases from the recovery boiler are brought into contact with the liquor, resulting in a transfer of water from the black liquor to the gas and a reduction of the gas temperature.

Three types of equipment are used: cascade evaporator, cyclone evaporator and venturi scrubber.

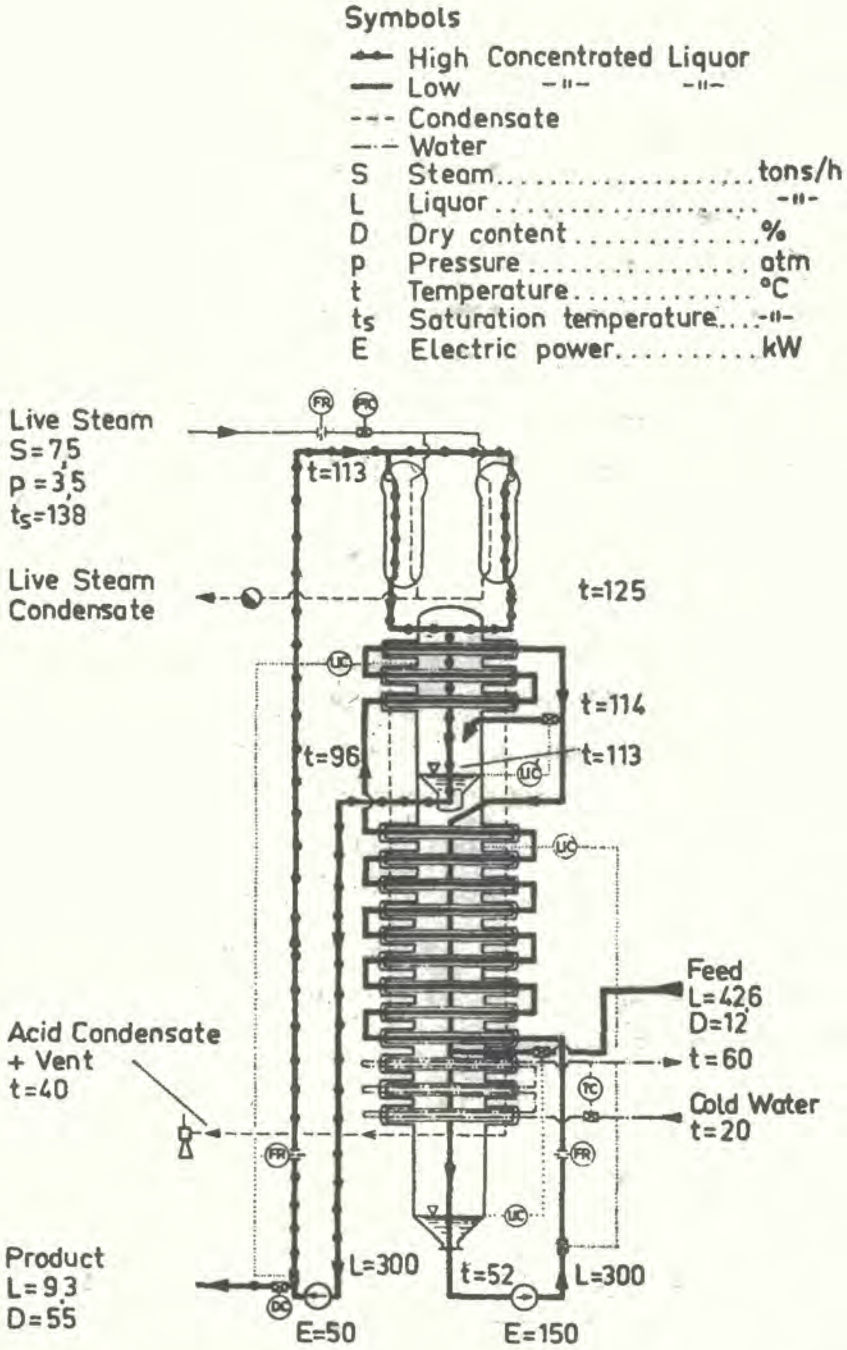


Figure 5.6. Lockman evaporator at Grycksbo sulphite mill (Stora Kopparberg-Bergvik) in Sweden

In the <u>cascade evaporator</u> (<u>Figure 5.7</u>) the black liquor i picked up on dishes or steel tubes and rotated through th stream of hot flue gas to evaporate moisture; then the thickened black liquor is removed by allowing the tubes t pass through the liquor held in the lower half of the evaporator, called the tank. By continuously recycling, the liquor in the tank is thickened and finally attains the uniform concentration suitable for burning in the furnace.

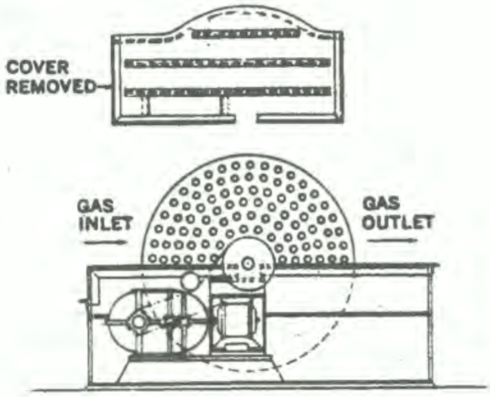


Figure 5.7. Cascade evaporator

The cyclone evaporator (Figure 5.8) is a vertical, cylindrical vessel with a conical bottom. Flue gas is admitted to the evaporator through a tangential inlet near the bottom. The velocity of its tangential entry causes the gas to take a whirling, helical path to the top of the cyclone, from which it leaves through a concentric outlet. Liquor to be evaporated is sprayed across the gas inlet. The liquor droplets mix intimately with the gas and are then thrown by centrifugal force to the cylinder wall. Recirculated liquor flowing down the wall of the cylinder carries the droplets and any dust thrown from the gas to the conical bottom, out through the drain, and into an integral sump. The interior walls are kept continuously wet to prevent localized drying on the wall surfaces.

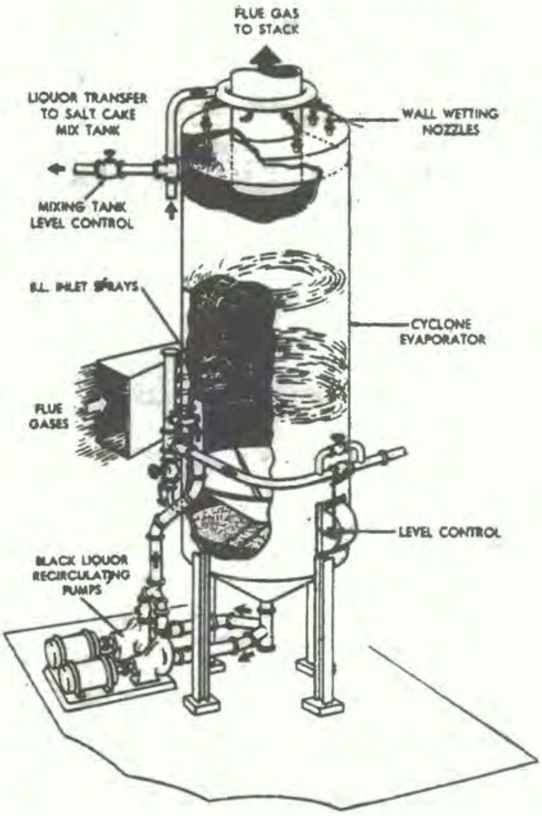


Figure 5.8. Cyclone evaporator

The venturi evaporator-scrubber (Figure 5.9) is a device designed to perform the functions of both a direct-contact evaporator and a fume collector. The scrubber operates on the principle of using the energy of the flue gas, accelerated in a venturi throat, to atomize streams of liquor injected at right angles into the high-velocity gas. The high relative velocity of the gas and fume with respect to the liquor results in an intense scrubbing action which causes the fume particles in the gas to adhere to the liquor droplets. At the same time, the heat of the flue gas is used for evaporation of water from the liquor, and the gas leaving the venturi is cooled to a value approaching the saturation temperature of about 80°C. The mixture of cooled flue gas and evaporator black-liquor droplets containing the recovered fume then goes to a cyclone separator, where the liquor droplets are separated from the flue gas.

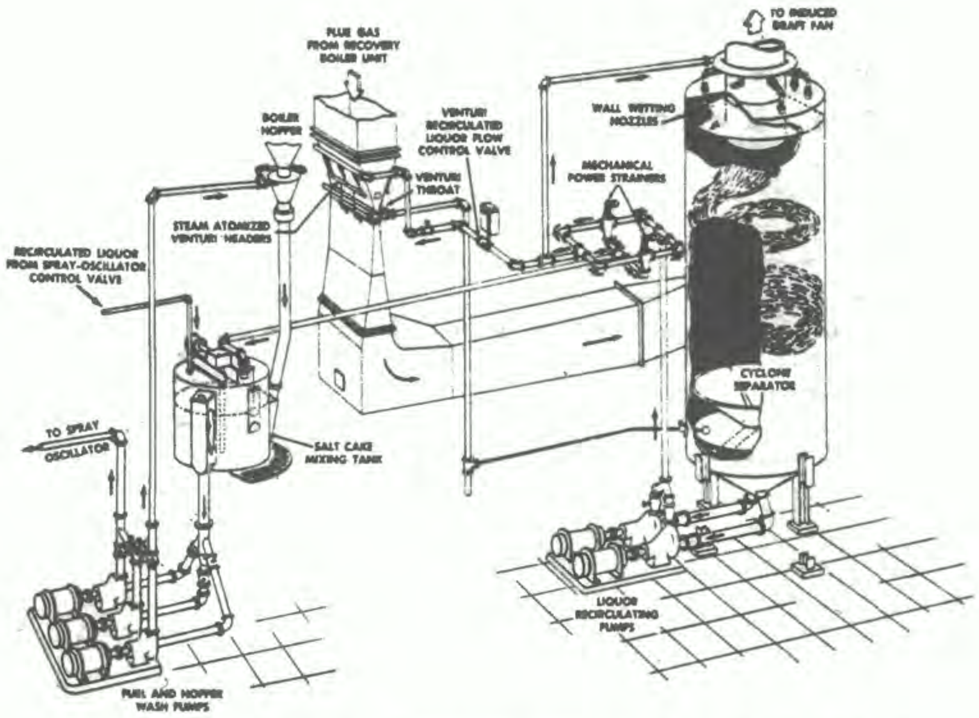


Figure 5.9. Venturi evaporator-scrubber

Because the flue gas temperature leaving the venturi is approximately 70°C lower than the usual 150°C leaving a direct-contact evaporator and entering a precipitator, more heat is available for evaporation and it is possible to lower the entering concentration of liquor while keeping the firing concentration at its usual value. Fume collection efficiencies of 90 to 95 % are continuously maintained.

5.2 Liquor composition and properties

The composition and physical properties of the black liquor depend on

- the composition of the raw material
- the yield of the pulp
- the cooking process applied
- the charge of chemicals
- the cooking time and temperature

The composition of the raw material is important for the evaporation and chemical recovery procedures. In Table 5.1 the size of fibres, content of lignin, pentosan, alpha-cellulose and ash and silica contents are listed.

Table 5.1. Composition of fibrous raw materials (8, 10, 16, 17)

Raw material	Size of fibres (averages) Length mm	Diameter um	Lignin-content	Pentosans	Alpha cellulose	Ash content	SiO_2
			%	%	%	%	%
Bagasse (depithed)	1,7	20	18-22	27-31	30-40	1-3	0,8-2
Cereal straw	1,5	13	16	25-28	35	6-9	4-6
Rice straw	1,5	9	12	25	30-35	16-20	10-13
Bamboo (Indian)	2,7	14	20-30	16-20	35-40	2-5	1-3
Reeds			18-22	28-32	35	3-6	2-4
Softwoods (Scandinavian)	3-5	36	28	10-15	40-45	0.1-0.3	0.01
Hardwoods	1,3	29	20-25	18-25	40-45	0.1-0.3	0.01

At a small mean fibre size the solids content in the black liquor from the washing is generally lower than for large fibres (higher dilution factor) and the risk for fibres following the liquor to the evaporation plant increases. High lignin content gives a higher heat value of the black liquor. An increasing pentosan content will increase the viscosity of the black liquor. High silica content is troublesome because of severe scaling problems caused by the silica.

The liquor viscosity depends primarily upon the liquor consistency but also on wood species, pulping process (kraft, soda), pulp yield, alkali content and liquor storage time.

5.2.1 Liquor from wood based mills

The composition of black liquor varies considerably between different mills. A composition of pine sulphate black liquor is shown in Table 5.2.

Table 5.2. Composition of kraft black liquor from pine (10)

	% of total solids
Alkali lignin	41
Extractives	3
Hydroxy acids and lactones	28
Acetates	5
Forminates	3
Methanol	1
Sulphur	3
Sodium	16
Total	100

The greater part of the organic matter removed from the wood during the cooking process is combined chemically with sodium, forming salts of resinous acid and other organic acids. Some resin soap compounds account for the intense foaming properties of the liquor.

Most of the sodium in black liquor is present as organic sodium compounds (50-60 %), sodium carbonate (15-20 %) and sodium hydroxide (15-20 %). The rest is present as sodium sulphide (about 4 %) and sodium sulphate (about 6 %).

Tropical hardwoods are often rich in silica rendering the black liquor also rich in silica, which causes serious problems in the evaporation plant (see paragraph 5.3.2).

Traces of other substances are also present in the black liquor, such as iron oxides, alumina and sodium chloride.

The physical properties of black liquors are much the same from the soda as from the sulphate process. The relationship between viscosity, temperature and concentration for Scandinavian black liquor from pulping of pine is shown in Figure 5.10. The viscosity increases with the concentration and decreases with increasing temperature.

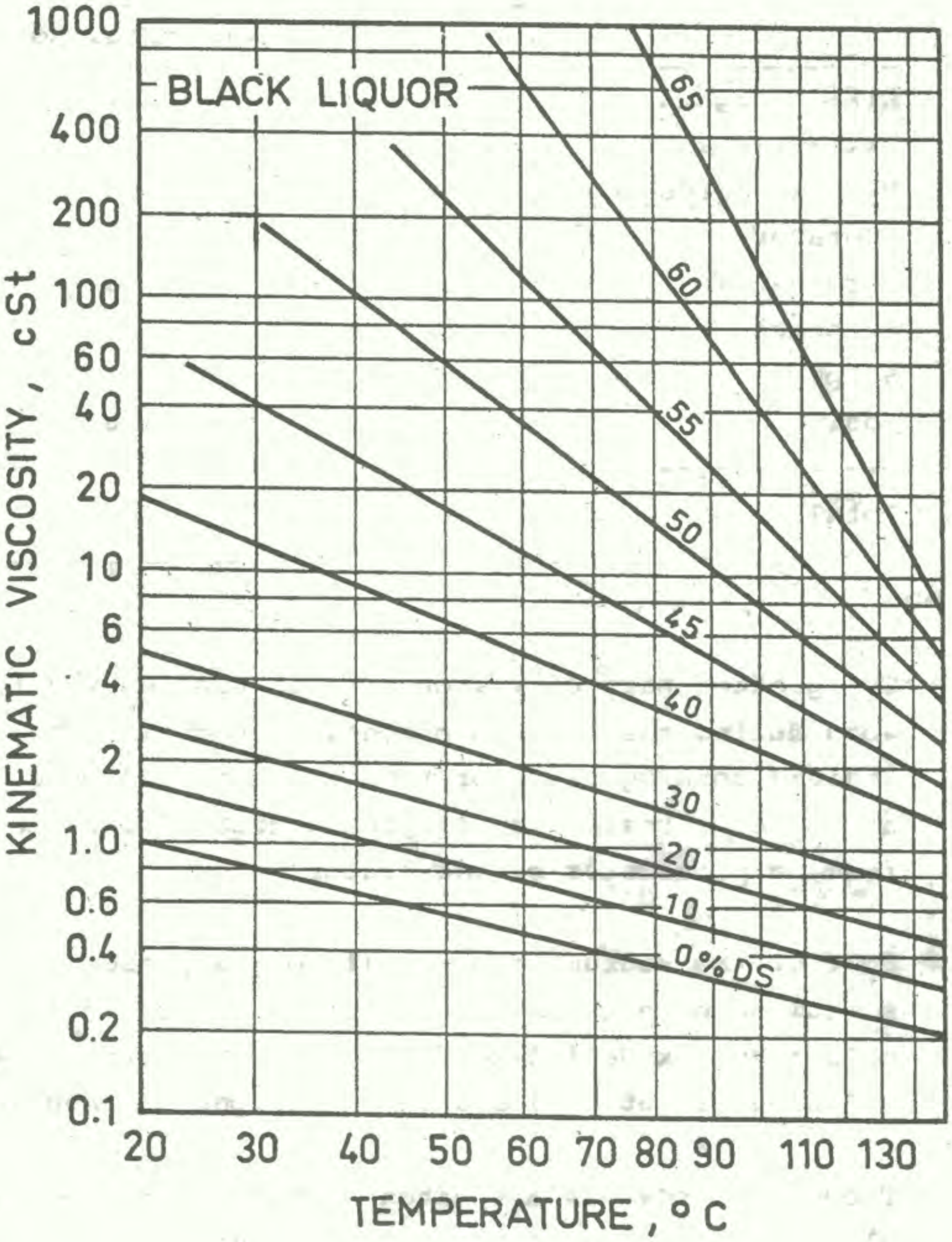


Figure 5.10. Viscosity of Scandinavian pine kraft black liquor (8)

Black liquor from hardwood pulping has a higher viscosity than that from softwood. Especially for eucalyptus black liquor the viscosity increases rapidly with increasing concentration (see Figure 5.11).

5.2.2 Liquor from pulping of non-wood fibrous materials

The composition of some black liquors from non-wood pulping is given in Tables 5.3 and 5.4.

Table 5.3. Composition of non-wood black liquors

Reference		5	11	12	8
Raw material		Bamboo (kraft)	Bamboo (kraft)	Bagasse (soda)	Wheat straw (soda)
Total solids	g/l	206	145	-	-
Total solids	%	18.8	-	8.13	13.6
Total alkali as Na_2O	g/l	49	34.7	-	24.96
Free alkali as Na_2O	g/l	8.4	7.4	1.16	2.56
Total sulphur as S	g/l	6.0	-	-	1.78
Silica as SiO_2	g/l	8.0	5.65	-	-
Silica in the solids as SiO_2	%	-	-	1.2	-
Ash content in solids	%	48	-	38.7	36.98
Calorific value of black liquor solids	cal/g	3340	3200	-	-
Sodium carbonate as Na_2O	g/l	-	-	7.24	-
Sodium sulphide as Na_2O	g/l	-	-	1.7	-

Non-wood liquor has, compared to wood black liquor, usually a lower lignin and soap content. The inorganic compounds are similar to those of wood black liquor. The silica content in non-wood black liquor is usually high, originating mostly from the raw material used but also from the lime used for causticizing (15).

Table 5.4. Analysis of black liquors (6)

Species	pH$^{a)}$	Organic. Inorganic	Lignin		Carbo-hydrates		Silica	
			(b)	(c)	(b)	(c)	(b)	(c)
Bamboo	12.2	57:43	37.0	24.7	48.5	32.3	7.3	4.9
Bagasse (kraft)	11.2	66:34	35.0	23.4	63.5	42.7	6.9	4.7
Bagasse (soda)	11.8	59:41	30.4	20.2	58.4	38.8	3.6	2.4
Eucalyptus (prehydrolysis kraft)	11.9	70.30	65.5	43.6	40.0	26.6	1.0	0.6
Eucalyptus, pine, salai (75:15:10)	11.4	61:39	57.4	38.1	34.4	22.9	1.2	0.8

a) Weak black liquor 15 %, 30°C
b) Concentration, g/l
c) % black liquor solids

The concentration of silica in some analysed non-wood black liquor solids is given in Table 5.5. A silica content of 2-5 % is very common in black liquor from non-wood pulping. For rice straw the silica content is extremely high, 16-30 % (8). Because of that only part of the lime mud is reburned. If all the lime mud were to be reburned the silica content in the recovery system would reach an unacceptable level.

Table 5.5. Concentration of silica in spent black liquors (8, 10, 16) as percentage of total dry solids

	%
Rice straw	16-30
Cereal straw	3-6
Reeds	2-6
Bamboo	2-5
Bagasse	1-3
Softwoods	0.01
Eucalyptus	0.01-0.8

The physical properties of non-wood black liquors differ in some ways from wood black liquors. It is not as foamy and the viscosity is usually higher due to the high amount of pentosans in the raw materials used. Figure 5.11 shows the viscosity of black liquors at 90°C from pine, eucalyptus, bamboo, bagasse and straw.

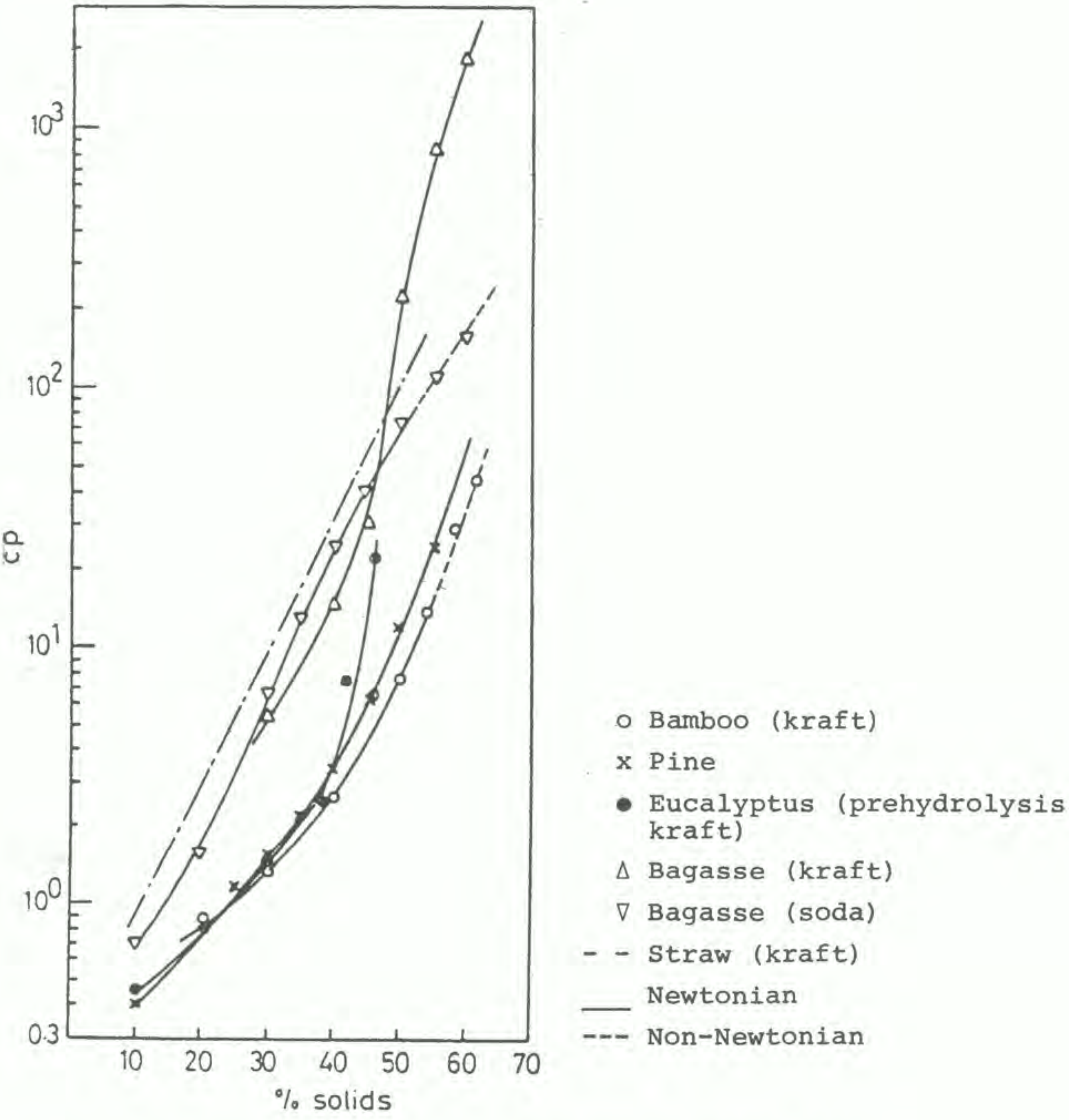


Figure 5.11. Viscosity of black liquors at 90°C (4)

The concentration of the weak black liquors from non-wood pulping is usually lower than that from pulping of wood. Reported concentrations of black liquors from existing bagasse mills are in the range of 8-12 %. From straw mills the figures are somewhat higher, 10-14 %. Bamboo weak black liquor usually has a concentration between 15 and 18 %, i.e. comparable to weak wood black liquor.

5.3 Specific problems

For wood black liquors the evaporation is a well known technique and usually does not create any operating problems. For non-wood black liquors, however, the evaporation is troublesome, due to high viscosity and high silica content.

5.3.1 Viscosity

The viscosities of some non-wood black liquors are shown ir Figure 5.11 and discussed in paragraph 5.2.2.

An efficient method in reducing the problems of both viscosity and scaling is to keep the concentration of free alkali in the black liquor above a certain level.

Operating experience has shown that the optimum concentration of free alkali is 12-13 g/l NaOH in a weak black liquor with concentration of total solids of 13.5 % obtained from wheat straw pulping (8). Exceeding this figure is undesirable because it upsets the critical ratio between organic and inorganic content in the dry solids of black liquor for satisfactory combustion in the furnace.

Figure 5.12 shows the effect of free NaOH on wheat straw black liquor at 90°C and 60 % total solids concentration. Usually a free alkali content of 8-10 g/l NaOH in the weak liquor is sufficient to control the viscosity and the scaling problems.

A high alkali concentration in the weak black liquor can be maintained either by addition of white liquor or of fresh caustic liquor. In soda mills recycling of white liquor with 100 g/l NaOH to maintain free alkali 12-13 g/l in the weak black liquor will increase the evaporator feed-rate approximately 10 %. Consequently the evaporating system has to be enlarged. The amount of alkali that has to be added to the black liquor to reach a free alkali content of 12-13 g/l corresponds to the make up required for a soda mill with a total alkali recovery efficiency of about 80 % (8). If the recovery is better than 80 % there will be an alkali surplus in the mill and consequently the alkali level has to be maintained with white liquor.

5.3.2 Scaling

Scale formation results in reduced capacity of the evaporators and, in time, if not given proper attention, it may cause plugging of the tubes.

In order to minimize the risk of deposits a high causticizing efficiency and, for kraft liquors, a high degree of reduction in the recovery boiler must be maintained. If not, Na_2SO_4 and Na_2SO_3 might precipitate in the evaporator tubes, especially at high solids contents and high temperatures. The scale is generally easy to remove by washing with weak liquor or water.

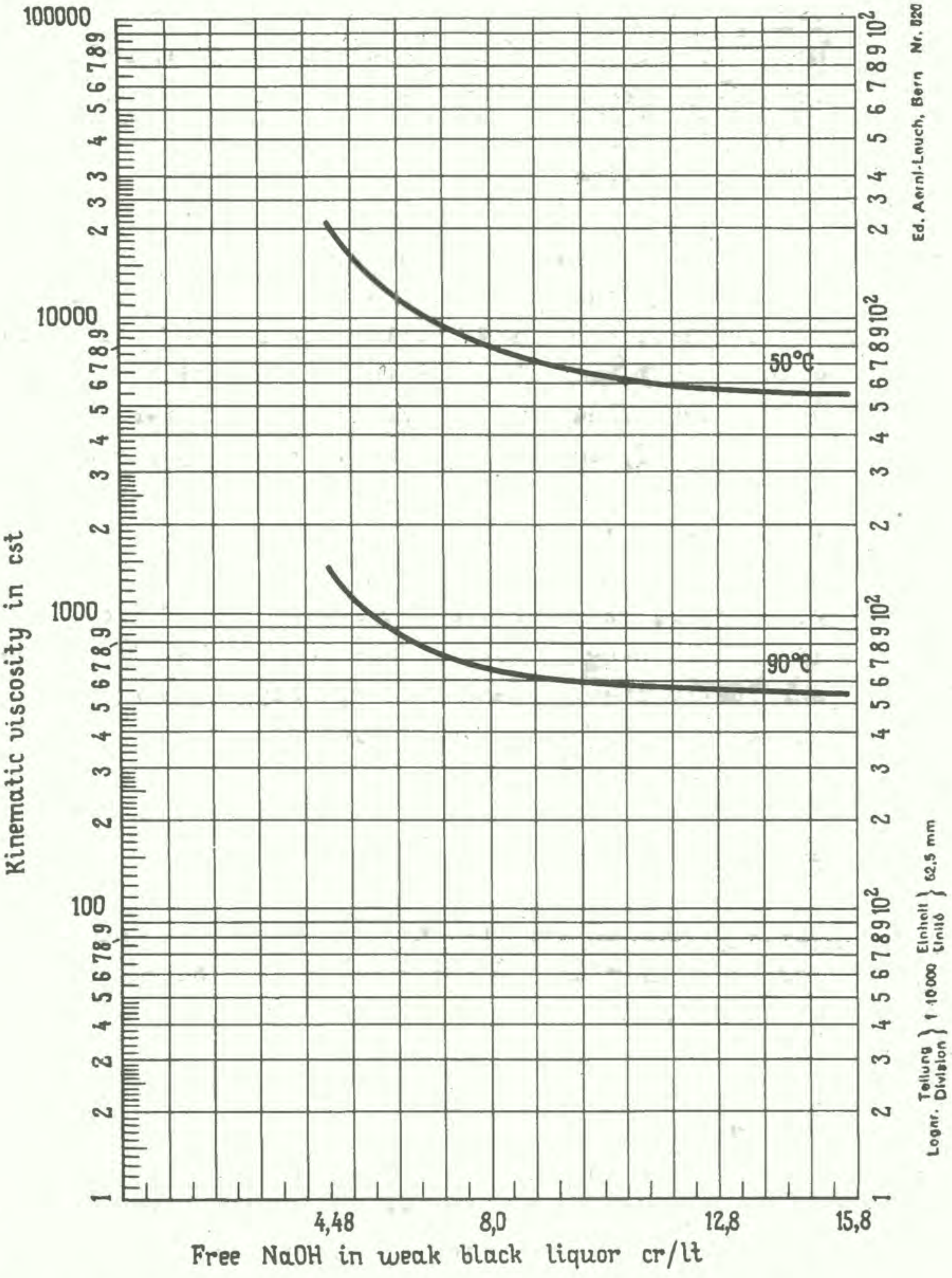


Figure 5.12. Effect of free NaOH in a wheat straw black liquor on viscosity at 60 % total solids and 50 and 90°C (8)

Incrustration of calcium compounds, precipitated because of inadequate clarification of the white liquor are difficult to remove. For these compounds treatment with chemicals is required, for example with hydrochloric acid (HCl) at 4 % concentration (12). Using acid for cleaning requires that the plant is made of stainless steel

Lignin may precipitate, for instance if the pH gets low as may happen if black liquor is mixed with liquor from semi-chemical pulping (cross recovery).

Fibres in the liquor can also form deposits. A filter should be installed if required for the black liquor entering the evaporation plant. A fibre content of 20 mg/l on an 80 mesh screen is an acceptable upper limit. Non-wood black liquors, due to the inherent amount of short fibres in non-woods, contain more fines and the fibre content recommended may be difficult to reach. 50-100 mg/l is not uncommon in such liquors (12, 3).

The main problem with non-wood black liquors is the formation of silica scales. Hard scale deposits form inside the tubes of the evaporator units, especially when the liquor consistency reaches above 30 % solids.

With increasing concentration of the liquor the solubility limit of silica is reached (around 30-40 % liquor solids (15) for many non-wood black liquors) and it precipitates from the liquor. According to scale analyses in different effects in one bagasse liquor evaporation plant (12), the organic matter deposits in the first bodies in contact with the weak black liquor, the calcium carbonate scale deposits in the middle of the evaporation plant and the silica precipitates in the last bodies of the plant.

The following precautions are recommended to decrease formation of silica scales in the evaporation plant:

- High caustic content in weak black liquor
- Maintain the temperature conditions in the plant and the viscosity of the black liquor as constant as possible
- Minimize storage time of black liquor to avoid precipitation of silica compounds
- Washing of the chips to reduce the input of silica is recommended
- As explained later (paragraph 7.5.10) it may be necessary to discharge a certain amount of the lime mud in order to avoid a cumulative effect of silica in the recovery system

Some methods in use for cleaning evaporation plants in pulp mills are listed in Table 5.6. Mills which are cooking wood with low silica content normally use washing with water followed by treatment with 10 % H_2SO_4 + inhibitor or 15 % HNO_3. In case of abnormal scaling problems, treatment with sulfamic acid + inhibitor + hydrofluoric acid can be used. Intermittent use of steam and cold water is useful to crack the scale deposit making it better available for subsequent chemical treatment. In mills which use raw material with very high silica content, the scaling problems are of such an order that mechanical drilling is used regularly. The time between each complete cleaning operation varies between one and two months.

Scale reducing chemical additives can be added to the thin black liquor. Normally these agents do not solve the problems but do slow them down. The way to decrease the scale forming tendency is to keep the ions of silica, alumina, carbonate, sulphate and other "dangerous" ions at such levels that the solubility limits for the scale forming compounds are not exceeded.

Table 5.6. Methods used for cleaning of evaporation units

A. Swedish mills cooking softwoods

A1: Periodical washing with cold water in a hot unit to achieve cracking of already formed scales

A2: Periodical cleaning with:

a) high pressure water
b) water
c) 10 % H_2SO_4 + inhibitor at 80°C

If organic material is involved 15 % HNO_3 at 80°C is recommended instead of H_2SO_4.

For units of mild steel 3 % sulfamic acid + inhibitor is used.

B. Indian mill cooking bamboo or pinewood

Mechanical cleaning once a month of first and second effects. The other three effects are cleaned once a year.

C. Mill cooking 80 % bamboo + 20 % mixed hardwood

The thick liquor body is cleaned every day by water boil out (2 hrs). The spare body is cleaned between cycles (each cycle of 15 days). The whole evaporation plant is cleaned and mechanically drilled every 50 days, total shut down 48-72 hrs).

D. Mill cooking wheat straw and bagasse

Boiling with water 2-3 times a week
Boiling with caustic 4-6 hrs a week
Shut down for general cleaning every third week

Deposits on the steam side of the tubes occur on carbon steel tubes by rust and scale. Such problems are avoided by using stainless steel tubes in the plant.

5.4 Air pollution

The odorous gases at kraft mills are chiefly hydrogen sulphide (H_2S), methyl mercaptan (CH_3SH) and organic sulphides. These are dissolved in the black liquor and to some extent flashes to the condensates or to the vents.

Soda mills without lime reburning have very little sulphur in the chemical recovery system and consequently odour problems do not occur. However, in soda mills where lime burning is practised sulphur enters the system through the oil fired lime kiln. If the discharges to air and water are low, the system will soon reach such a sulphur level that odour problems occur, comparable to those in kraft mills (2).

5.4.1 Discharges from indirect evaporation

The amount of odorous gases emitted from the evaporation plant is 0.1-1 kg S per ton of pulp (14). The gases from a multiple-effect evaporator have to be collected and destroyed in a suitable way. This technique will be discussed in paragraph 5.6.

5.4.2 Discharges from direct evaporation

When the flue gas from the recovery boiler passes over the unoxidized kraft black liquor in a direct-contact evaporator, malodorous gases are emitted due to the following reactions.

$2\ NaHS + SO_2 + H_2O \rightarrow Na_2SO_4 + H_2S$

$Na_2S + SO_2 + H_2O \rightarrow Na_2SO_4 + H_2S$

As a result, the concentration of total reduced sulphur (TRS) compounds could be in the range of 80-500 ppm (17). This TRS emission is unacceptable from an environmental point of view. If a black liquor oxidation system with an efficiency of 98-99 % is installed the concentration of TRS compounds can be reduced to 5-10 ppm (17). Another way to reduce the TRS emission is to replace the direct contact evaporator with added multiple-effect capacity.

Black liquor oxidation: Black liquor can be treated with oxygen or air to convert the sodium sulphide to sodium thiosulphate and reduce the release of hydrogen sulphide and mercaptans. For wood liquors containing a lot of soap, the oxidation must be carried out after the multiple-effect evaporator where the soap is skimmed off; thus foaming is avoided.

In one US mill (9) black liquor oxidation is carried out in a two-stage system (Figure 5.13). Approximately 85 % oxidation efficiency is achieved in the first stage and after the second stage the efficiency is more than 99.5 %. The average TRS emission from the recovery unit after an evaporative scrubber was 2.3 ppm as H_2S, over a six month period.

Black liquor in the direct-contact evaporator serves as an absorber of both sulphur dioxide and sodium sulphate. Particulate emissions from a furnace firing oxidized or unoxidized liquor appear to be similar. Cascade and cyclone evaporators can be expected to remove about 15 % of the dust before it reaches an electrostatic precipitator (17). Evaporative scrubbers have been reported to reduce sulphur dioxide emission by 50-80 % and dust emission by 15-25 % (9).

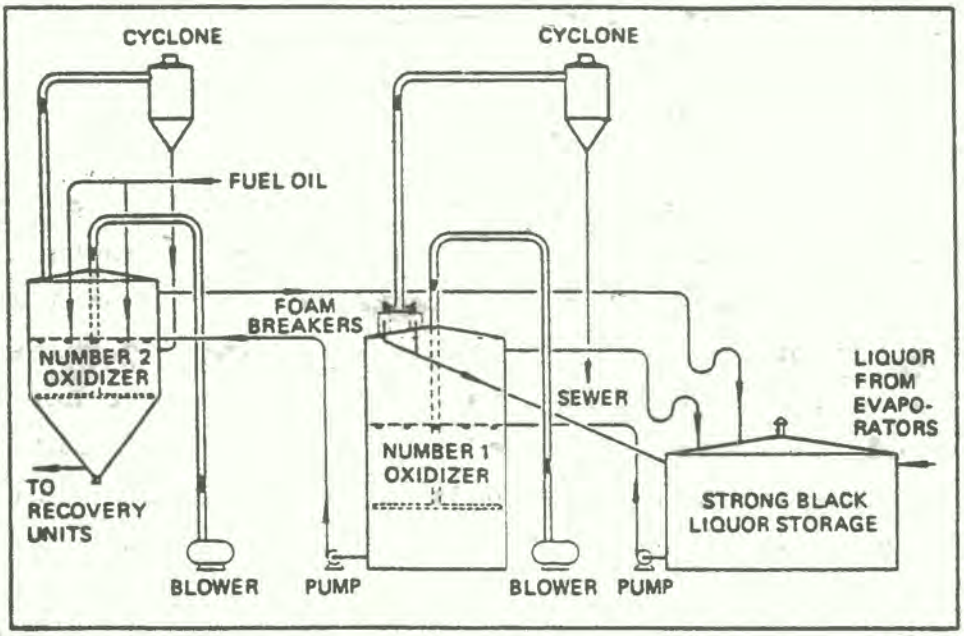


Figure 5.13. Decrease in black liquor heat value on oxidation to 0.2 g/l of residual Na_2S (as sodium) (17).

The black liquor oxidation is an exothermic reaction and the heating value of the liquor is decreased as a function of the amount of sodium sulphide in the liquor and the extent of oxidation (Figure 5.12). The oxidation also means an increase in solids weight. This addition of inorganic solids has no heating value but carries more water to the recovery boiler. For a normal kraft black liquor (containing 32 g/l sodium sulphide) the steam production in the recovery unit will be reduced by about 9 % when the heating value is corrected for both the exothermic reaction and the increase in solids (17).

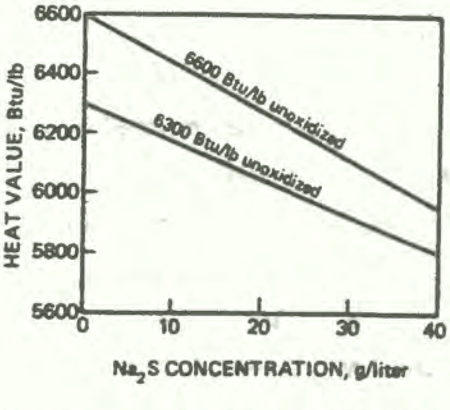


Figure 5.14. Decrease in black liquor heat value on oxidation to 0.2 g/l of residual Na_2S (as sodium) (17)

5.5 Water pollution

The water pollution from an evaporation plant originates from the liquor condensate. The condensate from all the stages but stage one, which is the live steam condensate, are more or less heavily contaminated with methanol, sulphur compounds and sometimes also black liquor. The methanol raises the oxygen consumption of the condensate and the sulphur compounds impart an offensive smell. Under certain conditions small amounts of black liquor are carried over as droplets from the stage before.

Occasional water pollution is caused at the cleaning of the evaporation effects either by washing or by mechanical treatment.

The amount of oxygen consuming substances (BOD) in the condensate depends on the raw material for pulping, and on the digesting equipment. In a mill with batch digesters the BOD of the condensate is lower than in a mill with a continuous digester. However, the total amount of BOD in the digester condensate and the evaporation condensate is approximately the same for the two cooking techniques.

Water pollution from a new evaporation plant can be greatly reduced if proper consideration is given to the following:

- The liquor quality which is influenced by the raw material
- Scaling and scale removal methods
- Carry over of solids in separators
- Instrumentation and control equipment
- Separation of condensates from different parts of the plant

5.5.1 Carry over of solids in separators

Carry over of black liquor solids markedly increases the BOD and COD of the condensates. To keep a low level of carry over the expansion vessels have to be suitably large and preferably equipped with cyclones in the separators. A further improvement is the installation of a secondary profile seprator (Euroform), which may be inserted in the separator in the steam line. The liquor removal efficiency of such equipment is usually about 90 %. A profile separator is more efficient, especially on small drops, than a cyclone separator or a mesh demister. The pressure drop of a mesh demister may be rather high because of its tendency to clog.

The separator of the first stage in an evaporation plant has, on average, twice as much carry over of liquor as the sum of all the other stages. It is therefore especially important to arrange the equipment well in this stage. An example on the installation of drop removal equipment in the last stage of an existing five stage evaporation plant is shown in Table 5.7. Comparison is done between a demister, a low efficiency and a high efficiency profile separator. When installing a new evaporator plant it is important to specify a low (100 t/t_{90}) carry over of black liquor.

5.5.2 Control equipment

The purpose of instruments and control equipment is to promote the optimal utilization of the capacity and to avoid operational disturbances.

To avoid water pollution when disturbances occur, conductivity meters should be provided in the condensate output lines. The instruments should be equipped with automatic switches for the condensate, switching it to a collecting vessel if the conductivity gets high.

Some interlocking connections are used to prevent damage to the plant. For instance to avoid dry cooking in the thick liquor apparatuses the live steam valve should close automatically if the liquor feed pumps stop working.

Table 5.7. Implications of inserting a demister after the last stage of a 5-effect evaporating plant with a capacity of 8 t/t of pulp

Mill capacity	t/d	300
Assumed conditions		
Evaporating capacity	t/h	100
Before demister		
Solids loss	g/t evaporated H_2O	200
Solids loss	kg/t pulp	1.6

		Demister etc[a]	Profile separator Low efficiency	Profile separator High efficiency
After demister				
Solids loss	g/t evaporated H_2O	(100)	25	2
	kg/t pulp	(0.8)	0.2	0.02
Pressure drop	mm H_2O	60	20	80
Temperature drop	°C	0.8	0.2	1.0
Gain in BOD_7	kg/t pulp	(0.3)	0.4	0.5
Installed costs				
Demisters	USD	18000	15000	23000
Expansion of evaporating plant	USD	15000	5000	18000
TOTAL	USD	33000	20000	41000
Annual gain in solids	USD/yr	(6000)	10000	12000
Economic outcome				
Annual cost (capital cost 16.3 %)	USD/yr	-600	-6700	-5300
Specific cost	USD/t of pulp	-0.006	-0.07	-0.05
Specific cost	USD/t of BOD_7	-20	-170	-110

a) In the case of cyclone separators or demisters placed at the steam inlet the efficiency may be taken as roughly equal to that for a demister. The installed costs will then be lower, about 50 and 10 % respectively, of those for a demister.

Note. The solids contents expressed in grams per ton of evaporated water are calculated on the whole amount of evaporated water

5.5.3 Condensate from different stages

The main part of the oxygen consuming substances in the condensates such as methanol, ethanol, mercaptanes and other sulphur compounds is volatile. Because of the distillation effect in an evaporation plant, the BOD is not distributed evenly in the condensates from different stages. See Table 5.8.

Table 5.8. Amounts of condensates and pollutant levels from a mill with continuous cooking (14). Feed of weak liquor is to third effect

	Condensate t/t	BOD_7 kg/t	Sulphur compounds kg S/t
Source of condensate			
Evaporation stage 2 and 3	3.2	0	0
Evaporation stage 4 and 5	4.5	7	0.2
Primary condenser			
Secondary condenser			
Vacuum pump well	0.3	2	0.3
TOTAL	8.1	9	0.5

Figure 5.15 shows an example of the methanol distribution in an evaporation plant, with the liquor passing the stages in the order 3-4-5-1-2. The distribution of methanol in the streams of the plant has been calculated, using general rules of distillation, and then verified by condensate analysis in an existing evaporation plant. Thus 30-40 % of the methanol is found in a small quantity of condensate, about 6 % (i.e. about 0.5 ton of condensate per ton of pulp). The methanol concentration is in the order of 2-5 g/l and the condensate originates from the liquor preheater in stage 4 and from the secondary surface condenser. The amount and methanol concentration of these condensates make them suitable for treatment in the condensate stripper, where most of the methanol is removed (see paragraph 4). A further reduction of water pollution from the condensate can be obtained by recirculating the condensates from stages 4 and 5, that contain more than 50 % of the total methanol in the evaporation plant, to the causticizing department (and the pulp washing). By this recycling of condensate the methanol level in the mill systems will increase to a certain extent, but not so much that problems will occur, as long as a large part of the methanol is removed by stripping.

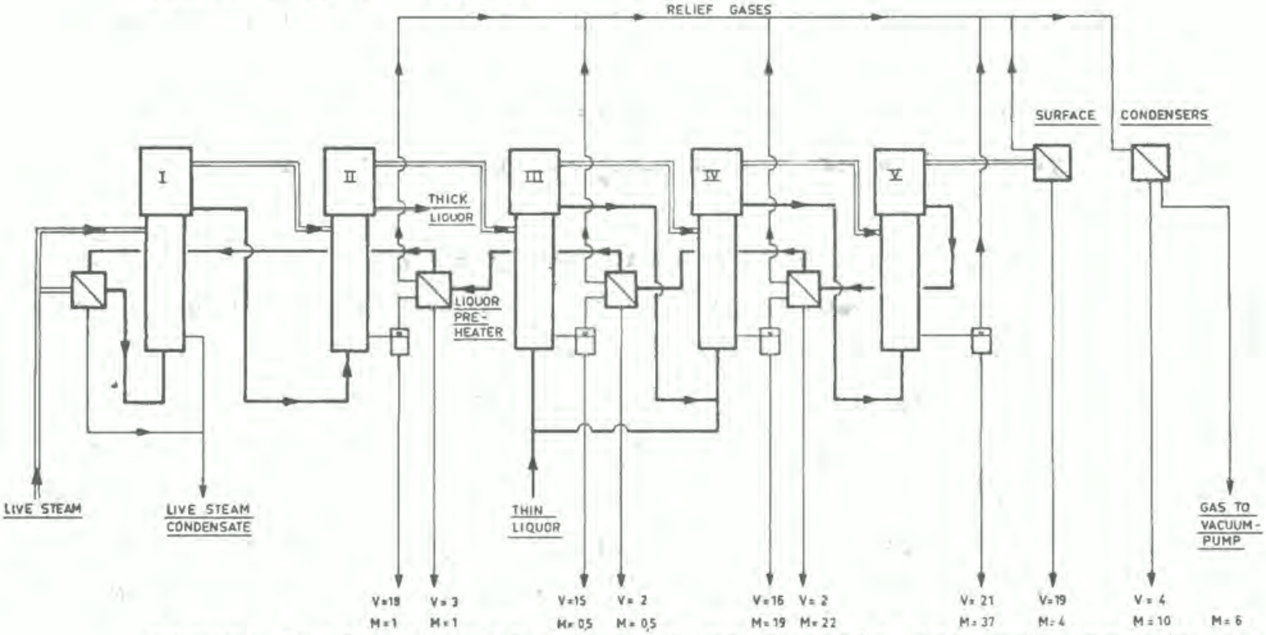


Figure 5.15. Distribution of condensate and methanol in an evaporation plant. V = Condensate flow, % of total amount. M = Methanol, % of total amount (1).

The main part of the condensate, about 60 %, contains very small amounts of volatile impurities and may be recycled in the mill as a substitute for clean hot water.

Depending on the liquor feed order and arrangement of liquor preheaters and condensers the methanol distribution may be completely different in another plant. But the same principle of calculation of the methanol distribution can still be used, to find the best way of dividing the condensate between stripping and various ways of re-use.

Some equipment and ways of arranging the equipment are essential for reduction of the water pollution from condensate. The relief gases have to be drawn to a separate part of the surface condensor. The condensate from the liquor preheaters, if any, should have a separate outlet from the stages where the methanol content is high. The condensate system has to be divided into two or three sections, with a separate collection tank for each section.

Guiding principles for recycling of condensates are:

- A small amount of condensate, 0.5-1.0 ton per ton of pulp with high BOD content should be treated in a stripper

- Another part of the condensate, 30-50 %, should be recycled, preferably to the causticizing plant

- The rest of the condensate is practically pure and can replace hot water in the mill or be sent to the sewer

The condensate stripper may be combined with the evaporation plant to reduce the consumption of live steam (see paragraph 5.6). The stripper is then usually run on steam from stage No 1 in the evaporating plant and the stripper condenser is used as heater for the liquor in stage No 4.

5.6 Treatment of malodorous gases and contaminated condensates

A quite substantial amount of malodorous gases are formed during the kraft pulping process. These gases have normally been released to the atmosphere resulting in the typical odour of a kraft mill. The major malodorous gas components are reduced sulphur compounds like hydrogen sulphide, methyl, mercaptan, dimethyl sulphide and dimethyl disulphide.

These components are dissolved in the condensates from the digester and evaporator departments. These condensates also contain methanol, formed during the cooking process, representing a high share of the total BOD discharge from the mill.

Today there are several different process solutions available to decrease the emission of the bad smelling sulphur components to the atmosphere and to reduce the BOD discharge via the condensates.

5.6.1 Treatment of malodorous gases

The major sources of bivalent sulphur compounds creating the odour from a kraft mill are:

- non condensable gases from the digester and evaporator departments
- flue gases from the recovery boiler and lime kiln
- vent gases from the brown stock washers, tall oil digester and the thin liquor condensate and soap tanks

In Figure 5.16 the total amount of TRS (total reduced sulphur) per tonne of pulp emitted from a kraft mill is shown. The figures correspond to 30 % liquor sulphidity and a production of softwood pulp. The figures are lower at lower sulphidity. Measurements made of the total sulphur emission show that these correspond to 3-4 % of charged sulphur in the digester.

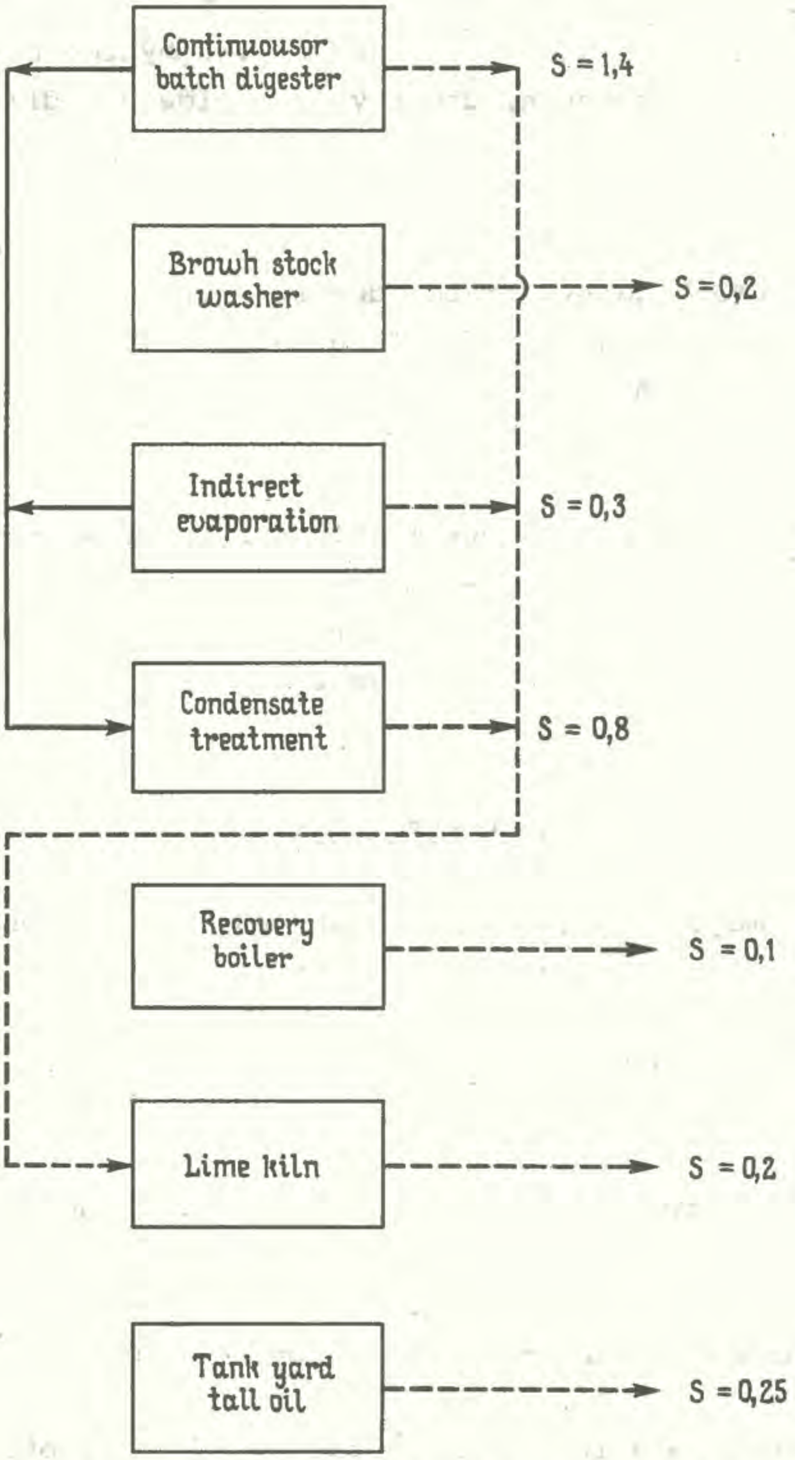


Figure 5.16. Emitted TRS (as kg sulphur per tonne of pulp) from a kraft pulp mill. The recovery boiler is not equipped with a direct evaporator.

Of the above mentioned sources the emissions from the recovery boiler, the lime kiln and the brown stock washers depend to a determining extent upon the design and operation of the equipment, these sources will not therefore be discussed further in this chapter.

Treatment of non condensable gases from the digester and evaporator departments

The major sources of odour from a kraft pulp mill are the ventpipes from the digester and evaporator departments. The emitted gases contain a significant amount of neutral sulphur compounds not soluble in caustic solution. For that reason scrubbing with white liquor or fresh caustic will not effectively control the odour. The most effective process solution is to oxidize the sulphur compounds to sulphur dioxide through burning. Safety will be the major concern in treating these gases with an oxidation process since the sulphur compounds are rather toxic as well as potentially explosive in air over a wide concentration range (see Table 5.9.).

Table 5.9. Explosion limits for gaseous compounds in air

Compound	Explosive concentration range in air, % by volume
H_2S	4.3-45.5
CH_3SH	2.2-9.2
$(CH_3)_2S$	3.9-21.8
$(CH_3)_2S_2$	-
Turpentine ($C_{10}H_{16}$)	0.8-
CH_3OH	6.7-36.5

Within the explosive limits an explosion can either be started spontaneously if the gases are heated up to about 200°C or ignited by a spark or flame. In a gas collection system there will be potential sources of ignition present, so that it is essential to keep the gases in non explosive conditions to minimize the risk of explosion. This can be accomplished by excluding air; by keeping the gases above the upper explosion limit, or by diluting the gases with air to bring them below the lower explosion limit. Below different solutions of treating the non condensable gases from the digester and evaporator departments are described.

Gas collection without dilution with air (see Figure 5.17)

The main principle of this solution is to collect the non condensable gases from the digester and evaporator departments in a concentrated form above the explosion range. In order to achieve this, the ventpipes are blocked with safety valves.

Collecting the gases from batch digesters is more complicated due to the widely fluctuating flow and composition. The solution is to use a gas holder working at a constant pressure to collect and even out the flow of gases, and at the same time keep them non explosive.

The flow of non condensable gases from the digester and evaporator departments is about 2 standard cubic meters/-tonne of pulp from each. Due to these small gas flows the major advantages with this type of system will be:

- The digester gases will be effectively washed with water in order to remove turpentine and other explosive extractives

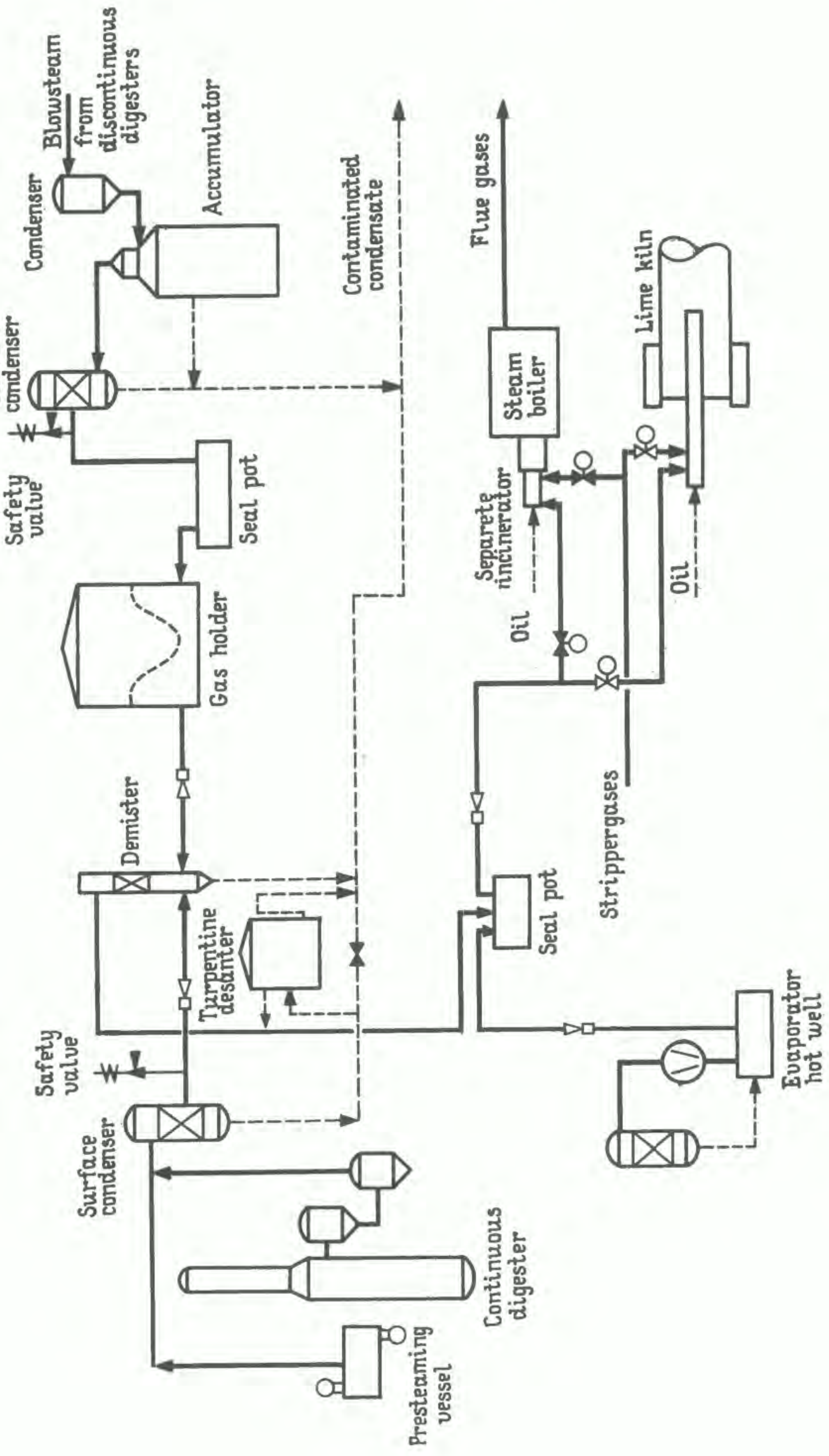


Figure 5.17. Gas treatment system without air dilution

- Gas transportation can more economically be carried out with steam ejectors instead of fans which will eliminate the risk of ignition

- Small dimensions of the gas pipes

Once the flows and composition of the gases have been evened out while keeping them non explosive the alternatives available for oxidizing will be burning in the lime kiln or in a separate incinerator.

Due to the small gasflows the gases can be safely introduced into the lime kiln in concentrated form through a high velocity nozzle. The heat released by combustion of the waste gases will result in savings of oil. The SO_2 generated is absorbed in the lime and recovered to 60-70 % in the white liquor.

The separate incinerator burning system has the major advantage that the system is not tied into any other department in the mill. One of the two different installation types that can occur with a separate incinerator is as a stand-by unit for the lime kiln burning where the gases only will be cooled from 800°C to 400°C before exhausted to atmosphere. The other is a continuous burner placed in a steam boiler, when the energy in the flue gases will be recovered in the steam boiler.

With this type of system there will be a reduction of TRS emitted to the atmosphere of 75 %. With the amount released from the contaminated condensates included, the figure will be 80 %. The rest is discharged from the recovery boiler (without direct evaporator), the wash plant, the lime kiln and as diffuse discharges. In Table 5.10 the investment cost is shown.

Table 5.10. Gas collection and burning system. No air dilution

Operation data

Gas flow for burning	10 standard cubic meters/ tonne of pulp
Steam consumption	2-3 kg/tonne of pulp
Combustion energy in gases	100 MJ/tonne of pulp
Oil consumption in separate incinerator	10 kg of oil/h

Investment cost (in million USD) for turn-key installation

Gas collection system		
Batch digester	50 tonnes of pulp/day	0.32
	100 "	0.35
	300 "	0.40
Continuous digester	50 tonnes of pulp/day	0.22
	100 "	0.24
	300 "	0.27
Gas burning system		
Lime kiln	50 tonnes of pulp/day	0.08
	100 "	0.08
	300 "	0.08
Separate incinerator at steam boiler or ejector cooler	50 tonnes of pulp/day	0.32
	100 "	0.32
	300 "	0.32

Gas collection with air dilution (see Figure 5.18)

In this solution the non condensable gases from the digester and evaporator departments are collected in a diluted form below the lower explosive limit. In order to maintain the dilution the ventpipes are connected to the atmosphere and the transportation fans dimensioned to transport a higher gas flow than the amount of produced non condensables.

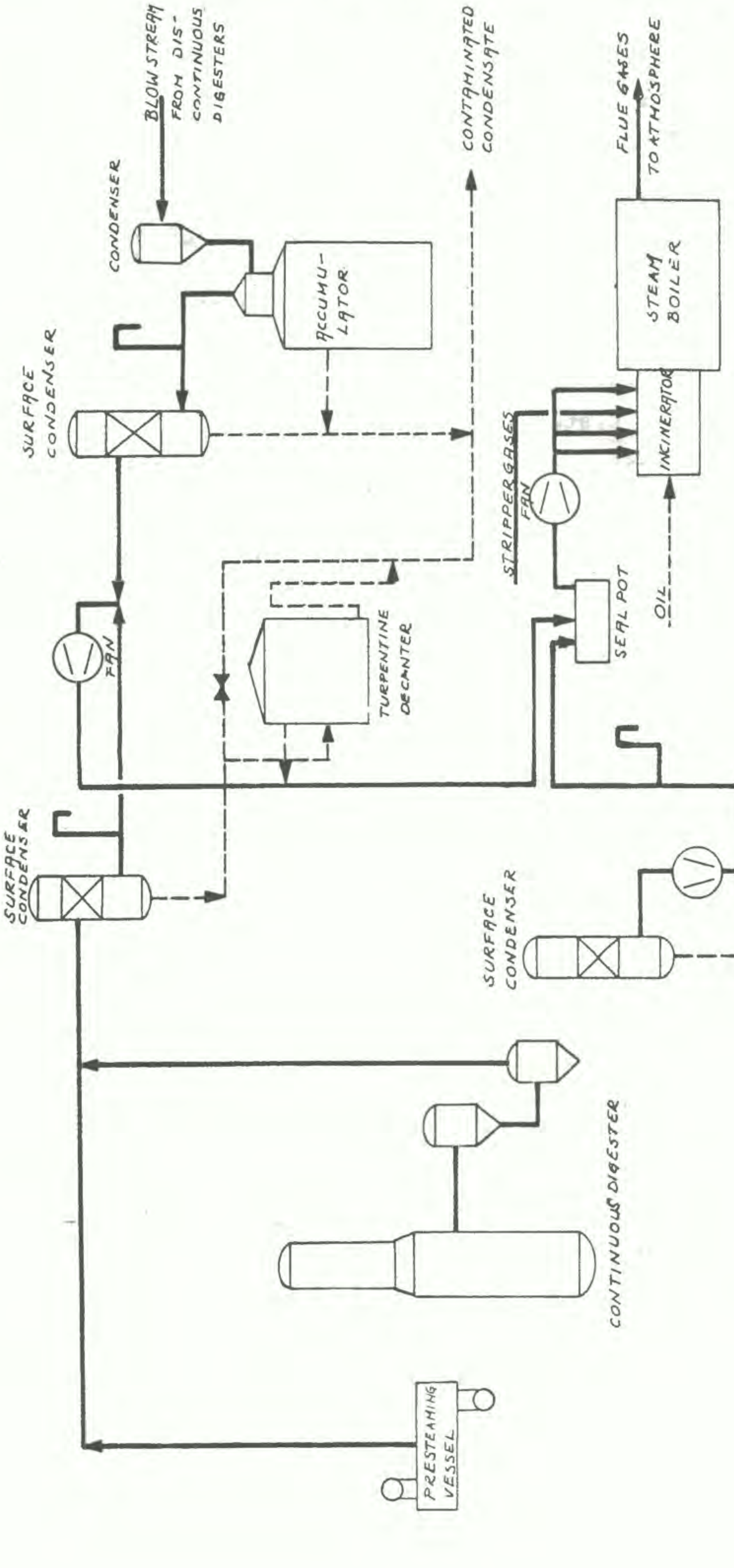


Figure 5.18. Gas treatment system with air dilution

The collection from the batch digesters has to be designed for the peak flow at the beginning of a blow.

Oxidation of the gases will be carried out in a separate incinerator installed in connection to a steam boiler.

Due to the risk of not diluting the gases enough the system has to be equipped with flame arrestors and rupture discs in order to avoid damage to personnel and equipment, in case of an explosion.

The major advantage with this system is its simple operation. The reduction of TRS will be the same as for the system working with concentrated gases.

In Table 5.11 the investment cost is shown.

Table 5.11. Gas collection and burning system. Air dilution

Operation data			
Gas flow for burning from:			
Discontinuous digester	800	standard cubic meters/ tonne of pulp	
Continuous digester	160	"	
Combustion energy in gases	100	MJ/tonne of pulp	
Oil consumption in incinerator:			
Discontinuous digester	25	kg oil/tonne of pulp	
Continuous digester	5	kg "	
Investment cost (in million USD) for turn-key installation			
Discontinuous digester, prod	50	tonnes of pulp/day	0.32
	100	"	0.35
	300	"	0.40
Continuous digester, prod	50	tonnes of pulp/day	0.24
	100	"	0.26
	300	"	0.30

Treatment of the evaporator gases

The gas from the evaporator department contains a high share of acid sulphur compounds. As a complement to the above described gas collection systems this gas can easily be treated with an alkaline solution in order to absorb the hydrogen sulphide and methyl mercaptan.

In Figures 5.19 and 5.20 two different solutions are shown using weak wash or white liquor as scrubbing agent.

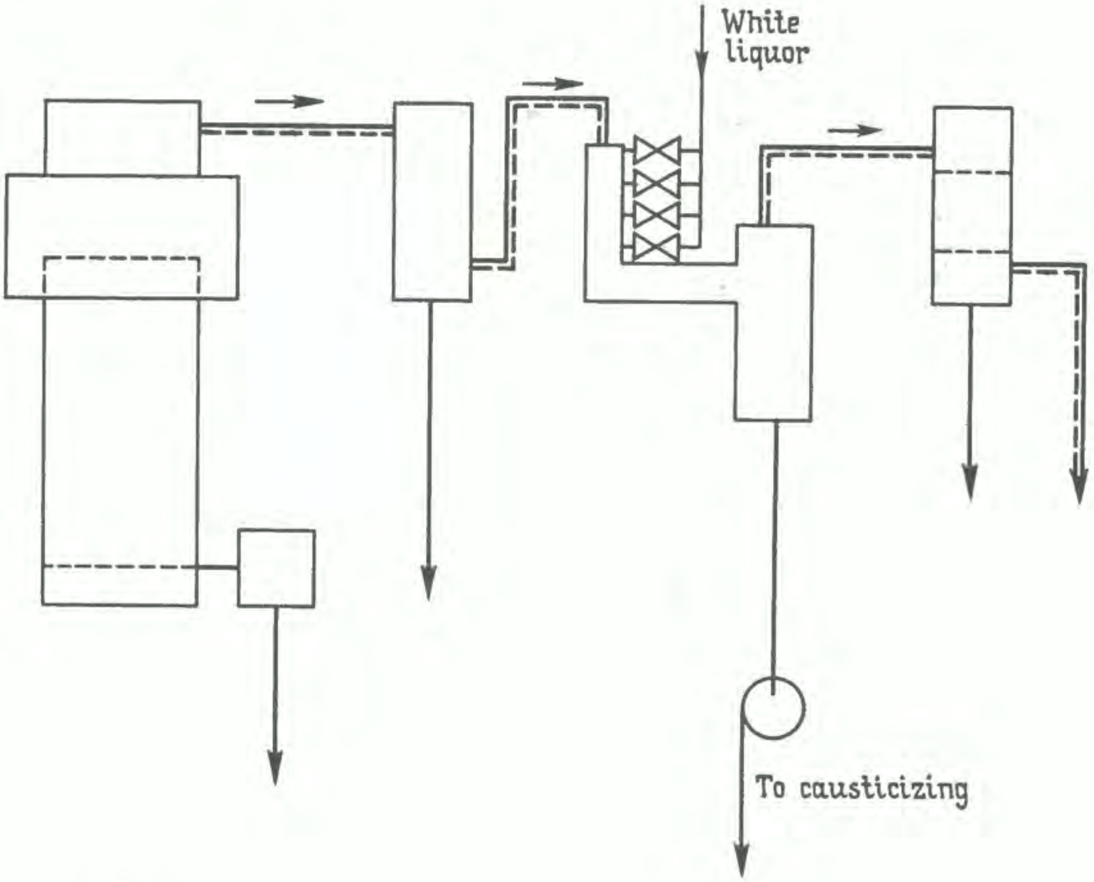


Figure 5.19. Venemark scrubber

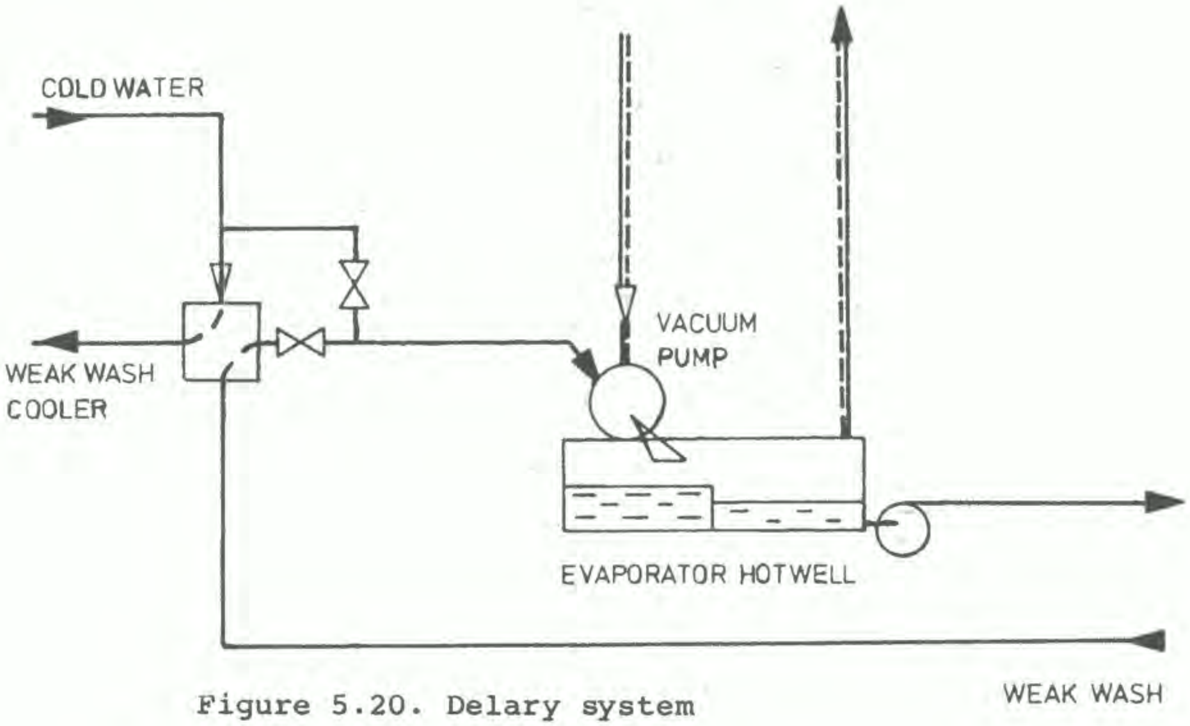


Figure 5.20. Delary system

The advantage with this solution is that hydrogen sulphide is recycled as an active chemical to the white liquor. The absorbed amount of TRS is 70-75 % of the total emitted sulphuric gases from the evaporators. Investment costs for these systems are shown in Table 5.12.

Table 5.12. Scrubber systems for evaporator gas

Operating data		
Venemark scrubber:		
gas flow	2	standard cubic meters/tonne
white liquor flow	0.03	m^3/h
Delary system:		
gas flow	2	standard cubic meters/tonne
weak wash flow	1.5	m^3/h
Investment cost (in million USD) for turn-key installation		
Venemark scrubber	0.05	
Delary scrubber	0.02	

Treatment of diffuse gases from the tank yard and tall oil digester

The emission of TRS from the tank yard originates mainly from the thin liquor-, contaminated condensate- and soap tanks. It is impossible to collect these gases together with gases from the tall oil digester without diluting them with air. The recommended solution is therefore to treat the gases with an alkaline solution before venting to the atmosphere so as to avoid the explosion risks in a gas transport system with a burner.

The principle of the system is shown in Figure 5.21.

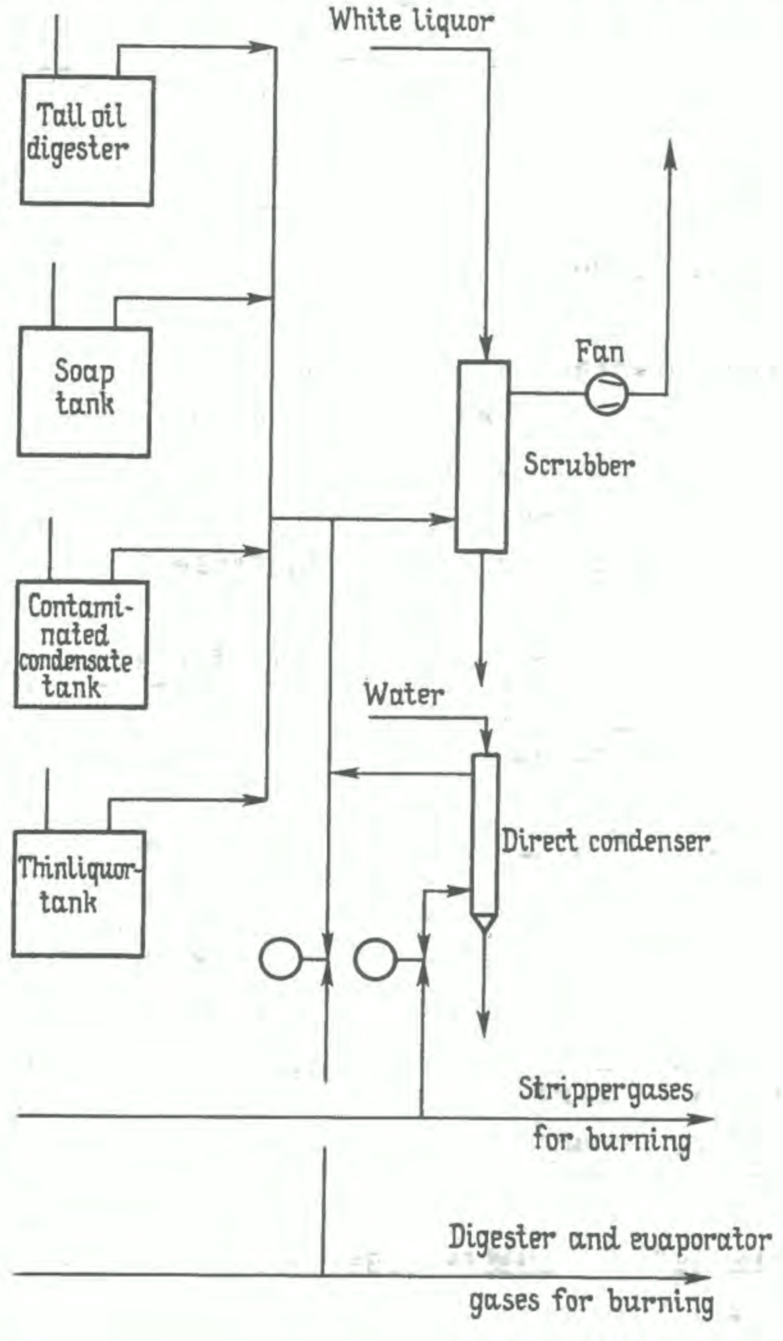


Figure 5.21. Gas treatment system for diffuse emissions

In order to minimize the odour peak from vented gases that can escape when some disturbance occurs in the gas collection or condensate treatment systems, it is recommended that vented gases be treated in the same alkali scrubber as the diffuse gases. The reduction of hydrogen sulphide and methyl mercaptan will be 90-95 %.

In Table 5.13 the investment costs for this system is shown.

Table 5.13. Scrubber for diffuse gases

Operating data	
Gasflow to scrubber	5000 standard cubic meters/h
White liquor flow	0.3 m^3/h
Investment cost (in million USD) for turn-key installation	
	0.12

5.6.2 Treatment of contaminated condensate

The main sources of contaminated condensate are the multiple effect evaporation and digester plants. The contaminants in the condensate are the same compounds which may be vented to the atmosphere from these departments and include hydrogen sulphide, methyl mercaptan, methyl sulphide, methyl disulphide, methanol and traces of other organic constituents liberated from the wood during the digesting process.

Although these condensates account for less than 15 % of the total volume of mill effluent if discharged to a sewer, they account for about 30 % of the BOD based on bleached production. The subject of pulp mill toxicity is very complex, but generally speaking it is well recognized that the compounds that are dissolved in liquor condensates and listed above are very toxic. Furthermore, the contaminated condensates are a source of odour when sewered.

In order to reach an acceptable level of BOD discharge via the condensates, without too high operating costs, the solution will be a combination of re-use and treatment of the condensates. The main principle will be to re-use the cleanest and hottest condensates from the evaporation in the brown stock washing and causticizing departments and only treat the most contaminated condensates from the evaporation plant together with condensates from the digester. In an ordinary 6-stage evaporation plant the segregation will be (see Figure 5.22):

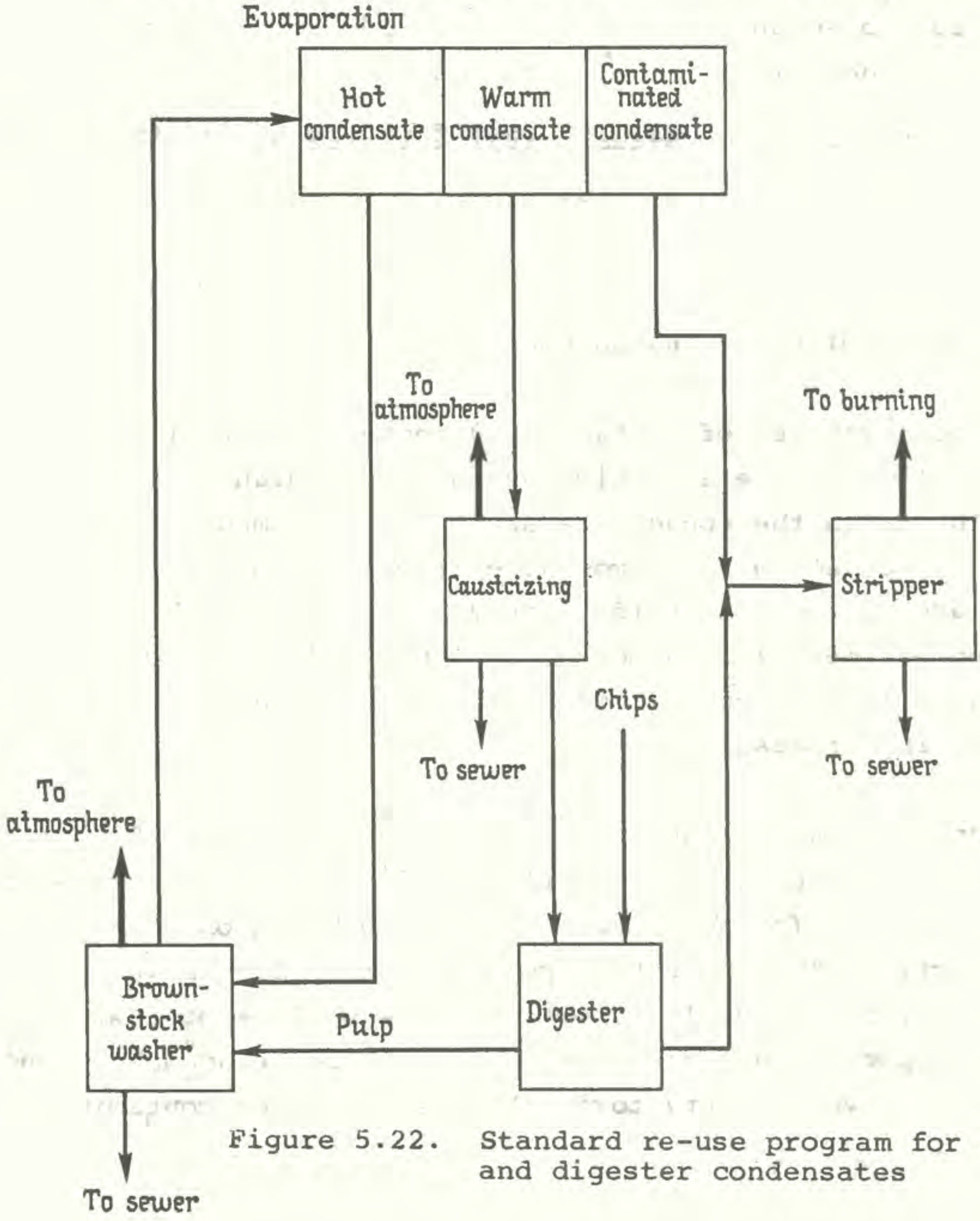


Figure 5.22. Standard re-use program for evaporator and digester condensates

- condensate from effect 2, 3 and 4 to brown stock washers
- condensate from effect 5 and 6 and from the surface condenser to the causticizing plant
- condensate from the 5th effect liquor preheater, after condenser and the evaporator hotwell for treatment in a stripper

The general rule is to treat condensate from the liquor preheater to the effect after the feeding effect together with the condensate from the aftercondenser, evaporator hotwell and the digesters. Table 5.14 shows how the BOD is split in various departments of the mill.

In Table 5.14 the condensate flows from the evaporators and digesters are also shown.

There are two different ways of treating the contaminated condensate; stripping and burning or biological degradation. These solutions are described below.

Contaminated condensate treatment with steam stripping

The usual method of treating the most contaminated condensates is to steamstrip them in a tray column. The condensates are preheated with hot stripped condensate before entering the column. Steam is fed to the stripper by flow ratio control with the incoming condensate so that a constant L/V-ratio is maintained in the stripper. The vapour leaving the column will be partially condensed either in a liquor preheater or in a watercooled condenser. The vapour is condensed at 85-90°C which at atmospheric pressure corresponds to a methanol concentration in the uncondensed gases of about 40 %. These gases are transported either to the lime kiln or to a separate incinerator

Table 5.14. Approximate condensate flows and split of BOD in various mill departments

Evaporation	
Part of incoming BOD to:	
- washing	5 %
- causticizing	55 %
- condensate treatment	40 %
Condensate to:	
- washing	3.8 t/t of pulp
- causticizing	3.7 t/t of pulp
- condensate treatment	0.5 t/t of pulp
	8.0 t/t of pulp (including residual liquor 1.0 t/t)
Causticizing	
Part of incoming BOD to:	
- digester (white liquor)	40 %
- atmosphere	50 %
- sewer	10 %
Cooking	
Part of volatile BOD formed in discontinuous digesters to:	
- washing (with the black liquor)	50 %
- condensate treatment	50 %
Continuous digester to:	
- washing (with the pulp)	70 %
- condensate treatment	30 %
Condensate to treatment:	
- batch digester	1.2 t/t of pulp
- continuous digester	0.4 t/t of pulp
Washing	
Part of incoming BOD in last stage shower water to:	
- evaporation	40 %
- atmosphere	20 %
- pulp (finally ends up in the sewer)	40 %
Assumed washing efficiency of BOD in pulp	98 %

for burning. The sulphur compounds of the dirty condensates will be stripped off completely and 90 % of the methanol is stripped off at a steam consumption of 18 % of the feed (Table 5.15).

Table 5.15. Steam stripper for contaminated condensate

Operating data		
Contaminated condensate for treatment:		
- batch digester	1.7 t/t of pulp	
- continuous digester	0.9 t/t of pulp	
Steam consumption for 90 % BOD removal:		
- batch digester	0.30 t/t of pulp	
- continuous digester	0.16 t/t of pulp	
Combustion energy in stripper gases	180 MJ/t of pulp	
Investment cost (in million USD) for turn-key installation		
Batch digester, prod	50 tonnes of pulp/day	0.17
	100 "	0.20
	300 "	0.24
Continuous digester, prod	50 tonnes of pulp/day	0.15
	100 "	0.17
	300 "	0.20

As stripping media either live steam or liquor steam can be used. In Figure 5.23 three different solutions of how to connect the stripper are shown.

Contaminated condensate treatment with the ENSO-BIOX method

This method biologically breaks down the sulphur compounds as well as the methanol in the contaminated condensate.

The supporting medium of the micro organisms is softwood bark, which already contains many valuable nutrients

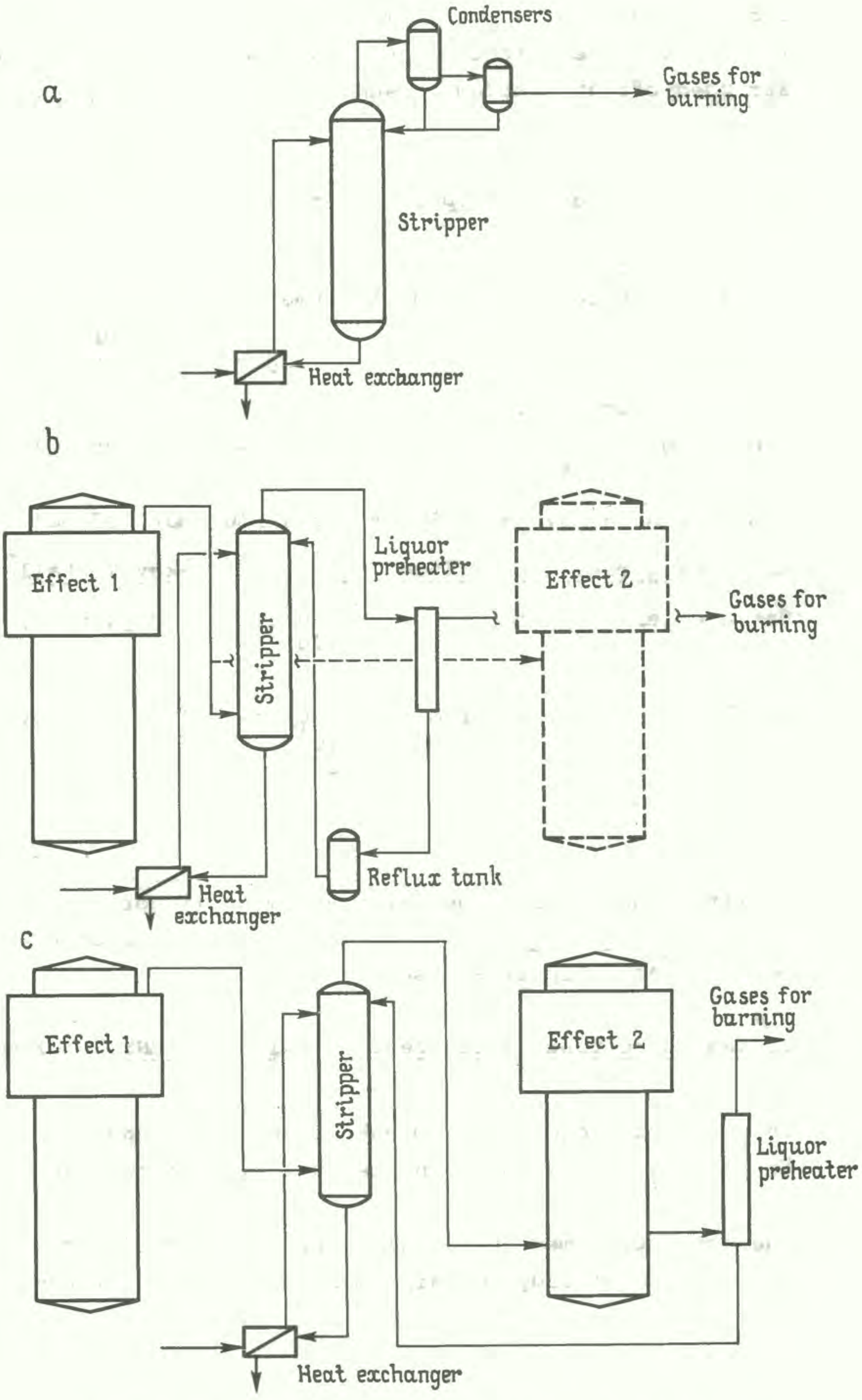


Figure 5.23. Alternative stripper installations

required for the functioning of organisms. Because of the aerobic function of these micro organisms the bark medium must be aerated. The biological filter system consists principally of three operating units, which are filled with bark. The first two units, called liquor filters are fed with the contaminated condensate in series (see Figure 5.24). The required air enters from below. In the first liquid filter the sulphur bacteria will oxidize the malodorous compounds. The condensate is then fed to the second liquid filter, where methanol is broken down. The air leaving the liquid filters is a little contaminated with malodorous compounds. This air is passed through the third filter, the gas filter, where it is purified in the same way as in the liquid filters. End products will be SO_2 and CO_2.

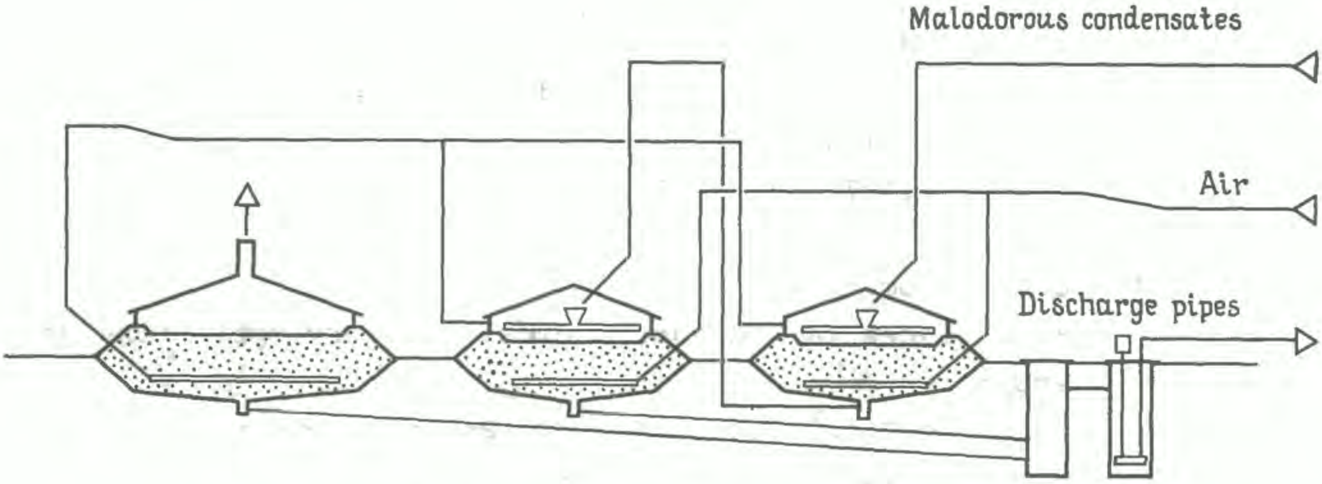


Figure 5.24 ENSO-BIOX method for purifying kraft pulp mill condensates using two liquid filters in series

With this type of solution 95 % of the incoming sulphur and methanol will be oxidized.

In Table 5.16 the investment cost for the system is shown.

Table 5.16. The ENSO-BIOX method

Operating data		
Contaminated condensate for treatment:		
- batch digester	1.7 t/t of pulp	
- continuous digester	0.9 t/t of pulp	
Investment cost (in million USD) for turn-key installation		
Production	50 tonnes of pulp/day	0.17
	100 "	0.19
	300 "	0.23

Literature reference list, chapter 5

(1) Arhe H., Bergkvist S.:
Methanol distribution in an evaporation plant
Svensk Papperstidning 76(1973):10 380-382

(2) Brown R.W. et al:
Black liquor evaporation and odour control in "sulphur-free" alkaline pulping
Tappi 58(1975):4, 94-97

(3) Camilo Gomez E.:
Experiences in bagasse chemical recovery operations at Propal
Non-wood Plant Fibre Pulping, Process Report No 8, 8-12
Tappi, Atlanta, Georgia (1977)

(4) Ghalke S.N., Veeramani H.:
Viscosity of bamboo, bagasse and eucalyptus black liquors
Non-wood Plant Fibre Pulping, Process Report No 8, 33-40
Tappi, Atlanta, Georgia (1977)

(5) Kalyanasundaram K. et al:
Problems encountered in processing bamboo black liquor in recovery installations in India
Tappi CA Report No 43 (1972) 79-117

(6) Lengyel P.:
Investigation and technical experiences in the recovery of straw black liquor
Proceedings of the symposium on "Recovery of Pulping Chemicals". Held in Helsinki, May 13-17, 1968

(7) Olausson L.:
Heat economy improves with Lockman pre-evaporation using digester flash steam
Pulp & Paper Canada, Vol. 80, No 3, March 1979, 45-48

(8) Misra D.K.:
Installation and operation of chemical recovery system in soda pulp mills utilizing wheat straw and bagasse as raw material
Tappi CA Report No 43 (1972) 119-175

(9) Padfield D.H.:
Control of odour from recovery units by direct contact evaporative scrubbers with oxidized black liquor
Tappi 56(1973):1, 83-86

(10) Rydholm S.A.:
Pulping Processes
Interscience Publishers, N.Y. 1965

(11) Sadawarte N.S. et al:
Studies on desilication of bamboo kraft green liquor
Non-wood Plant Fibre Pulping, Progress Report, No 9, 97-103
Tappi, Atlanta, Georgia (1978)

(12) Salaber J., Maza F.:
Bagasse black liquor recovery
Tappi CA Report No 43 (1972) 55-57

(13) The SSVL Environmental Care Project
Stockholm, Sweden 1974

(14) Skogsindustrins luftvårdsproblem (in Swedish)
Statens Naturvårdsverks Publikationer 1969:3

(15) Veeramani H.:
Significance of silica during pulping chemical recovery in bamboo kraft paper mills
Non-wood Plant Fibre Pulping, Progress Report No 8, 13-22
Tappi, Atlanta, Georgia (1977)

(16) Veeramani H.:
Design properties of bamboo and bagasse black liquors
Non-wood Plant Fibre Pulping, Progress Report No 9, 97-103
Tappi, Atlanta, Georgia (1978)

(17) Winklepleck R.G., Suda S.:
Considerations in converting existing kraft recovery units for air emission control
Tappi 56(1973):6, 73-77

(18) Jönsson S-E.:
The Lockman Evaporator, a new liquor evaporation system
Proceedings of the Symposium on Recovery of Pulping Chemicals, Helsinki May 13-17 1968, 137-155

6. THE COMBUSTION OF SPENT LIQUOR

6.1 Principles

The spent liquor contains valuable chemical compounds which can be recovered and used for preparing new cooking liquor. The heat content of the dissolved organic matter can be utilized to produce steam and electricity. A modern sulphate or soda pulp mill with recovery boiler and back pressure turbine can in fact produce steam and electricity enough to be self supporting.

In the recovery process of a sulphate pulp mill the chemicals for new cooking liquor have to be produced from sodium carbonate (Na_2CO_3) and sodium sulphide (Na_2S) as raw materials. Unfortunately, the chemistry involved prohibits direct conversion of black liquor inorganics into sodium hydroxide, NaOH. The process has to be run in such a way that the losses to the environment are reasonably low. The sulphur is recovered as sodium sulphide and the heat content of the black liquor is utilized.

In the case of non-wood pulping, because of lower heating value of the spent liquor, supporting firing with other fuels will be required.

The chemical recovery process of the soda pulp mill is simpler as it is in principle sulphur-free and no sulphur needs to be recovered.

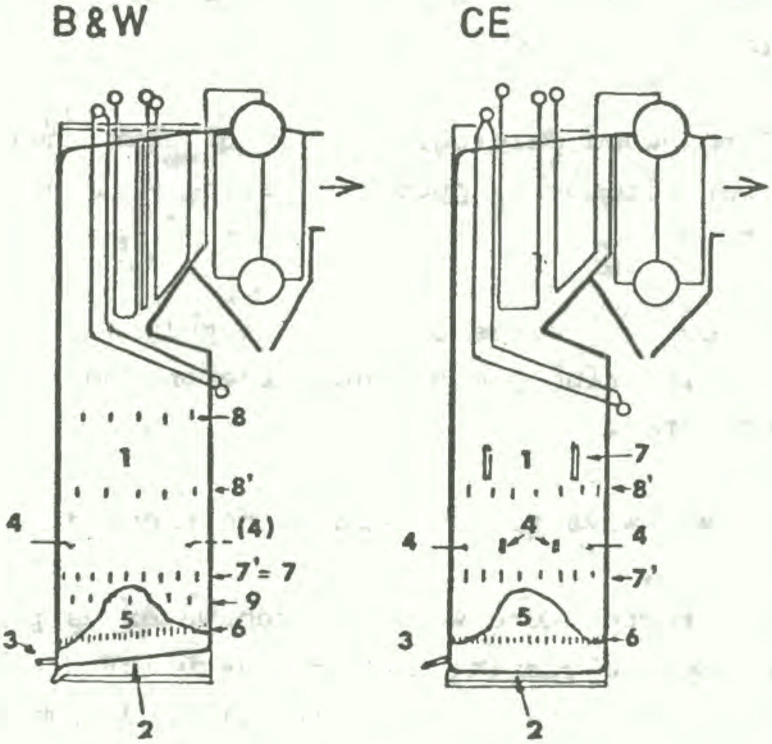
There are two basic ways to regenerate the chemicals:

- The "dry" high temperature way: as much water as possible is evaporated before burning in a recovery furnace. The product is a smelt containing sodium compounds (mainly Na_2S and Na_2CO_3) which is dissolved in water (or weak liquor) producing green liquor.

- The "wet" way: the compounds in the black liquor are decomposed at moderate temperature and high pressure without or with only partial evaporation of the water. The product is green liquor.

6.2 High temperature recovery furnace

In about 1930 the modern type of recovery furnace was developed, the Tomlinson furnace (Figure 6.1). This furnace is in principle a big steam boiler, with water-cooled walls and water and steam-cooled tubes in the roof. The liquor which is concentrated to 60-65 % dry substance is sprayed into the furnace and a bed of substance is formed on the bottom. Air is blown into the furnace through ports on the walls and the surface of the bed burns. The molten sodium salts flow from the bed and out through the smelt spout(s) down into the dissolving tank.



1. Furnace
2. Bottom
3. Smelt spont
4. Liquor gun (s)
5. Bed
6. Primary air
7. Secondary air (USA, Canada)
7'. Secondary air (Sweden)
8. High secondary air (USA, Canada)
8'. High secondary air (Sweden)
9. High primary air

Figure 6.1. The Tomlinson type recovery furnace. Babcock & Wilcox, and Combustion Engineering

In the upper part the flue gases are reacted with excess air and brought to in the heat recovery part of the boiler. To diminish the heat and chemical losses with the flue gas, the recovery boiler is often equipped with an electrostatic precipitator and a scrubber.

The furnaces of the two suppliers, Babcock & Wilcox and Combustion Engineering differ only in certain details.

Figure 6.2 shows the main parts of the kraft recovery system. The thick black liquor from the evaporators should have a high content of dry substance, 60-65 %. 50-55 % is often mentioned as the limit for safe firing. Below 50-55 % dry substance the risk of explosions is said to increase. The ash from the ash hoppers and the electrostatic precipitators is circulated back and mixed with the black liquor, which is sprayed into the furnace. If the dry content is low, or the furnace is operated at a low load, it may be necessary to use additional oil or gas firing. In this case the oil supply must be carefully controlled to prevent an oil-gas explosion.

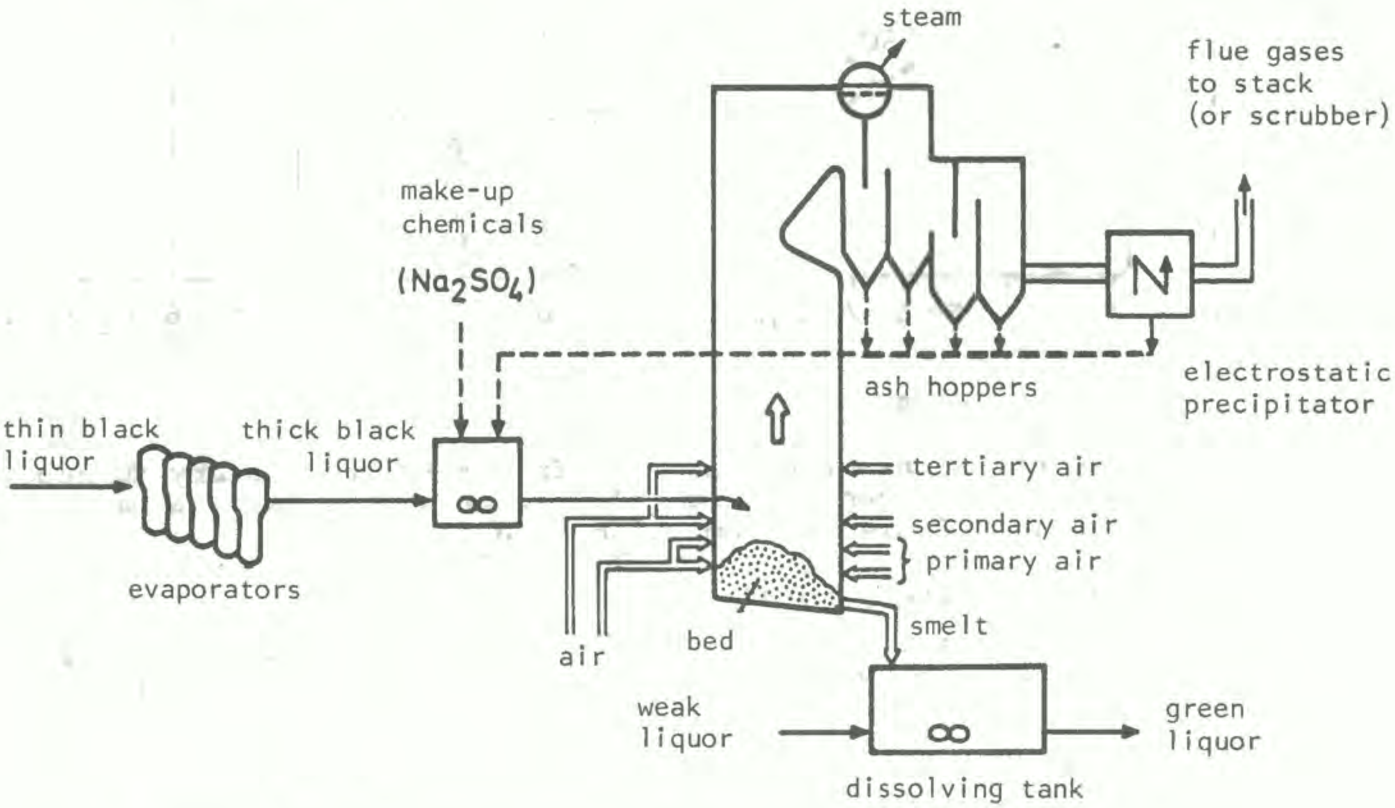
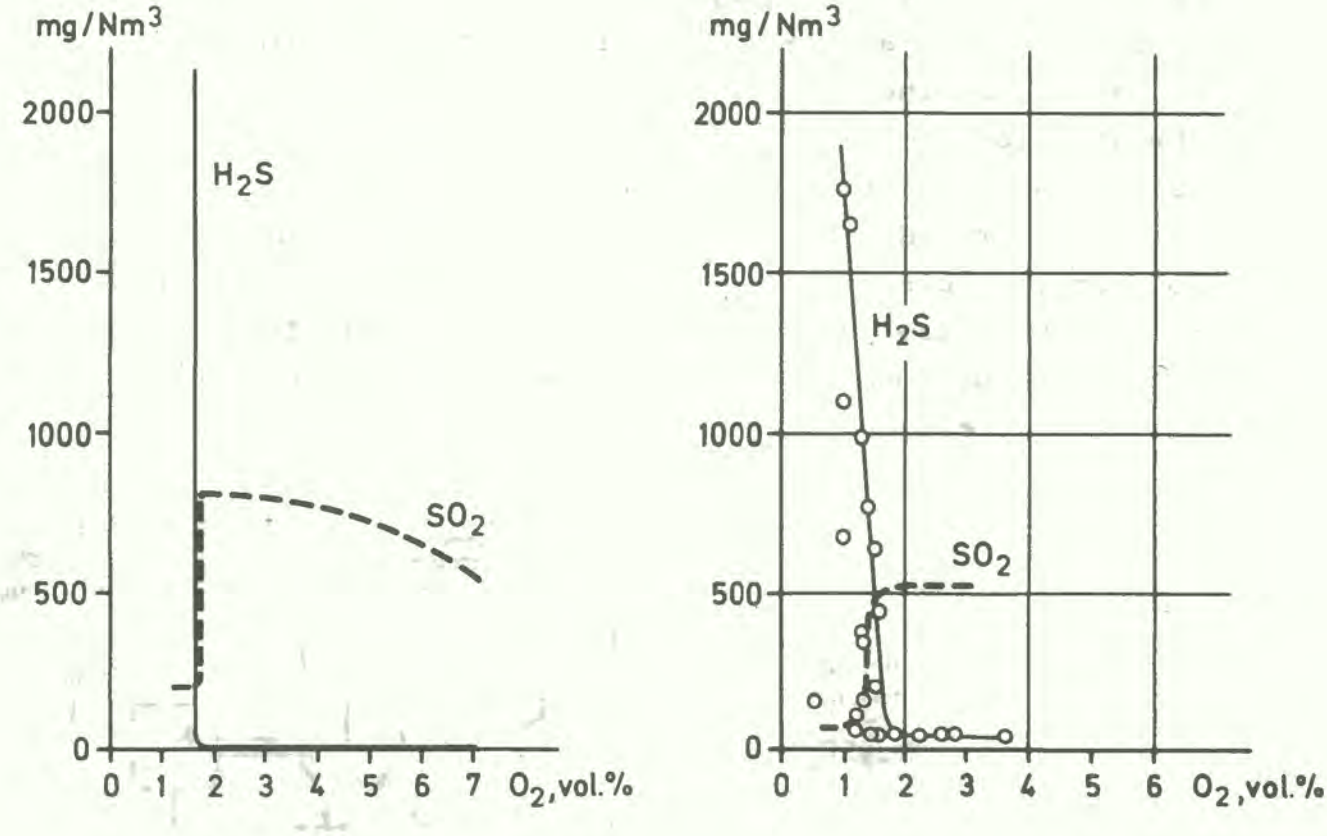


Figure 6.2. The main parts of the kraft recovery furnace

The emission of hydrogen sulphide (H_2S), can be minimized by a proper regulation of the air supplied to the furnace. The total excess air should correspond to about 2-5 % oxygen in the flue gas. Each recovery furnace has an individual limit. See Figure 6.3. To get a low emission of reduced sulphur gases in the flue gas, it is important to have a high pressure and high impulse on the tertiary (or high secondary air). This provides a good mixing of the gases in the furnace and the odorous gases are burnt to SO_2.



Figures 6.3a and 6.3b.

The emissions of H_2S and SO_2 from a kraft recovery furnace. When the oxygen content of the flue gas is below a particular figure, the emission of H_2S is high.

3a calculated, 3b measured

(Warnqvist B.: Chemical equilibria in the kraft recovery furnace (in Swedish). Svensk Papperstidning 76(1973):12, 463-466.

The ratio of sulphur to sodium and the total chemical balances of sulphur and sodium determine the emission of sulphur dioxide (SO_2) from a recovery furnace without scrubber, and the amounts of dust which are formed in the furnaces. These two flows, the SO_2-emission and the dust formation are linked together by the chemistry in the recovery furnace. Figure 6.4 shows the connection. It is based on theoretical calculations and data from a limited number of recovery furnaces. Individual variations occur. The parameter dry content of the liquor (DS) is intended to be a measure of the heat value of the liquor. The heat value as such is unsuitable as a short-term control parameter because it is time-consuming to determine.

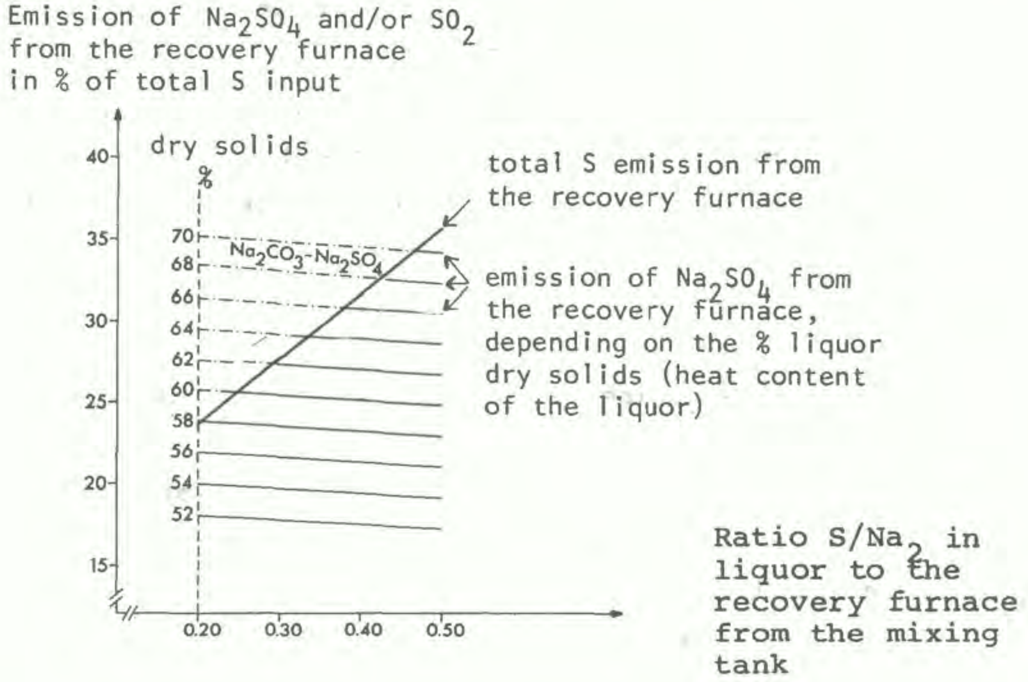


Figure 6.4. The emission of sulphur (SO_2) from a kraft recovery furnace at nominal load

The input parameters of Figure 6.4 are thus the dry content of the liquor (the heat content) and the sulphur/sodium ratio (roughly equal to the sulphidity).

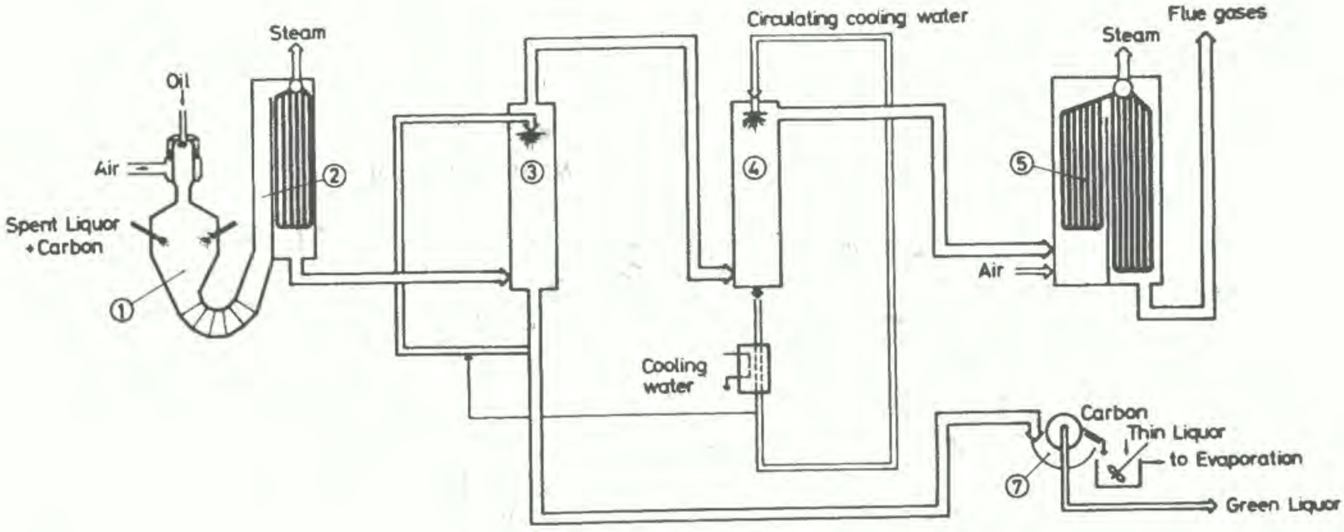
This gives the primary formation of fly ash dust (Na_2SO_4). The main part of the fly ash is separated in the dust hoppers and the electrostatic precipitator. The difference between the total primary sulphur emission and (the S-content of) Na_2SO_4 dust emission is the emission of sulphur as sulphur dioxide (plus hydrogen sulphide). At high DS levels and low sulphur/sodium ratios the dust formation may get so high that it will consume all sulphur primarily emitted. The dust will then contain sodium sulphate and sodium carbonate, and practically no sulphur dioxide will be emitted from the recovery furnace. As the conditions in the recovery furnace depend on the dry substance load, the emissions from it will vary with the load.

To minimize the emissions and to maximize the steam output from the recovery furnace a computer system is sometimes used. There are a few systems commercially available today. Some recent developments of the kraft recovery furnace have been described by Vegeby (13). Literature referred to (5, 7, 11).

6.3 High temperature combustion - other processes

The modern kraft recovery furnace is often designed for a mill capacity of several hundred tons of pulp/day. For small mills, the complete system of a recovery boiler is comparatively expensive. Today there is no self-evident alternative, but several processes have been proposed and some have been tested.

The SCA-Billerud process was originally developed for sulphite-NSSC chemical recovery, but has also been adopted for kraft and soda recovery. The process has been operating for several years as complement to an over-loaded small kraft recovery furnace in Spain (Figure 6.5). The product is an ordinaty green liquor and the heat recovered corresponds to 87 % of that recovered in an ordinary recovery boiler. The reduction efficiency is lower than that of an ordinary recovery boiler (8, 9).



1. Reactor
2. Flue gas heat recovery
3. Gas and dust scrubber
4. Cooling tower
5. Steam boiler
7. Carbon separation filter

Figure 6.5. The SCA-Billerud recovery process in sulphate pulping

For soda pulp liquor recovery a process based on the fluidized bed concept (Figure 6.6) can be used. The heat and sodium content of the liquor can be recovered. Typical for the fluidized bed process is that the temperature of the fluidized bed cannot be permitted to exceed the melting point of the inorganic salts, in this case the mixture sodium carbonate-sulphate. Combustion with deficiency of air (pyrolysis) will in this case give high losses of sulphur to the flue gas.

With this process, only the heat can be recovered in case of a kraft process. The product is a mixture of sodium carbonate and sodium sulphate (Na_2CO_3, Na_2SO_4). In a kraft mill, this kind of process can of course be used to reduce the overload in a small kraft recovery furnace but the final reduction of sulphate to sulphite is carried out in the recovery furnace.

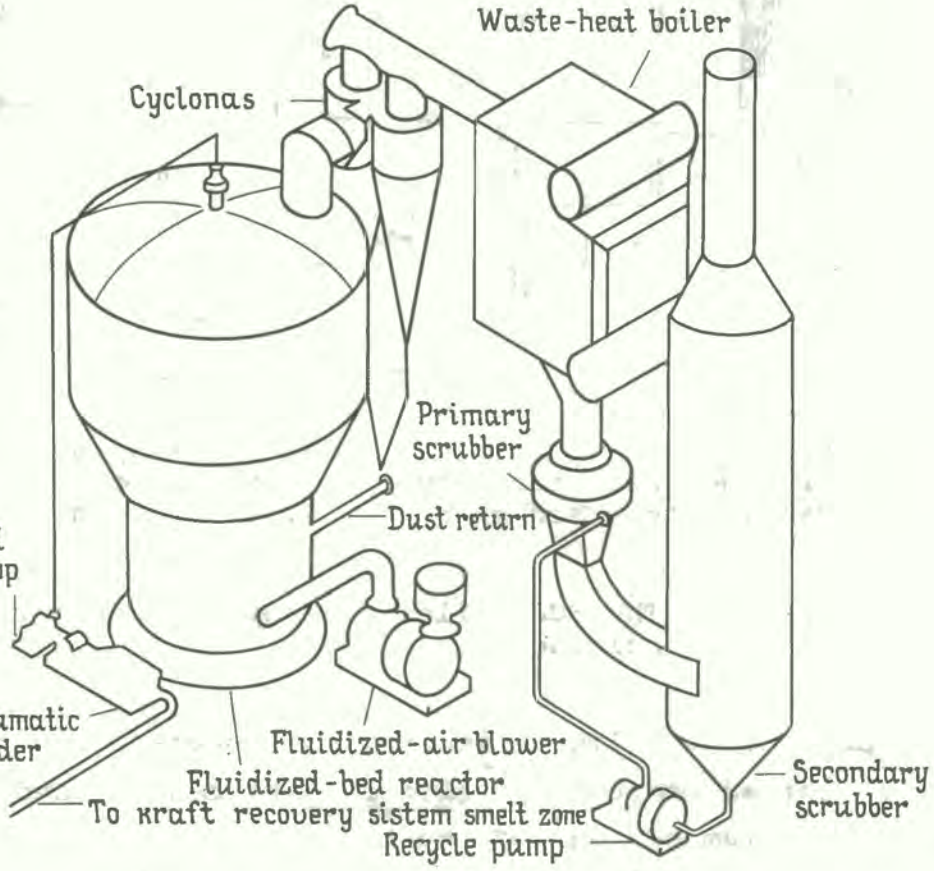
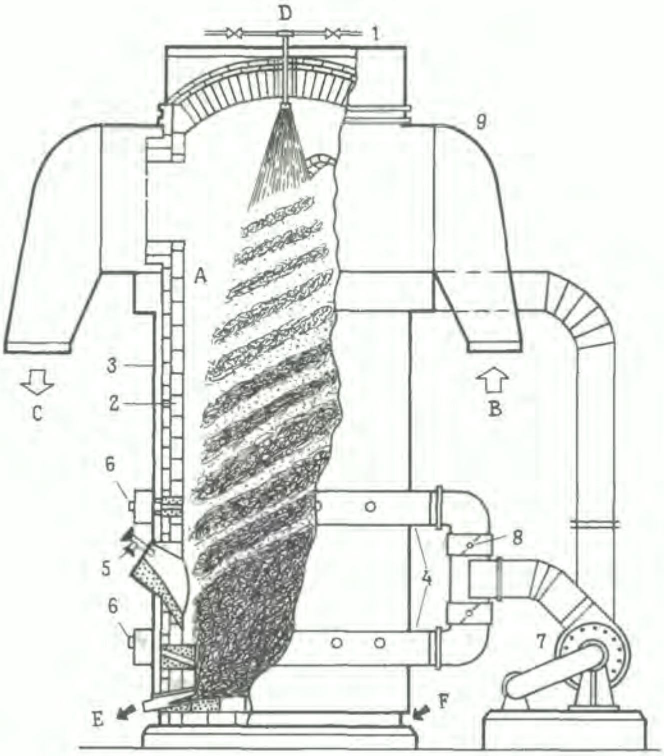


Figure 6.6. Fluidized bed combustion of sulphate liquor

The combustion of the black liquor can also be carried out in a relatively simple brick-lined uncooled shaft furnace. One example of this is the "Broby Smelter" which can be adapted to both kraft and soda pulping. Figure 6.7 shows the combustion chamber and Figure 6.8 a simple flow-sheet. When soda cooking is practised, the "Broby System" makes it possible to achieve an almost complete recovery. For kraft pulping it may be necessary to install an SO_2-scrubber.



A Combustion gases (1070°C)
B Dilution gases (130°C)
C Outlet gases (350°C) to evaporator
D Thick liquor inlet
E Smelt outlet
F Combustion and cooling air inlet
❶ Thick liquor injector
❷ Brickning
❸ Cooling air space
❹ Air distribution box
❺ Oil burner
❻ Sight glasses
❼ Combustion air fan
❽ Regulating throttles
❾ Gas mixing box

Figure 6.7. The "Broby Smelter"

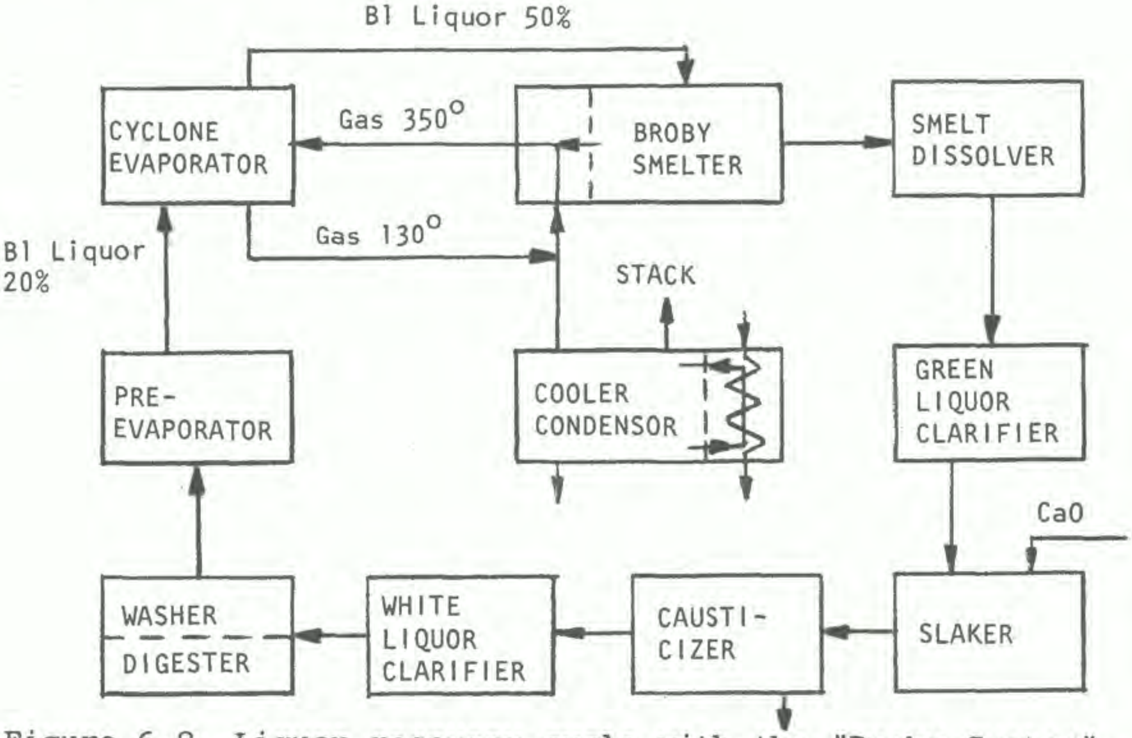


Figure 6.8. Liquor recovery cycle with the "Broby System" for chemical recovery

6.4 Low temperature processes - wet pyrolysis, wet combustion

Wet air oxidation technology is today commercially used for soda recovery (3, 10, 14, 15). One mill has been successfully operating a system since 1966.

Wet air oxidation is based on the principle that organic material, suspended or dissolved in water, can be oxidized in the presence of oxygen (air) under pressure. The degree of oxidation depends upon temperatures and pressures applied. The system is completely closed, assuring high levels of chemical and energy recovery.

In a typical wet air oxidation system, the black liquor, pre-evaporated to about 20-30 % dry solids, is brought to pressure by a high pressure pump. The liquor passes through heat exchangers, receiving heat from the out-going flow, and is then mixed with air from air compressors. The liquor - air mixture is injected into a reactor where the temperature is 250-300°C and the pressure up to 20 MPa. Under these conditions the organic compounds in the liquor are decomposed to simple compounds and the products are a steam-saturated "flue-gas" and green liquor.

A soda pulp system has no problems with the recovery of sulphur compounds. A system for kraft liquor chemical recovery including sulphur has recently been developed to the pilot-plant scale by the St. Regis Company in USA.

6.5 Emissions

The kraft recovery furnace can be operated with low emission of hydrogen sulphide or TRS but there is usually an emission of sulphur dioxide.

With good design and a proper distribution of air to the different levels, the emission of hydrogen sulphide can be kept very low. Less than 10 mg/m^3 norm can be maintained more than 90 % of the time. Because of the physical and chemical processes inside the kraft recovery furnace there are often peaks in the emission for instance when the load of the recovery furnace is changed.

The main part of the dust in the flue gases (mainly sodium sulphate) can be separated in the electrostatic precipitators and circulated back to the thick black liquor. Modern plants are equipped with two or three precipitator chambers giving a separation of more than 99.0 % equal to an emission of 0.3-0.5 kg dust/ton of pulp. With one of them closed the separation is 95.0-98.5 % (emission of 1-3 kg dust/ton of pulp).

The kraft recovery furnace can thus be operated at a low emission of hydrogen sulphide, but to be sure of very low emissions of sulphur dioxide it is necessary to install a scrubber (see paragraph 5.4.2).

This scrubber usually consists of a high and narrow tower with a number of intermediate partitions arranged so that the wash water and gases come into intimate contact with each other. A sodium hydroxide solution is usually employed as washing agent. White liquor or green liquor should be avoided because of the risk of hydrogen sulphide emission. The main reason for a scrubber is the occasional increase of the sulphur dioxide content of the flue gases. There is also some trapping of dust that has passed through the electrostatic precipitator. Hot water can be generated in the upper part of the scrubber.

If the plant is equipped with a direct contact evaporator the conditions are somewhat complicated (see chapter 5). The direct contact evaporator acts as an absorber with respect to sulphur dioxide and dust. If the oxidation of the black liquor is not arranged for the content of obnoxious reduced sulphuric gases in the flue gas will increase. From this point of view, the indirect contact evaporator is preferable to the direct contact system.

For the soda pulping process, conditions in the recovery process can be fully oxidizing and the problem of hydrogen sulphide (or TRS) is thus avoided. But there are still problems with sulphur dioxide and dust. The sulphur input is usually not zero, and an equilibrium level will build up in the system. The sulphur input ought to be kept low, for instance by using low-sulphur fuel oil or natural gas in the lime kiln. The sulphur dioxide can be absorbed in a scrubber and the scrubber liquor discharged, thus turning an air emission into a water pollutant. The dust emission can be handled in the same way as in the sulphate recovery system. Literature referred to: (13).

6.6 Costs

The kraft recovery furnace is a big and expensive piece of equipment. A soda recovery furnace is a little simpler, but it is still expensive. For small mills, this solution must be considered to be uneconomical.

Table 6.1 shows the options studied by Domtar Ltd in 1973. Option 4 was chosen and the fluidized bed has been operated since 1976 (2).

Table 6.2 (1) and Figure 6.9 (9, 16) give some data on recovery boilers, the SCA-Billerud process and fluidized beds. Data from the different sources do not agree.

The study of the adoption of the wet air oxidation process to the recovery of chemicals and heat in an Indian pulp mill indicates that this process is of interest. A simple calculation indicates that it could be economical in a small mill handling only 40 tons of pulp/day. The main factors influencing the feasibility of installing a wet air oxidation plant are the costs of caustic soda, electric power and the capital costs (6).

Table 6.1.

Option	Description	Capacity total (tpd)	Estimated cost USD (1973)	Time to become operable	Risk	Thermal efficiency
1	New 500-tpd recovery furnace	500	15 million	3 years + 6 mo	low	59
2	New 200-tpd recovery furnace plus Existing 300-tpd recovery furnace	500	12 million	3 years + 6 mo	low	56
3	Rebuilt 175-tpd recovery furnace plus Existing 300-tpd recovery furnace	475	5 million	2 years + 3 mo	low	53
4	Used Copeland reactor of 200-tpd future capacity plus Existing 300-tpd recovery furnace	500	3 million	1 year + 12 mo start-up	high	29/53

Table 6.2. Approximate chemical recovery equipment investment for a 300 ton/day NSSC pulp mill (million USD)

SCA-Billerud	Kraft recovery boiler	Fluidized bed	
		Without heat recovery	With heat recovery
5	8	4	5.5

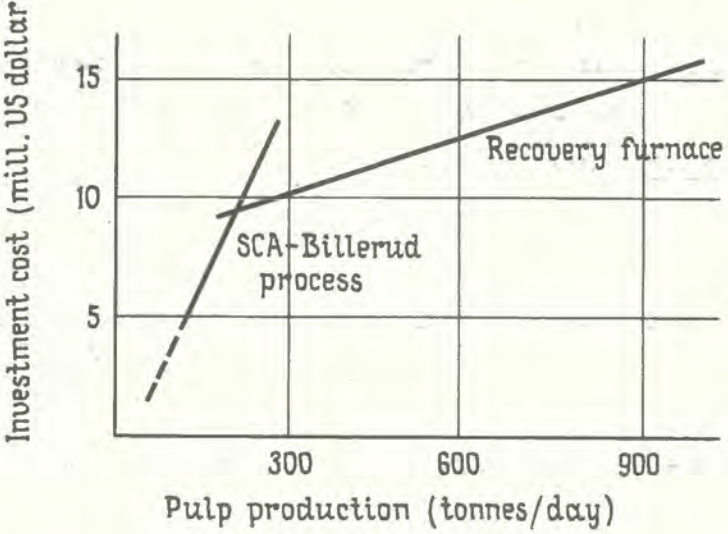


Figure 6.9. Investment costs for chemical recovery as a function of pulp production (9, 16)

The simplest recovery system, i.e. some kind of combustion chamber likt the "Broby smelter", has the lowest investment cost, but as shown in Table 6.3 the degree of heat recovery will determine the operating cost.

Table 6.3. Difference in operating costs for various chemical recovery systems for a 300 ton/day NSSC pulp mill in comparison with the SCA-Billerud reactor (USD/ton of NSSC pulp)

	SCA-Billerud	Kraft recovery boiler	Fluidized bed Without heat recovery	 With heat recovery
Steam prod	-	-10	+50	-
Capital costs	-	+5	-1.5	+1
Sub-total	0	-5	+48.5	+1

Literature reference list, chapter 6

(1) Annergren G. and Horntvedt E.:
NSSC or sulfur-free pulp methods for corrugating medium
Pulp & Paper International 16(1974): 6, 58-61

(2) Anon.
New approach to kraft recovery utilizes fluidized-bed reactor
Pulp & Paper 51(1977):10, 68-70

(3) Anon.
Wet air oxidation comes of age
Environmental Science & Technology 9(1975):4, 300-301

(4) The Broby Smelter. Information from Apparatkemiska AB
AKA, Box 15071, S-104 65 Stockholm, Sweden

(5) Borg A., Teder A. and Warnqvist B.:
Inside a kraft recovery furnace - studies on the origins of sulfur and sodium emission
Tappi 57(1974):1, 126-129

(6) Brunes B.:
The possibility of applying the wet air oxidation process to the recovery of chemicals and heat in Indian pulp plants
Indian Pulp & Paper 31(1976):1, 17-20

(7) Chamberlain R.E. and Wostradowski R.A.:
Key to recovery boiler performance is an understanding of variables
Pulp & Paper 52(1978):3, 96-101

(8) Horntvedt E.:
Chemical recovery according to the SCA-Billerud process
Sodahuskonferensen 1972 (in Swedish)

(9) Horntvedt E. and Grommi J.V.:
Use of SCA-Billerud recovery process for sodium based liquors
Paper Trade Hournal (1974):22, 32-34

(10) Morgan J.E. and Saul C.M.:
The Zimmerman process in a soda pulp mill recovery system. Development of a commercial process
Appita 22(1968):3, 60-75

(11) Rydholm S.A.:
Pulping processes, 1965

(12) The SSVL Environmental Care Project
Technical Summary
Stockholm 1974

(13) Vegeby A.:
How to burn black liquor efficiently - design and operation of Swedish recovery boilers
Swedish Pulp and Paper Mission to North America, Novermber 23 - December 7, 1973

(14) Watkins J.J.:
St. Regis study finds hydropyrolysis more beneficial than Tomlinson furnace
Southern Pulp and Paper Manufacturer 41(1978):4, 20-25

(15) Watkins J.J.:
Hydropyrolysis offers operational savings of $ 3.8 Million on 1000 TPD production
Southern Pulp and Paper Manufacturer 41(1978:5, 26-34

(16) Personal communication from Götaverken Ångteknik AB

7. CAUSTICIZING AND LIME CIRCULATION

7.1 Principles

The sodium carbonate (Na_2CO_3) in the green liquor has to be converted to sodium hydroxide (NaOH), the active chemical in the white liquor.

First the green liquor from the dissolving tank must be clarified from particles to reduce problems during causticizing. The green liquor sludge is washed to recover sodium compounds and the sludge can then be deposited.

Quick lime (CaO) is then mixed with the green liquor. The quick lime in a first step forms calcium hydroxide ($Ca(OH)_2$) which then reacts with the sodium carbonate (Na_2CO_3) to sodium hydroxide (NaOH) and calcium carbonate ($CaCO_3$) which is removed in the white liquor circulation.

$$CaO(S) + H_2O \rightarrow Ca(OH)_2(s)$$
$$Ca(OH)_2(s) + Na_2CO_3(aq) \rightarrow 2\ NaOH(aq) + CaCO_3(s)$$

Some impurities in the quick-lime are not dissolved but are separated from the liquor in an early stage of the causticizing. These grits are handled similarly to the green liquor sludge.

The calcium carbonate (lime mud) which is separated from the white liquor, is washed and then reburnt in a rotary kiln or fluidized bed to get fresh quick lime, which is used again.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

To compensate for the losses, make up lime is added, either as quick lime in the causticizing or as limestone to the lime kiln.

The lime kiln or the fluidized bed is usually fired with fuel oil or gas. The flue gas from the burning of the lime mud contains a high amount of carbon dioxide. The content of sulphur dioxide is low as most of it is absorbed in the lime. Emission of hydrogen sulphide can occur. This can be minimized by efficient washing of the lime mud to a low sodium content and dewatering to a high dry content.

The lime circulation is also discussed in paragraph 7.5.

7.2 Processes

Figure 7.1 is a simplified flowsheet showing the liquor preparation cycle.

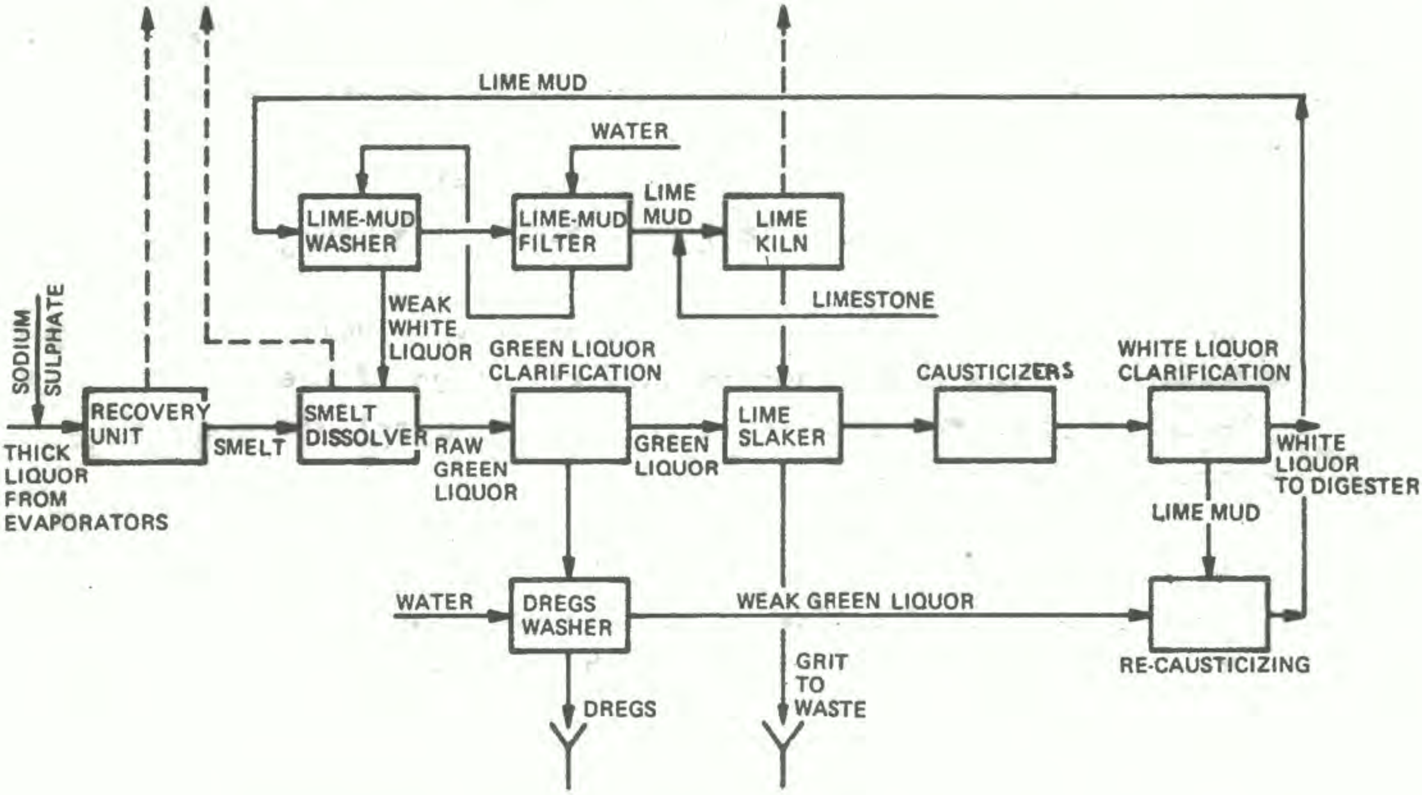


Figure 7.1. Chemical recovery system in a kraft mill

At least three different systems can be used for separation of the lime mud from the liquor. The conventional one is based on gravity settling in the clarification tanks, see Figure 7.2. The white liquor overflow is taken to white liquor storage tanks. The lime mud contains some alkali that is separated in mud washers which are of practically the same construction as the white liquor clarifiers. The overflow from the mud washers goes to the weak liquor storage and from there to the smelt dissolving tank.

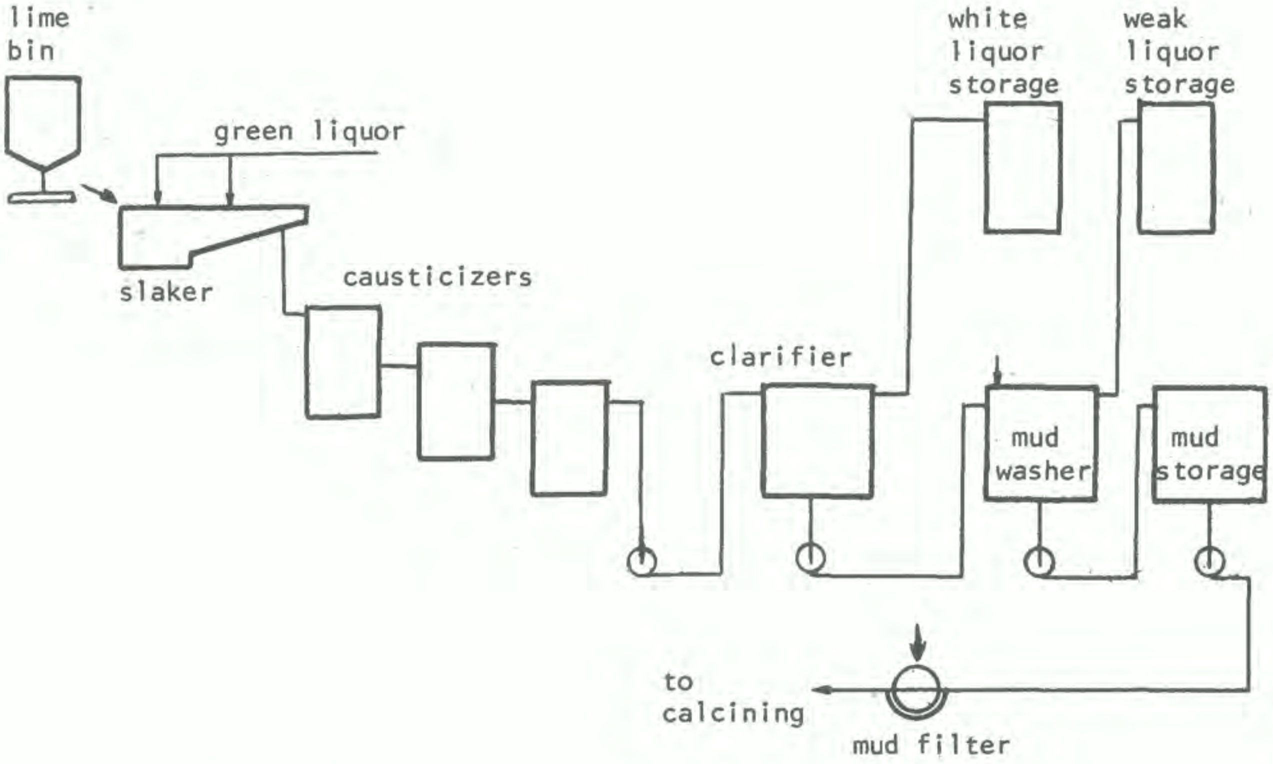


Figure 7.2. Conventional liquor preparation system

Figure 7.3 describes the flow scheme of a system in which the settling tanks are replaced by two belt filters. In the white liquor filter the lime mud is washed with a small amount of water, giving clear white liquor as the filtrate. Mud washing continues on the mud filter, where the rest of the alkali is washed out and the lime mud is dewatered to its final moisture content.

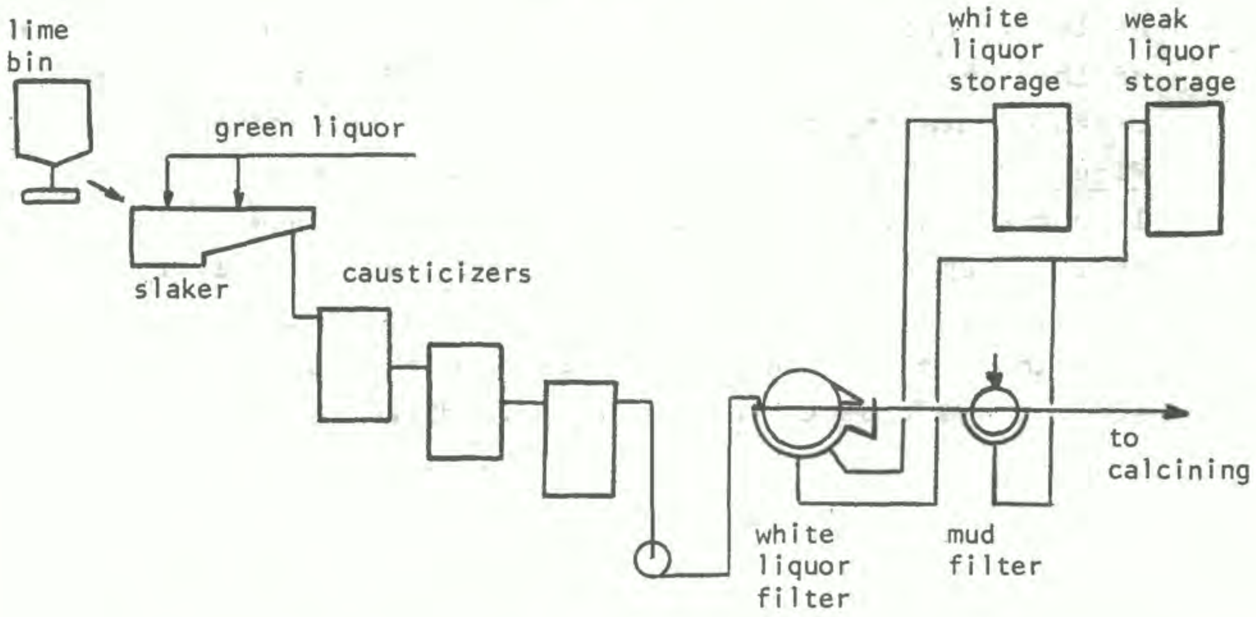


Figure 7.3. Liquor preparation system with belt filter

The white liquor filter in Figure 7.4 is a pressurized filter (Clarifil) giving a white liquor with a low particle content.

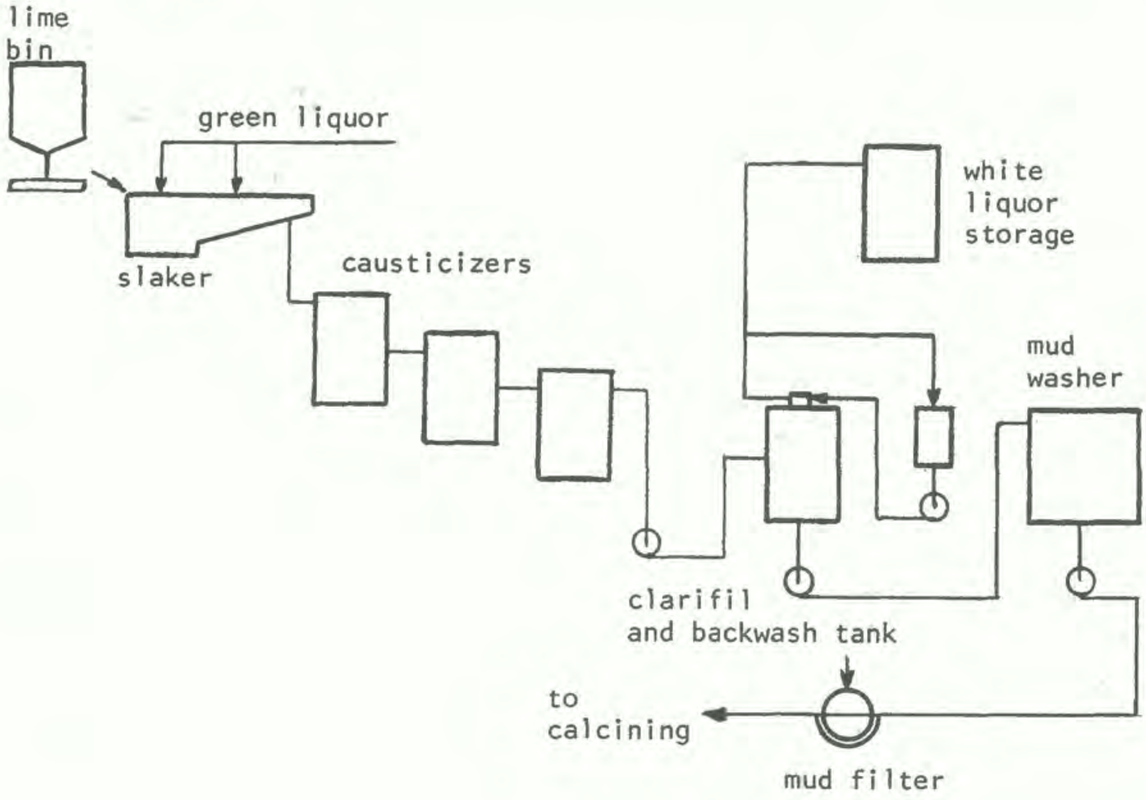


Figure 7.4. Liquor preparation system with pressure filter

The lime mud can be reburned in either a rotary lime kiln or a fluidized bed (Figures 7.5 and 7.6).

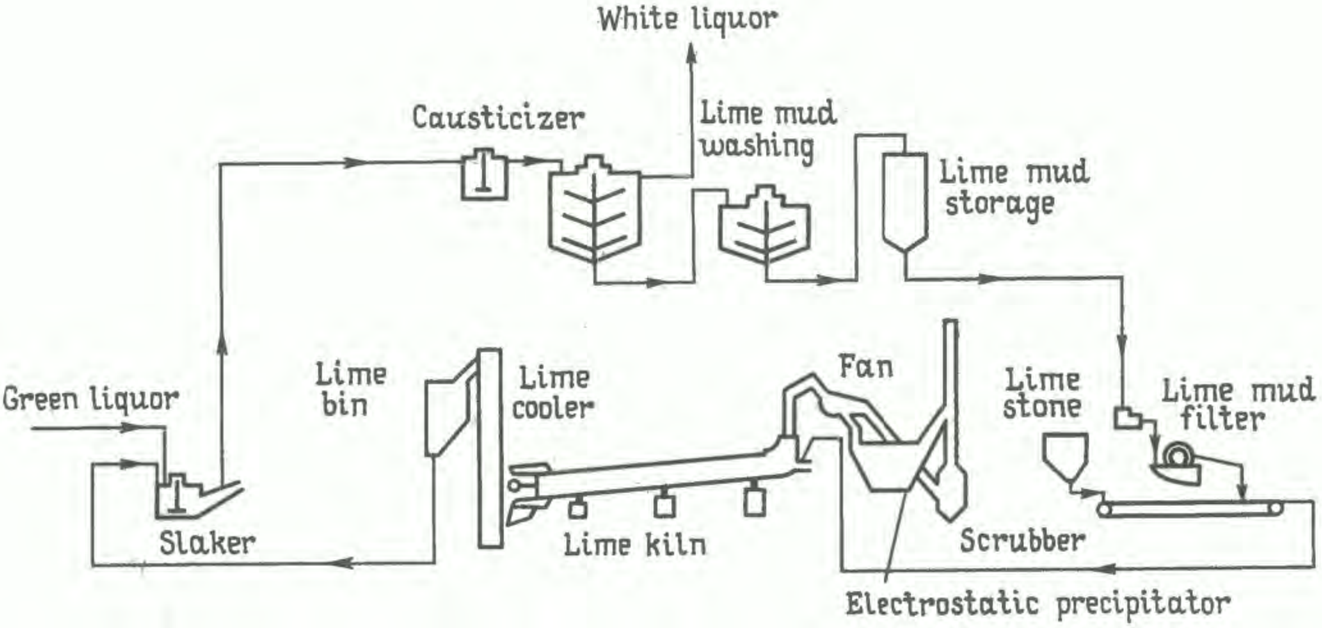


Figure 7.5. The lime kiln and causticizing department

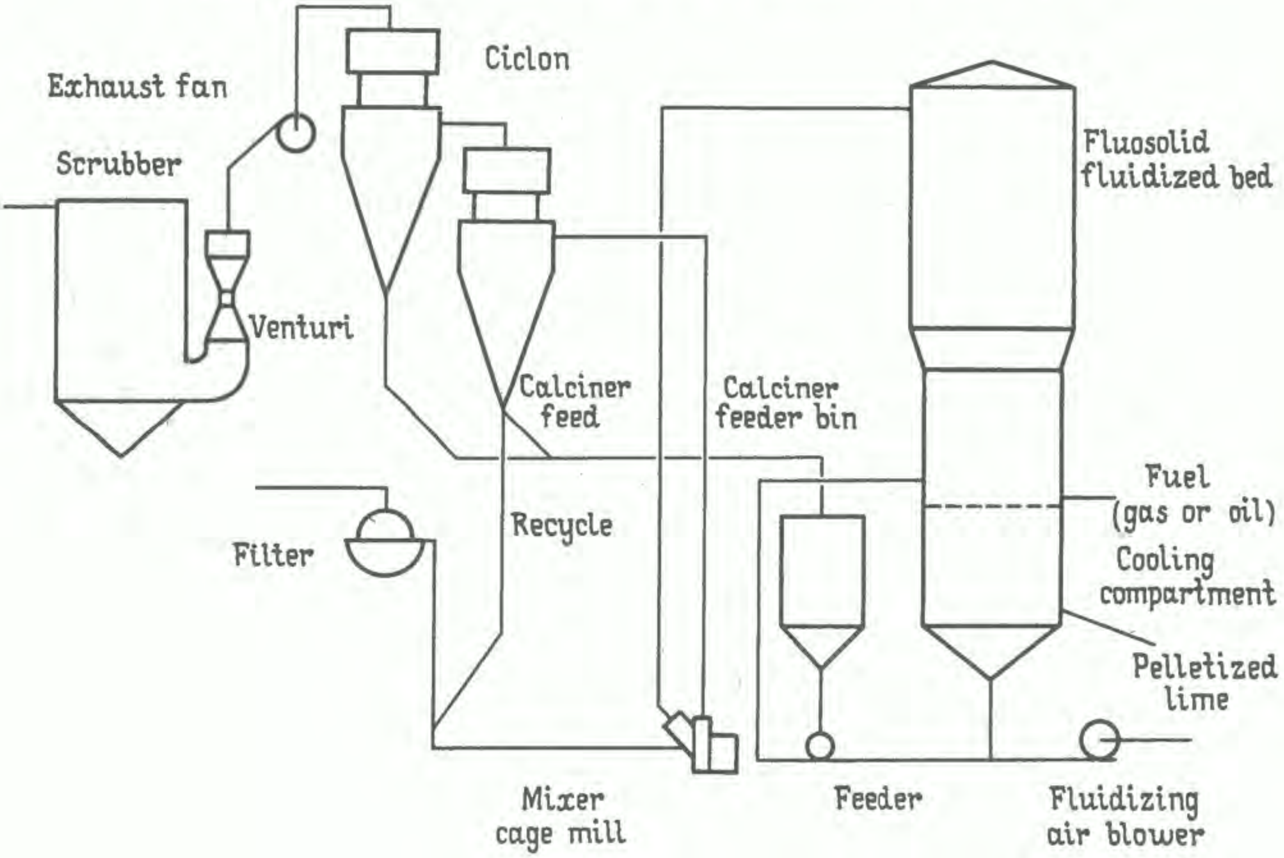


Figure 7.6. Lime mud reburning system with fluidized bed

7.3 Discharges

The normal discharges from this department are the flue gas from the lime kiln and the dregs and grits from the green liquor clarifier and the slaker. Discharges of lime mud are necessary in some mills because of high silica content of the fibrous raw material used.

One problem is the accidental discharges caused by, for instance, overflows from tanks. These can be minimized by making the storage tanks, located at strategic places in the system, big enough. It is also important to have proper control of the liquor levels and flows in the system.

The flue gases from the lime kiln are usually scrubbed or sometimes passed through an electrostatic precipitator to remove the main part of the dust. The dust consists mainly of calcium carbonate and sodium sulphate and carbonate. It can be discharged or circulated back to the system. If the scrubber liquor is discharged it can be used to neutralize other acid effluents.

If the lime kiln is fired with fuel oil containing sulphur, about three quarters of the sulphur input will be absorbed by the lime. Some more will be absorbed in the scrubber after the kiln. A discharge of 5-300 mg SO_2/m^3 norm is normal. The fluidized bed is a more efficient SO_2-absorber than the lime kiln, and the emission of SO_2 will be lower.

Sometimes there is a considerable emission of hydrogen sulphide from the lime kiln. One part of it originates from the remains of sodium sulphide in the lime mud. Part of this sulphide is driven off as hydrogen sulphide when the mud is dried in the low temperature part of the kiln. This emission can be minimized by a careful washing of the lime mud and by dewatering the lime mud to a dry solids content of 60-65 % before it is fed into the lime kiln.

High hydrogen sulphide emissions may take place if the lime kiln is not fired with the correct proportion of air to fuel in the flame. If this happens the combustion of fuel will not be complete and reduced gases, containing hydrogen sulphide, will pass through the long lime kiln giving high emissions. This can be avoided by controlling the air fuel ratio to the burner.

Sulphide containing liquor, for instance unclean condensates, must not be used in the scrubber after the lime kiln. Obnoxious gases will be driven off.

The emission of hydrogen sulphide in the flue gases is usually between 0 and 400 mg H_2S/m^3 norm, but it can be kept below about 50 mg/m^3 norm by steps mentioned above.

The discharge of green liquor sludge and grits from the causticizing is usually not a problem. The content of calcium carbonate is so high that it can be deposited without problems. If the lime mud is not burnt and circulated in the mill but discharged, problems may occur mainly because of the large quantities. Literature referred to (3, 8, 10).

7.4 Costs

The causticizing department consists mainly of relatively simple equipment, such as pipings, pumps and tanks and some kind of filters as described above.

An interesting part is the choice of lime kiln versus fluidized bed. The operating costs of these two alternatives have been compared under North American conditions (1967). For a mill with the capacity of about 400 tons of pulp per day or more, the capital investment for a lime kiln will be lower. For smaller mills, the fluidized bed will be cheaper. The operating costs compared for a 150 tonnes per day lime output are shown in Table 7.1. The investment cost for a lime kiln for 150 tonnes/day pulp production is 2-3 million USD.

Table 7.1. Comparison of operating costs. Burnt lime production 150 tonnes/day

	Rotary kiln %	Fluo solids %
Fuel	64.6	53.2
Electric Power	2.9	10.0
Labour	7.1	7.1
Maintenance	25.4	12.7
Total	100.0	83.0

7.5 The silica problem

7.5.1 Introduction

The main input of silica is usually the fibre raw material, but the make-up lime can also be a considerable source. The silicates give heavy scaling problems in the evaporators and also cause problems in the causticizing department. Several processes have been proposed to get rid of the silica but no process seems to offer a complete solution to the problem.

It appears, however, that the problem can be contained by limiting the inputs of silica and discharging some of the lime mud to keep the silica concentration below an acceptable limit.

7.5.2 Silica in the raw material

The large silica input to the pulping process comes with the raw material. Some tropical wood species contain high amounts notably the bamboo and annual plants.

Table 7.2 shows some data for different raw materials. Three groups can be identified with respect to silica content:

- low silica woods	0.01 % SiO_2
- high silica woods	0.1-3 % SiO_2
- non-wood plants	1-13 % SiO_2

Table 7.2. Ash and SiO_2 in some wood and non-wood materials (1)

Raw material	Ash, %	SiO_2, %
Scandinavian hardwoods	0.1-0.4	0.01
Scandinavian softwoods	0.1-0.4	0.01
Tropical hardwoods	0.3-3	0.01-3
Reed	3-6	2-4
Bamboo (India)	2-5	1-3
Rice straw	16-20	10-13
Cereal straw	5-10	4-6
Bagasse (depithed)	1-3	0.8-2

It is known that the content of trace-elements in growing plants and trees to a great extent depends on soil conditions. The content of various trace-elements can vary within very broad limits for samples of the same species.

The input of silica with the raw material can to some extent be influenced by the methods used in handling the raw material. It should be stored and handled in such a way that a minimum of soil, clay and sand is entrained to the process. An effective way is to wash it before or after the chipping.

For some raw materials the content of silica is higher in one of the fractions from the chip screening. For instance, the fines from chipped bamboo contain three times more ash than the accept (2). The input of unwanted elements, e.g. silica, therefore to some extent can be reduced by screening the chips.

7.5.3 Preparation of raw material

It is theoretically possible to remove the major part of the silica with an alkali treatment before the cooking. Experiments with bamboo (1) showed that 76 % of the silica could be removed by an alkali treatment with 2.0 % NaOH at 100°C during 24 hours. If the time was extended to 72 hours 85 % was removed. The chemical charge in fact corresponded to nearly one third of the chemical charge of normal kraft pulping of bamboo chips. Furthermore, the pretreatment caused a substantial degradation of the organic material, the yield of chips was 80 and 75 %, respectively. The high content of both sodium and organic material in the extraction liquor makes it necessary with a recovery of heat and chemicals, if this pretreatment process is used.

7.5.4 Cooking

During the cooking of the raw material, the silica is dissolved in the cooking liquor. As the alkali is consumed, silica compounds are precipitated on and within the fibres and follow the pulp through the washing and screening plants. However, the ability of the pulp to carry the silica with it appears to be limited. The surplus silica accumulates in the chemical cycle of the mill.

Laboratory experiments have shown that the formation of precipitate is strongly affected by the presence of aluminium. A certain amount of silica is thus precipitated on the pulp by aluminium ions. The distribution of silica between pulp and black liquor is affected by several factors. The total content of both silica and aluminium influences the distribution. The cooking conditions are also important, especially the amount of residual alkali.

7.5.5 Bleaching

If the pulp is used for unbleached paper grades, silica usually causes no problems.

With respect to trace elements the bleaching of the pulp can be regarded as an acid wash. This is also valid for the silica compounds. About 90 % is found in the effluent from the bleach plant, the main part in the effluent from the first acid stage. Closing the bleach plant can be expected to cause problems with the formation of deposits, if the streams are mixed in such a way that solubility limits are exceeded. This problem is not specific for silica compounds.

7.5.6 Desilication of the black liquor

Several methods of desilicating the black liquor have been proposed and tested. The silicate is precipitated by the addition of lime, magnesium salts, sulphuric acid or treatment with carbon dioxide. These processes all have in common that not only the silica compounds are precipitated, but also part of the lignin content. The precipitate that is formed is very difficult to dewater.

The pH of the black liquor can be decreased with sulphuric acid or carbon dioxide to a level where silicates precipitate. Precipitation of silica compounds is not very selective and is difficult to control. The process is not known to be used in mill scale (4, 6, 7, 9, 11).

The use of burnt lime to precipitate silicates has been successfully tested in laboratory and pilot plant. There are, however, no reports published from a planned full size plant (6).

The investigations reported here all dealt with black liquor from bamboo. The black liquors from bagasse and straw have higher viscosity and in these cases the precipitate may be even more difficult to separate and dewater (or wash) to recover some sodium and organics.

7.5.7 Silica scale formation in evaporation plants

The scaling in evaporation plants when concentrating black liquor is discussed in paragraph 5.3.2.

Today there is no ultimate solution to the silica scaling problem, but it can be minimized by keeping the silica content low and the pH of the black liquor high (NaOH or white liquor can be added).

7.5.8 Combustion

The problems found at the combustion of the liquor are mainly connected with high viscosity and low heating value of the liquor.

The viscosity is especially high for straw and bagasse black liquors. These must consequently be fired at a lower dry solids content, which lowers the thermal efficiency. It may be necessary to fire additional fuel in the recovery furnace to avoid black-outs. The high ash content of the liquors also contributes to a lower heat value of the liquor.

Silica containing deposits, which are difficult to remove, can also lower the thermal efficiency of the recovery unit.

7.5.9 Desilication of the green liquor

In the green liquor clarification heavy metals and some other unwanted elements are removed with the green liquor sludge. The content of silica and aluminium is almost unaffected.

If the mill operates without recovery and recirculation of lime, the green liquor clarification is not required, but if the lime mud is burnt and recirculated it is essential to remove as much of the impurities as possible in order to facilitate operation of the causticizing process, the lime kiln and the evaporation plant.

A method for precipitation of silica in green liquor with CO_2 has been tested in a pilot plant (4, 7, 11). The process is only suitable for soda pulping since H_2S will be formed when treating kraft green liquors.

7.5.10 Causticizing

The presence of silica in the causticizing process will have an influence on the chemical reactions and physical operations. The velocity of sedimentation is lower when silica compounds are present. These are colloidal and will also tend to block filter fabrics.

It is known from laboratory and mill experiences that the lime mud precipitated in the slaker is enriched in silicates. This has been confirmed by theoretical calculations. This fact has been used in the proposal for a two-stage causticizing process (7, 9, 11). The conditions in the first stage are controlled to give a maximum precipitation of silicate. In the second stage the causticizing is continued to give a white liquor (with a high degree of causticizing). However, this process is difficult to combine with lime mud burning.

An advantage in the attempt to keep the silica content of the system down is to use only make-up lime with low content of silicates. The quick lime and the green liquor are two sources of silica in the causticizing plant. If the silica content of the quick lime is kept to a sufficiently low level, there is a better chance of controlling the problem in the whole mill.

The essential thing is to limit the inputs of silica to the digesters. The fibre raw material has been discussed previously. The silica content of the other silica source, the white liquor, must be kept to the lowest possible level by efficient white liquor precipitation and separation of the silicate compounds.

It has been shown that even if the silica content of the green liquor from the recovery boiler is rather high the content of the white liquor can be kept reasonably low. This is because the major part of the silica is precipitated by the lime and follows the lime mud to the lime kiln. The silica is accumulated in the lime cycle as its two discharge flows, grits from the slaker and dust from the lime kiln, are not sufficient to expell more than a minor part of the silica. By operating the causticizing plant at constant conditions with good flow control over the green liquor and lime fed to the slaker and good white liquor mud sedimentation, it should be possible to maintain a high silica to lime ratio in the lime cycle, thus avoiding an unnecessarily high silica level in the clarified white liquor.

However, if the silica input to the lime cycle gets too high, which it usually does when pulping bamboo, straw, bagasse etc. it is necessary to discharge part of the lime mud and replace it with fresh quick-lime with a low silica content. This is a simple and safe method of keeping the silica level under control. The necessary discharge of lime mud, to keep the silica concentrations in the liquor streams below a certain limit, can be calculated when the silica content of the fibre raw material is known, and assuming certain values of the operating parameters.

Fluctuating causticizing efficiency ($\frac{NaOH}{NaOH+Na_2CO_3}$) has shown to have an unfavourable influence on the scaling problems in the recovery cycle. An important scale reducing measure is therefore to keep the conditions in the slaker and causticizers constant by controlling the lime and green liquor flows.

Literature reference list, chapter 7

(1) Baba M.A. and Veeramani H.:
Silica mass balances for kraft pulping of alkali pretreated bamboo chips
Tappi Nonwood Plant Fibre Pulping, 1978, 91-95

(2) Chaudhuri P.B.:
Machine manufacturer's viewpoint of pulping as applied to Indian conditions
Ippta 7(1970):2, 117-127

(3) Dalley O.T.:
Comparison of rotary kiln and Fluo Solids lime reburning system
Indian Pulp and Paper 22(1967):1, 91, 93-97, 104

(4) Idrees M. and Veeramani H.:
Conservation of lime by desilication of kraft green liquor
Ippta 12(1975):4, 336-339

(5) Sundkvist A. (IVL-Consulting Ltd):
Internal report, 1979

(6) Kalyanasundaram K. et al:
Problems encountered in processing bamboo black liquor in recovery installations in India
Tappi CA Report No 43 (1972), 79-117

(7) Misra D.K.:
Installation and operation of chemical recovery system in soda pulp mills utilizing wheat straw and bagasse as raw material
Tappi CA Report No 43 (1972), 119-175

(8) Osterman O.T.:
A new look at recausticizing
Pulp and Paper 36(1962, July 9):14, 41-46

(9) Sadawarte et al:
Studies on desilication of bamboo kraft green liquor
Tappi Nonwood Plant Fibre Pulping 1977, 23-32

(10) The SSVL Environmental Care Project
Technical Summary
Stockholm 1974

(11) Veeramani H.:
Significance of silica during pulping chemical recovery in bamboo kraft paper mills
Tappi Nonwood Plant Fibre Pulping 1979, 13-22

8. TEMPORARY AND ACCIDENTAL DISCHARGES

8.1 Introduction

The total discharges from a kraft pulp mill to its water recipient may be divided into the process discharges and the temporary and accidental discharges.

It is relevant to discuss temporary and accidental discharges of chemicals from those mill sections that have some form of chemical recovery. Temporary and accidental discharges from mills or mill sections without chemical recovery systems are of no interest since the chemicals are to be discharged anyway.

It is relevant to discuss temporary and accidental discharges of fibre since the mill always aims at having all incoming fibre in their product.

Surveys have indicated that 20-70 % of a mill's total discharges are temporary and accidental discharges. As the process discharges decrease with, among other things, better equipment and more closed systems, the relative importance of the temporary and accidental discharges will increase.

8.2 Definition of discharges

A mill's total discharges are divided into the process discharges and the temporary and accidental discharges.

Depending on the time duration of the discharges they are divided into peak and level discharges. A peak discharge is a distinct rise of the discharge for a short period of time while a level discharge shows only small variations over a given time (Figure 8.1).

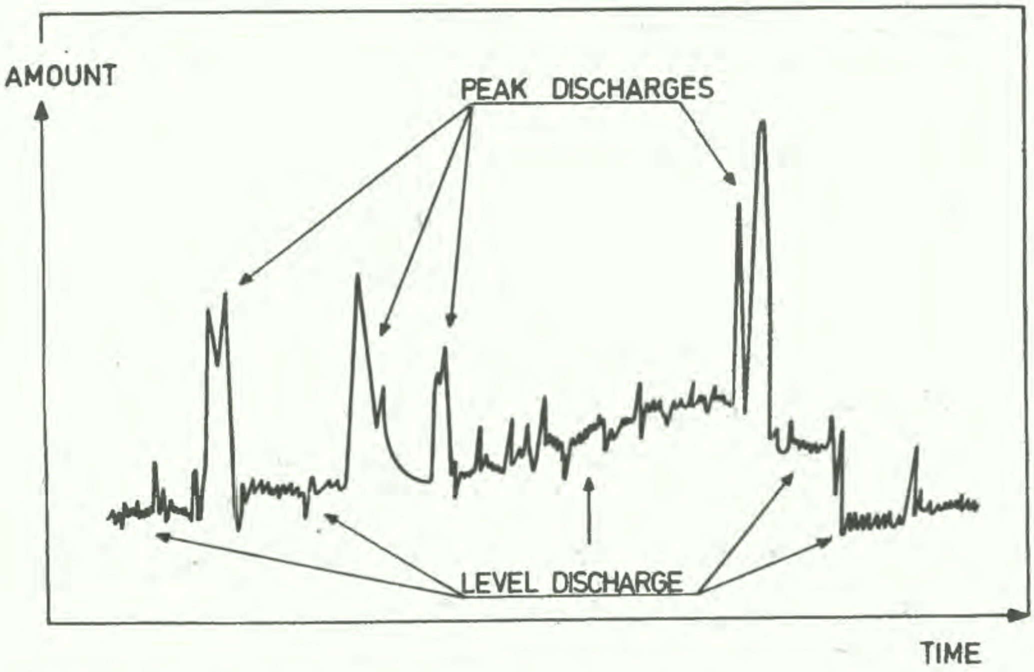


Figure 8.1. Example of level and peak discharges

The process discharges are "normal" discharges that cannot be avoided. The discharge level depends on the size and type of equipment used, the process design and the normal production variations (e.g. change of product quality). Emission of dust from the recovery furnace is an example of a level type process discharge. Peak type process discharges can occur, for example, when emptying discontinuous digesters. The process discharges can be predicted.

The temporary and accidental discharges are the discharges that substantially exceed the normal discharges for the process or equipment or are in any other way abnormal. They are caused by faulty equipment, incorrect process control strategy or by the human factor. The temporary and accidental discharges may be of peak as well as of level type and cannot be predicted (Figure 8.2).

Due to lack of information about the discharge causalities and of the process and effluent streams dynamics it is very difficult to separate the temporary and accidental discharges from the process discharges in short period effluent measurements.

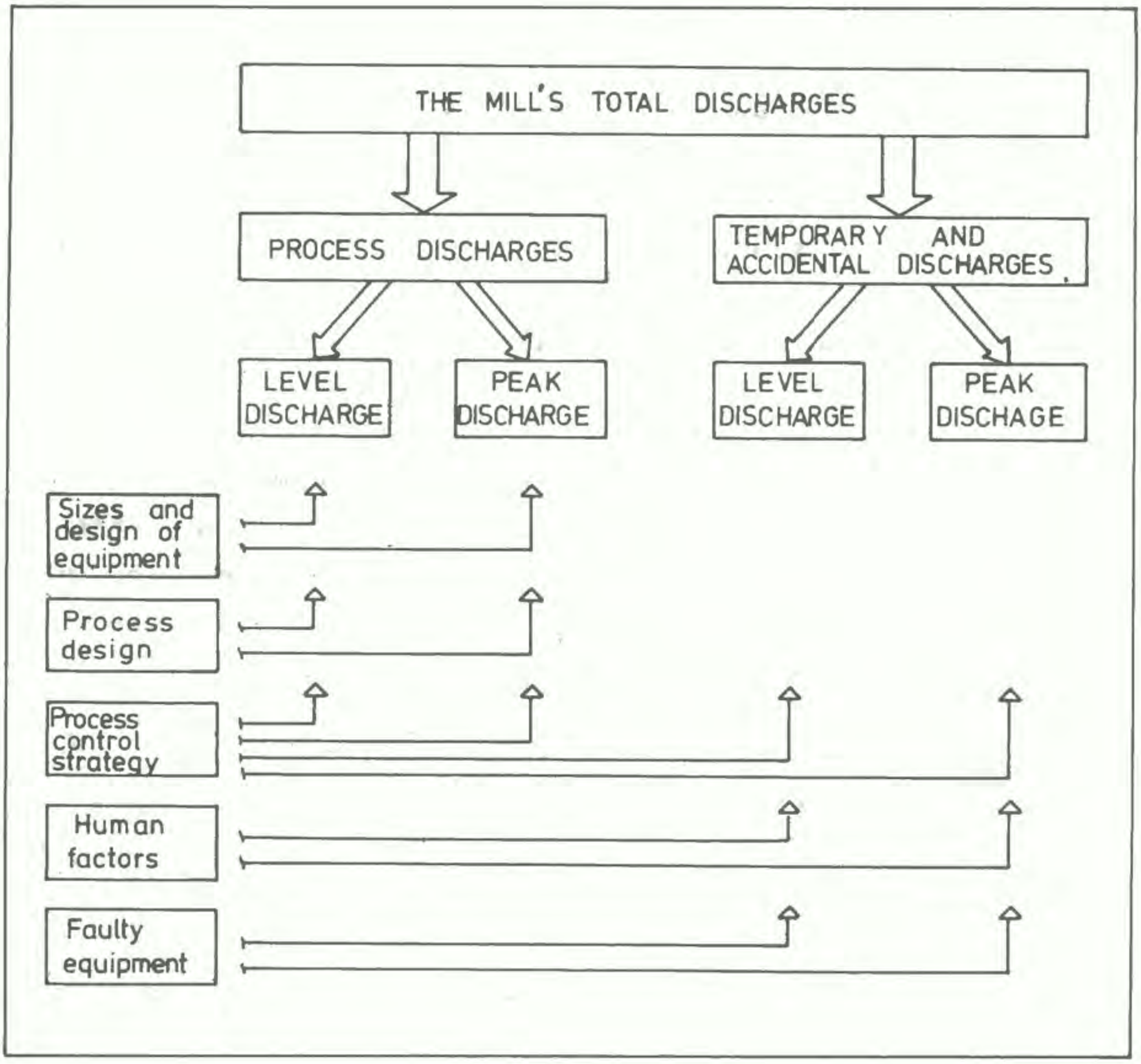


Figure 8.2. The segregation and causes of the total discharge

8.3 Nature of process discharges

In every mill there is a basic discharge level that is made up by the unavoidable process discharges. This basic discharge level differs between mills and depends on incoming wood, the chosen equipment, the mill's dimensions, the process design, the bleaching sequence, the desired product quality and several other factors.

The process discharges can be divided into:

- discharges of soluble substances
- discharges of suspended solids

The process discharge of soluble substances consists of dissolved organic substances and inorganic compounds that remain with the pulp after final washing or are generated in the bleaching stages or come with the condensate.

The quantity of soluble substances that remain in the pulp after final washing will be discharged in the bleaching effluent in the case of a closed screening system or will be divided between the screening and bleaching effluents if there is an open screening system.

The process discharge that is generated in the bleaching department depends on pulp grade, incoming pulp Kappa number, dissolved organic and inorganic substance with the incoming pulp, bleaching sequence and bleaching conditions.

The condensates contribute mainly with volatile organic substances. Use of condensate as replacement for warm water in the process and steam stripping of the most contaminated condensates will reduce their part of the process discharges to a minor one.

The process discharges of suspended solids consists of fibres and inorganic compounds. The fibres discharged are those fibres that pass through wire cloths and the fibre reject from the final screening stage. Hence the fibre process discharge is dependent on closure in the bleaching and screening departments and their filtrate surplus.

The inorganic suspended solids come from the recovery departments and are mainly lime, lime-mud and dregs from the green liquor clarifier. If there is a bark fuelled furnace, ashes from it may give a substantial contribution of suspended solids in the effluent.

The discharge from the rest of the mill should only consist of unpolluted cooling and sealing water and surplus warm water. There will, though, be a small discharge when mill departments are cleaned.

8.4 The temporary and accidental discharges

The temporary and accidental discharges are a very complex problem area. The observed discharge may be caused by an incident in a completely different part of the process and a relatively small disturbance can result in a considerable imbalance in the system and a big discharge.

To analyse the temporary and accidental discharges and to recommend measures to avoid or minimize them they will here be classified first according to the causes of the discharge and then according to its origin in the process.

8.4.1 Causes of temporary and accidental discharges

First the temporary and accidental discharges can be classified as to the reason for the discharge:

- faulty equipment
- human factor
- incorrect process control strategy

Generally one can assume that incorrect process control strategy as primary or secondary cause results in the biggest discharges. When faulty equipment or the human factor causes a discharge it is usually soon detected and is relatively simple to stop. Discharges caused by incorrect process control strategies are more difficult to detect and may take a very long time to correct.

Faulty equipment can cause discharges for various reasons at the same time. An example will illustrate this. A machine breaks down, which usually gives rise to a leakage. In order to repair the machine the pipe system around it must be emptied and, if there is no collecting system connected, this operation will result in a discharge. The production in the process section must be reduced and the buffer tanks earlier in the process will therefore fill and may overflow. At start-up there is always a risk of discharges before the system is in balance again. If the machine has to be re-started several times the risk of discharges is multiplied. This simple example shows how one single failure can result in several different kinds of discharge. The frequency of this type of temporary and accidental discharges can be reduced with a well developed system of preventive maintenance.

The human factor causes many temporary and accidental discharges due to lack of or misunderstood information, forgotten duties when more important matters require action, neglected repair and maintenance, etc.

Incorrect process control strategy is a more complex cause to discharges than the two earlier ones. The difficulty is to keep the right production rate in every section and in time adjust the production to changing conditions. It is quite usual for two sections, with a buffer tank between them, to run at different production speeds. This will result in the buffer tank overflowing or in one of the sections having to be stopped if the speed difference is not adjusted in time. Since some mill sections need a long time to adjust their production speed and buffer tanks are often too small or are already filled, this will lead to discharges that may have to go on for several hours.

If speed is changed in one section several others need to be adjusted. It is a complicated task to do this correctly because of different responding times to a change in different mill sections and to balance all the buffer tanks. Experience shows that there are often problems of this kind when mill sections are started or stopped which may happen many times in a week. Generally the lowest discharge level is reached when constant production at mill capacity is maintained.

8.4.2 Origin of the temporary and accidental discharges

Another way to classify the temporary and accidental discharges is according to their origin in the process.

- Liquor losses from the black side of the chemical line.

- Liquor losses from the white side of the chemical line.

- Losses from the fibre line after final washing.

The content of the discharges differs very much depending on the part of the process of their origin. It is therefore useful, in an analysis of temporary and accidental discharges, to distinguish between discharges from different sections of the process with regard to what is their primary contaminating substance.

Liquor lost from the black side of the chemical line contains both dissolved organic substances and inorganic compounds and sometimes also fibre. It is relevant to discuss losses of this liquor up to the final stage of the washing from which liquor is taken back to the evaporation and the recovery furnace.

Liquor lost from the white side of the chemical line contains mainly soluble and suspended inorganic compounds. If condensates are used in the causticizing sections organic substances can also be present in these liquors. The suspended inorganic compounds are lime, lime-mud and possibly dregs from the green liquor clarifier.

From the fibre line after final washing only fibres can be lost in temporary and accidental discharges. The discharges from the sections after the final washing stage contain both organic substances and inorganic compounds, but since there is no more recovery in the process, there is little relevance in discussing temporary or accidental discharges of these substances.

8.5 Strategies to reduce and control the temporary and accidental discharges

There are two levels of measures to reduce and control the temporary and accidental discharges:

- prevent the discharges from reaching the recipient
- prevent the discharges from occurring

The first level is of a concrete technical nature. The discharges are collected somewhere on their way from the process to the recipient and then returned. The cost of building and operating these collecting and returning devices are easy to calculate and the benefit of each installation is observable.

The second measure level is more a matter of organization, supervision, priority and education. This includes planning of production, preventive maintenance, correct use of the total buffer capacities, thorough process check-up and elimination of discharge sources wherever possible, continuous investigation of the discharges and the make-up chemical consumption and education of all personnel concerned. It is much more difficult to calculate the costs and to quantify the benefits of this kind of measure. It is almost impossible to specify the outcome of any particular measure.

Building a system that collects and returns discharges to the process will reduce the mill's total discharge significantly but the operating costs can be very high, for instance when diluted discharges are returned to the evaporation plant. To achieve a low level of temporary and accidental discharges at reasonable costs, measures must be applied, primarily, on the second level.

8.5.1 Preventing the dischages from reaching the recipient

Liquor losses

Measures to collect and return liquor losses include:

- Diking around tanks and equipment where concentrated liquors are handled. A discharge is collected within the walls and can be returned directly to the process since there is no dilution or contamination of the discharged liquor (Figure 8.3).

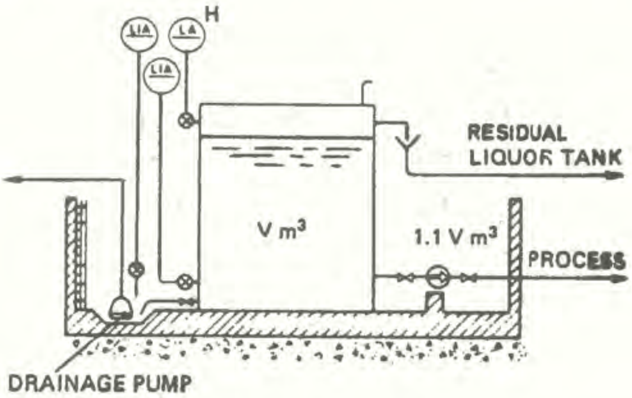
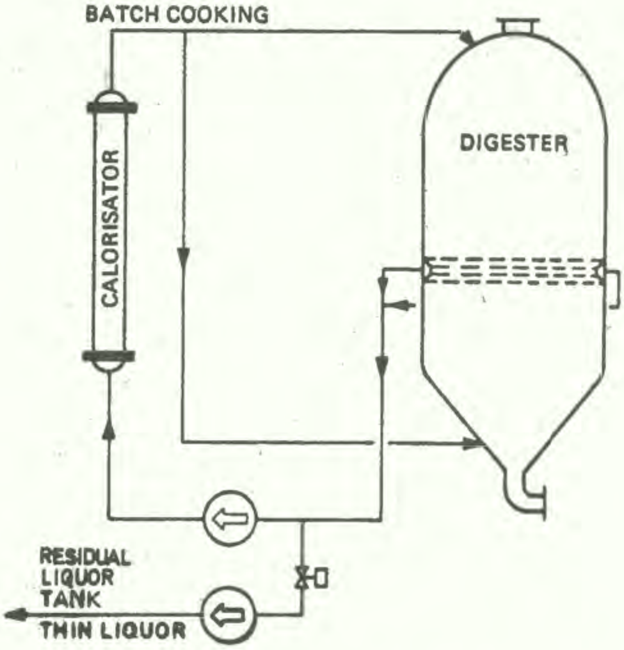


Figure 8.3. Diking around tanks and equipment

Drainage systems for tanks and machinery take care of remainig process liquors when there is a need for emptying and repair work. The process liquors are brought to a residual liquor tank and then returned directly to the process instead of being discharged to the sewers (Figure 8.4).



Residual liquor in the circulation system is pumped to the residual liquor tank

Figure 8.4. Clearing the circulation system in batch digesters

- Separation of the sewer system into sections and supervision of the effluent contamination with conductivity gauges. Discharges that reach the sewer system are detected by the conductivity gauge. When the conductivity rises above a given limit a pump starts and the effluent stream is returned to a residual liquor tank. The residual liquor is fed to the evaporation and recovery furnace to recover the chemicals and energy. In this kind of system the temporary and accidental discharges may get very diluted when returned to the residual liquor tank and the operating cost can be high because of the steam consumption required to evaporate all the excess water (Figures 8.5 and 8.6)

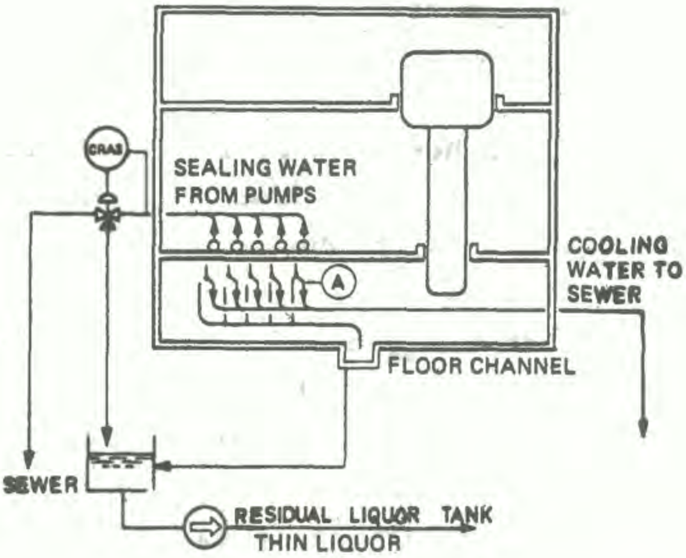


Figure 8.5. Sewer system from evaporating units

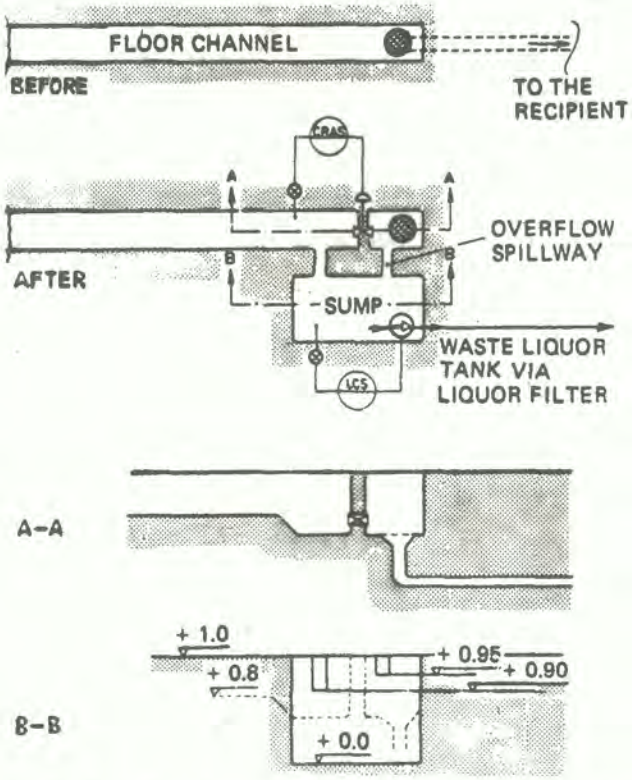


Figure 8.6. Design of sewers for cooking, washing, evaporating or causticizing plants

Building dikes and drainage systems to collect the concentrated process liquors directly where they are accidentally discharged and return them straight back to the process without any dilution or contamination are economically and environmentally well justified measures.

As a discharge reaches the sewer it is diluted with unpolluted effluents from other sections of the mill and may be contaminated with whatever is in the sewer. A discharge that is to be returned from this position must be taken to a residual liquor tank and then through the evaporation plant. There must be a concentration limit below which no effluent is returned. This implies that the discharge will never be wholly recovered. A system that recovers diluted discharges is expensive to operate and the operating costs rise with the energy prices.

For all kinds of installations aimed at preventing temporary and accidental discharges from reaching the recipient a general rule is that the discharges should be collected and returned as nearly as possible to the position from which they originated. The more diluted the discharges become, the higher the operating costs for returning them will be and the lower the quantity of the discharges returned will be.

Fibre losses

Fibre losses from the fibre line after the final washing stage are difficult to detect and return to the process. Recording instruments have not been available for measuring the fibre concentration in an effluent stream but new developments are under way. The big water volumes that accompany these discharges make them difficult to return directly to the process especially when the screening system is closed.

Fibres are lost by temporary and accidental discharges mainly in two ways.

Primarily fibres are lost with filtrates when there is a hole in the wire cloth or when the sealing band of the filter drum slacks or cracks. The solution with this kind of fibre discharge is to detect and stop it as soon as possible. Continuous measuring of the fibre content in the filtrate and the detection of the source of a discharge are problems that contribute to the size of these discharges. Because of the big filtrate volumes such discharges cannot be directly returned to the process. The filtrate must be brought to a sedimentation basin where the fibres are separated. Contamination with other suspended solids decreases the value of the recovered fibres. Since fibre losses, both as process discharges and as temporary and accidental discharges, influence the fibre content in the filtrate, the total loss of fibres is closely related to the filtrate surplus. By closing the screening and bleaching systems this loss can be reduced.

The second cause of temporary and accidental fibre discharges is by overflows of filters, tower tops and other fibre losses to the floor sewer system. These discharges can be recovered if the sewer system is connected to a filter that separates the fibres present. The recovered fibres are contaminated with everything else that comes to the floor sewer and must therefore be returned to the process in the pre-bleaching screening plant if this is an open one. If there is a closed screening system a separate screen must be installed. The profitability of a system like this depends on the extent of installations needed and on the amount of fibres that can be recovered.

8.5.2 Preventing the discharges from occurring

Measures to prevent temporary and accidental discharges from occurring include:

- Thorough investigation of the process and the equipment regarding the risk of discharges and elimination of discharge sources wherever possible. This investigation aims at detecting where the temporary and accidental discharges are frequent and deciding how to reduce them. Generally speaking no one really knows where the discharges come from or what causes them. When this can be determined it is relatively easy to eliminate the cause. Increased knowledge about the process and the mill is gained by this work and is of great value not only for reducing the discharges but also for reducing the energy and chemical consumption and for facilitating control of the whole process. It is of great importance that this kind of work gets priority and is continuously followed up.

- Preventive maintenance with the emphasis on discharge elimination. The maintenance of environmental protection instruments and equipment must not be separated in any way from the maintenance of other instruments and equipment. Badly maintained equipment will break down often resulting in accidental discharges. In the same way instruments that give negative or misleading information can cause discharges. A well organized preventive maintenance system and continuous follow-up of positions known to be troublesome will reduce temporary and accidental discharges. At the same time costly repairs of faulty equipment will be reduced and mill productivity will increase with fewer stops due to repair work.

- Planning, coordination and supervision of the production in different sections to achieve smooth production rate changes. The production planning is a very complicated process. The mill aims at producing a certain amount of pulp. The desirable way to achieve this is with the mill in a steady state condition. This is of course in reality impossible. Disturbances occur in the process and the person responsible for the production has to take decisions on how to meet these disturbances. The communication between the process sections must be good to provide for information passing as quickly as possible from one section to another. If the production speed is reduced in one section it will have consequences in other sections. To take the right corrective measures in these sections is difficult. Maintaining production and avoiding of discharges are areas of operation that often come in conflict with each other. Uncertainty as to when the original disturbance has been eliminated makes it difficult to undertake suitable process adjustments at the right moment. As long as maximum production is aimed at the decisions may not be too difficult to make, but when the environmental aspects must also be considered there is a great need for aids in the decision making. Such aids can be, for example, a display over the production and buffer situation in the mill at any moment and maybe a computor programme that can simulate what will follow different adjustments made in the process.

- Well dimensioned and correctly used buffer tanks. This is an important tool to keep production running smoothly in the mill. These tanks are supposed to buffer production alterations. Unfortunately they are mostly used as storage tanks that are kept full and in many cases only 10-20 % of their nominal buffer capacity is available. The optimum level in each buffer tank must be decided upon with regard to what it is supposed to buffer, how severe the consequences will be if that tank gets empty or full the capacities of the process sections before and after the tank.

Knowledge of the buffer tank levels at any moment is important for the production planning and the use of the buffer tanks as buffers, and not as storage tanks, will reduce the temporary and accidental discharges.

- Environmental education to all personnel. A large number of temporary and accidental discharges are influenced by the human factor and can be substantially reduced if all personnel are aware of the importance of these discharges. An educational programme should aim at giving the participants knowledge of the consequences of polluting discharges, both the process discharges and the temporary and accidental discharges. The strong possibility of an individual influencing these discharges must be stressed. It is important that not only operators and foremen are made aware of this, but all personnel at the mill. An important group is the service and maintenance personnel.

- Continuous follow-up of the mill discharges and the make-up chemical consumption. Where the discharges originate, what causes them and suitable measures to reduce them are important parts of this work. Tendencies to a rise in discharge level or new discharge sources must be investigated and preventive measures taken. The follow-up of the discharges could consist in measuring the sodium and the suspended solids content in the effluent. The sodium content should be compared with the make-up sodium consumption per month to make sure that all discharges are found.

  A monthly evaluation is recommended to avoid the possibility that changes in volume and concentration of the liquor stock affect the proposed comparison too much. A continuous follow-up like this will serve as a means of keeping personnel constantly aware of the problems as well as maintaining a high level of knowledge on how the mill is performing and where extra measures are needed.

8.6 Economic consequences

For a proper decision on how to treat the temporary and accidental discharges the costs to recover them must be analysed. Investments in collecting and recovering systems, operating costs for dewatering, evaporation and pumping and the value from recovered chemicals, fibres and the energy in recovered liquors are all relatively easy to calculate. Generally speaking devices that collect and return discharges at the source are low in investment and operating costs and the value of the recovered discharge is high. When the discharge has become diluted and contaminated in the sewer system the costs of recovery increase drastically and evaporation of diluted liquors is especially expensive.

Together with these investment and operating costs there are some other costs and returns that are more difficult to analyse. The more complex a system gets the higher is the risk of operating problems. Maintenance and control must be given priority. Increased information about the mill and the process is a valuable asset following from a thorough investigation of the mill's discharge sources. Fewer break downs reduce repair costs and increase productivity. There may also be a reduced need for external treatment of the effluents with reduced temporary and accidental discharges.

8.7 Conclusions

The total as well as the temporary and accidental discharges can be reduced to a much lower level than today's situation. This can be accomplished by the following measures:

- Thorough investigation of discharge sources and measures to eliminate or reduce them.

- Preventive maintenance aiming at reduced discharges.

- Build buffer tanks of sufficient size and use them as buffer tanks and not only as storage tanks.

- Build collection dikes around machinery and tanks where concentrated process liquors are handled. Return the discharges from these straight back to the process as close as possible to the discharge sources.

- Build drainage systems that take care of the process liquors when there is a need to empty any equipment.

- Develop an organized production planning system with necessary aids.

- Educate all personnel that in any way can influence the discharges.

- Review the discharge situation, make-up chemical consumption and steam consumption continuously to keep a clear view over the mill status and be prepared to act immediately as soon as anything starts to diverge.

9. ABBREVIATIONS

a Cl = active chlorine
ADMT = air dry metric ton
atm = atmosphere (unit for pressure)

bar = pressure unit (1 Bar = 10^5Pa = 1,013 atm)
BDMT = bone dry metric ton
BOD$_5$ = biochemical oxygen demand during 5 days
BOD$_7$ = biochemical oxygen demand during 7 days
BOD$_{20}$ = biochemical oxygen demand during 20 days

C = chlorine (Cl$_2$)
°C = degree Celcius (centigrade)
cal = calori
CC = chlorine compounds
CD = cross direction
C/D = chlorine/chlorine dioxide bleaching stage
COD = chemical oxygen demand
CSF = Canadian standard freeness

d = day. 1 day = 24 hours
D = chlorine dioxide (ClO$_2$) or dilution
D$_2$ = second chlorine dioxide stage
DR = displacement ratio

E = alkali (NaOH) stage
(e) = over-pressure

F = filter
°F = degree Farenheit
FW = fresh water

g = gauge. Sometimes used to indicate pressure relative to atmospheric pressure
Gcal = gigacalori. 1 Gcal = 10^3Mcal

h = hour
H = hypochlorite (NaClO or CaCL(ClO)) or Hi-Heat
H_{20} = dosage 20 kg hypochlorite/tonne of pulp
h.p. = high pressure

J = joule (unit of energy)

°K = degree Kelvin (unit for temperature)
Kcal = kilocalori. 1 Kcal = 4.187 x 10^3 J
Kg = kilogram
KwH = kilowatthour. 1 kWh = 3.6 x 10^6 J

l = litre
lbs = pounds (= 453,6 grams)
l.p. = low pressure

m = meter
M = chlorine monoxide
Mcal = Megacalori. 1 Mcal = 10^3 Kcal
MD = machine direction
MS = mild steel (black iron)

N = Newton (unit for force). 1 N = 0.1020 kp

O = oxygen (O_2)

P = Press or Peroxide (H_2O_2)
Pa = Pascal (unit for pressure). 1 Pa = 10^{-5} bar
ppb = parts per billion
ppm = parts per million
Pt = platinum. Comparison standard at colour determination
psi = pound-force per square inch (1 psi = 0.068 atm)

R = radial washer (continuous diffuser)

SCAN = Scandinavian standard procedure
sec = second
SF = screening plant filter (decker)
°SR = degree Schopper Riegler (unit for pulp freeness)
SS = suspended solids

t_{90} = tonne 90 % dry pulp
T = wash press
TOC = total organic carbon
ton = short ton (200 lbs)
tonne = metric ton (1000 kg)
TRS = totally reduced sulphur

USD = United States dollar currency

V = volt (1 V = 1 W/A)

W = watt (unit for heat power). 1 W = 1 J/s

y = year
Yr = year

304 = AISI 304 (lower stainless steel quality)
316 = AISI 316 (higher stainless steel quality)

APPENDIX 1

BASIC DATA FOR ECONOMIC CALCULATIONS

1. GENERAL

A common method for presentation of the economic calculations has been used in this manual. The calculations have all been based on standard basic data and on standard prices. All prices have been received from suppliers of equipment, chemicals etc. and from Swedish pulp and paper mills. The price level adopted is that prevailing during the 1st quarter of 1979.

2. PRESENTATION OF AN ECONOMIC CALCULATION

As far as possible the following pattern has been used in the presentation of an economic calculation.

	Alternative		
	1	2	3
Investment costs:			
Apparatus, insulated	....		
Buildings and foundations	....		
Pipes and fittings installed, insulated	....		
Electrical installations	....		
Instruments installed	....		
Secondary investments: electricity, heating, water and personnel	....		
Other secondary investments (workshops, offices, roads, trucks etc.)	....		
Total 1 thousands of US dollars			

Alternative
1 2 3

Total 1 ....

Project planning, control, administration (10 % of total 1) ....

Various unspecified equipment (7 % of total 1) ....

Total 2 thousands of US dollars

Alternative
1 2 3

Total 2 ....

Interest and insurance during the erection period ....

(1 year erection, 5 % of total 2) ....
(2 years erection, 10 % of total 2) ....

A) TOTAL thousands of US dollars

Alternative
1 2 3

Operating costs (gross):

Electricity ....

Heating ....

Chemicals, delivered at mill ....

Personnel ....

Maintenance of equipment (including related investments) ....

Costs of handling materials and chemicals within the mill ....

Refuse disposal costs ....

B) TOTAL thousands of US dollars

	Alternative		
	1	2	3
Operating income.			
Saleable products (ex mill)	....		
Other income	....		
C) TOTAL thousands of US dollars			

	Alternative		
	1	2	3
Economic result:			
Net operating costs (B minus C)	....		
Capital costs (16,27 % of A)	....		
TOTAL ANNUAL COST thousands of US dollars			

Investment costs have been assessed from estimates submitted or from data gained by experience.

Recovered fibres are valued as saleable pulp with a reduction for drying costs. Changes in capacity of a mill have been evaluated with the aid of the contribution to fixed costs resulting from the change in pulp production.

Capital costs include both interest and depreciation of invested capital. The residual value of environmental care investments has been set at zero.

3. MILL DATA, INTEREST AND DEPRECIATION

Capacity

Small mill unbleached, screened pulp (90 %)	100 tonnes/day
Large mill unbleached, screened pulp (90 %)	300 tonnes/day
Operating time	350 days/annum 8400 hrs/annum

Interest and depreciation

Depreciation period for both buildings and machinery	10 years
Annual interest rate	10 %
Annuity	16,27 %
Present value of an annual expenditure of one US Dollar	6.144 US Dollars

4. COSTS OF CHEMICALS

All chemicals are of technical quality and the chemical prices have been collected from Swedish manufacturers, suppliers and consumers. The prices given are purchase prices including delivery to mill.

	US dollars/tonne
Aluminium sulphate	70
Calcium oxide	115
Chlorine (per tonne of active chlorine)	170
Chlorine dioxide (per tonne of active chlorine)	320
DTPA	615
EDTA	525
Hydrogen Peroxide (100 % of H_2O_2)	870
Kaolin, filler	50
Kaolin, coating	100

	US dollars/tonne
Limestone	25
Magnesium oxide	250
Magnesium sulphate	90
NTA	460
Oxygen (liquid)	140
Sodium chlorate	340
Sodium hydroxide	170
Sodium hypochlorite (per tonne of active chlorine)	320
Sodium silicate	130
Sodium sulphate	65
Starch, surface sizing	310
Sulphur	70
Sulphuric acid	65
Sulphur dioxide (liquid)	90
White liquor, oxidized (oxidation cost)	60

5. ELECTRICITY, HEATING, WATER, PERSONNEL ETC.

The table below shows the costs of electricity, heating, water, personnel and building.

	Secondary investment USD	Maintenance USD/annum	Operating cost USD/ unit	USD/ annum
Electricity				
Low voltage power, 1 kW installed	340*	7	0,03/kWh	250
Heating				
HP-boiler with turbine, LP-steam 1 Gcal/h	150000	4500	6,90/Gcal	57000
HP-boiler without turbine, LP-steam 1 Gcal/h	105000	3200	11,90/Gcal	100000
Package boiler, LP-steam 1 Gcal/ h**	30000	900	13,30/Gcal	112000

	Secondary investment USD	Maintenance USD/annum	Operating cost	
			USD/ unit	USD/ annum
Water				
To drain (sewer) of warm water 1 l/min	115	2,3	-	120
Cold water to be evaporated in 5 effects 1 l/min	1150	34	-	685
Cold water passing recovery boiler	3400	68	-	685
Personnel				
1 man in 5 shifts	4500	90	-	130000
1 daily worked	4500	90	-	20000
Building				
Building volume of 1000-10000 m^3	100 USD/m^3	-	-	-
Large volumes	80 USD/m^3	-	-	-

* Including high voltage installation of 70 US dollars/kW

** 1 tonne of steam = 0,58 Gcal if the condensate is re-used in boiler house

1 tonne of steam = 0.68 Gcal if the condensate is lost

Notes to the table:

Electricity

The cost of electric motors is included in apparatus costs. Secondary investment costs include therefore only the equipment, or parts thereof, which are required to connect the motor to the high voltage supply to the mill. The figures relate to the installed effect.

Heating

Two alternative calculations are given, one for a high pressure boiler (67 atm, 475°C) in combination with a back-pressure turbine and one for a package boiler providing low pressure steam (4 atm, 150°C) directly to the consumer.

The investment costs are high in the first case, but the cost of the low pressure steam is reduced in proportion to the value of the electrical power generated. A low pressure steam consumer thus pays less for his heating, but pays the full competitive price for his electricity.

The calculations are based on the following data:

Boiler house investment including raw water treatment, buildings etc.	USD/t steam/h	70000
Investment for package boiler	USD/t steam/h	17000
Total turbine investment	USD/kW	230
Efficiency of high pressure boiler	%	90
Efficiency of package boiler	%	80
Energy generated (net after deductions for auxiliary machinery)	kWh/t steam	120
Oil	USD/m^3	140
Thermal value of oil	Mcal/m^3	9500
Fuel costs for high pressure steam	USD/Gcal	16,90
Corrected fuel costs for low pressure steam	USD/Gcal	9,80
Cost of back-pressure energy (fuel only)	USD/kWh	0,022

It is assumed that the steam requirement can always be met by oil firing. (The production of steam in liquor or reject fired boilers cannot be adjusted according to requirements to any great extent.)

Secondary heating (hot water, both generated and consumed) is included only for temperatures of 70°C and higher and then to a price per heat unit which is half that of low pressure steam, i.e. 4,90 USS/Gcal or 0,30 USD/m^3.

Personnel

Personnel costs include only direct operating personnel, except where the environmental care measures are so extensive that they necessitate new appointments in e.g. laboratories or central adminstrative positions. Secondary investments here include a portion of the changing rooms, wash rooms, dining rooms etc. The costs of barracks or other living quarters are not included. In the case of continuous five-shift operation, the investment relates to a complete shift team.

The salary costs are assumed to include social benefits and administrative costs. The costs of mill and company management, laboratories, sales etc. are excluded.

Water

The cost of connecting apparatus to the water supply and sewer system is included in the item covering costs of pipes etc.

Secondary investments include a portion of the pumping station costs, pipes for incoming water, chemical water treatment, treatment of effluent and sewers. If hot water is required, the cost of heating is added.

If the water is led to an evaporating unit instead of being discharged, the investment and operating costs for effluent treatment disappear. Instead the corresponding costs of increasing the evaporating and boiler house capacity are included.

The calculations are based on the following basic data:

Pump pressure for incoming and waste water	m (water gauge)	40
Heat consumption in evaporation unit	Mcal/t evap water	135
Electrical energy consumption in evaporation unit	kWh/t evap water	4
Personnel costs		negligible
Investment costs for evaporation unit	thousands of USD tonne of evap water water/h	22000
Maintenance costs, incoming and waste water	%	2
Maintenance costs, evaporating unit and boiler	%	3

Maintenance costs

In general the maintenance costs for apparatuses are assessed at 3 %, except for very corrosive service where a figure of 4 % has been adopted. For buildings where there has been no reason to expect a frequent need for rebuilding as a result of new technical developments (e.g. incoming water requirements) a figure of 2 % has been used.

Raw materials, etc.

The costs of receiving, storing and internal handling of solid and liquid chemicals are taken into consideration, although no standard figures can be given. Necessary costs for chemical storage space are included in the investment costs.

Solid waste

The methods of calculating the costs of waste treatment and disposal have been explained in the relevant sections.

Building costs

A figure of 100 USD/m^3 has been used for simple buildings of a normal pulp mill character and with a volume between 1000 and 10000 m^3. If the installation includes heavy machinery which requires a special foundation there are added costs of 5-7 USD/tonne load for piling and 150-200 USD/m^3 for the foundation itself.

In some cases the rate has been reduced to 80 USD/m^3 for larger buildings, even for buildings such as furnaces, turbine units etc. where very heavy machinery is involved.