Technologies for the stabilization of elemental mercury and mercury-containing wastes

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Technologies for the stabilization of elemental mercury and mercury-containing wastes

Final Report

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1   Executive Summary

As complementary input to ongoing UNEP's consideration on the issue of storage of mercury, the Gesellschaft für Anlagen- und Reaktorsicherheit (GRS), a Germany based independent expert- and research organisation on behalf of the German Federal Ministry for the Environment (BMU) has conducted a literature overview to identify and describe existing technologies for the stabilization/solidification of liquid (elemental) mercury and mercury-containing wastes. The goal of these methods is to chemically convert elemental mercury and mercury-containing waste into thermodynamically more stable and solid compounds with considerably less volatility and less solubility. Such compounds may pose a smaller risk to human health and the environment. This overview on stabilization/solidification methods is meant as contribution for further consideration how to facilitate national and (sub)regional efforts to manage, store and dispose waste mercury and mercury-containing wastes in an environmentally sound manner.

Based on an extensive literature survey, three existing stabilization approaches could be identified: conversion to sulphide / selenide, amalgamation, and stabilization within an insoluble mineral matrix. For each of these approaches a number of technological implementations were found which are described in detail. The degree of industrial scaling varied widely: some processes have been tested or, at least, documented, so far, only in laboratory, while others were already demonstrated in semi-industrial scale (~ 100 kg/d). Some are announced to reach full industrial scale (> 1000 t/a) in due time.

Key findings from the literature investigation include: Most processes succeeded in producing a chemically and physically more stable product. Standard leaching procedures showed that under defined conditions mercury concentrations in leachates were below regulatory standards (USA or Japan). The same result was often found when the vaporization of mercury from the products was tested. On the other hand some methods could be identified which, according to reviews in the recent ten years, were unable to reduce the leachability and volatility of mercury sufficiently. Unfortunately, for some procedures such investigations were insufficiently documented or not conducted, so far. Moreover, it seems to be questionable whether it is enough to apply standard leaching tests in order to assess the long-term behaviour of stabilized mercury-containing waste forms. The leachability and volatility of mercury in solids strongly depends on the physical and chemical pre-conditions at the place of storage.

These might not be the same as presumed in standard leaching procedures. Further experimental work assisted with geochemical modelling could be one way to identifying further suitable technological approaches that are tailor-made to the conditions of existing and potential future storage locations.

2   Glossary of some technical terms used in this report

Amalgamation

A chemical process unique to elemental mercury, in which another metal forms a semisolid alloy ("amalgam") with mercury. Mercury dissolves in the solid metal, forming a solid solution. The process is reversible, so that mercury can be released from these alloys by heating. Amalgams, although solid, show a significant vapour pressure and solubility of mercury. Both differ only little from pure liquid mercury.

Chemical stabilization

A chemical process that converts a chemical substance into another substance that is thermodynamically more stable, less soluble and less volatile under the geochemical conditions of the storage location.

Containment/ macroencapsulation

A technical process where a substance is contained into an impermeable matrix or an impermeable container. Once the matrix or the container is fractured or otherwise degraded, the containment completely looses is barrier properties.

Immobilization

Any chemical or physical process that leads to a lower mobility (leaching after contact with aqueous media or vaporization into the gas phase) of hazardous substances.

Solidification/ physical stabilization

A technical or chemical process that renders a liquid or paste-like material into a solid one with enhanced physical strength (e.g. compressibility).

NIOSH

US National Institute for Occupational Safety and Health. It has established a recommended exposure limit (REL) for mercury vapour of 0.05 mg/m^3 as a time-weighted average (TWA) for up to a 10-hour workday and a 40-hour workweek [46].

TCLP

The Toxicity Characteristic Leaching Procedure (TCLP) is designed by the US Environmental Protection Agency (US EPA) to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphasic wastes. The TCLP analysis tries to simulate landfill conditions. A waste or waste product is considered hazardous if one of the leachate concentrations exceeds certain limits defined in the Resource Conservation and Recovery Act (RCRA)/ Land Disposal Restrictions. The limit for mercury is set to 0.2 mg/l.

3 Introduction

3.1 Background

On its 25th session the Governing Council of the United Nations Environmental Programme (UNEP) decided on a mandate for an intergovernmental negotiation committee to develop a mercury convention, including provisions, among others, to reduce the supply of mercury and enhance the capacity for environmentally sound storage.

In 2005 about 1.760 - 2.360 metric tons of mercury was produced worldwide as a by-product of metal production, cleaning of natural gas, recycling operations and decommissioning of chlor-alkali plants. It is expected that in the course of declining global demand as well as national and regional export regulations, increasing amounts of elemental mercury will become obsolete [66]. Mercury that is no longer needed for use in products and processes would need to be stored in an environmentally sound way. Notably high safety requirements will have to be met in order to prevent serious contamination of the environment through volatilization of liquid mercury or leaching in aqueous media. At the moment only few such facilities exist worldwide, none of them in developing countries.

Stabilization/solidification processes are widely applied to treat hazardous waste. Their purpose is to convert waste into a product with higher physical and chemical stability that meets regulatory standards and can be utilized or stored without further treatment. In the case of mercury stabilization processes are employed to convert elemental mercury and mercury compounds into compounds with inherently more favourable chemical and physical properties (e.g. low leachability of mercury and low mercury vapour pressure). Such compounds may pose a smaller risk to human health and the environment - and could be handled and stored more safely. Thus stabilization/solidification methods may also be a means to facilitate national and (sub)regional efforts to manage, store and dispose waste mercury and mercury-containing wastes in an environmentally sound manner.

3.2   Objective of this report

The objective of the present report is to identify and to describe chemical stabilization processes for both elemental mercury and mercury-containing waste, but priority is given to the former. Methods of macroencapsulation (physical immobilization) that do not alter the chemistry of the waste form, but add an impermeable protective barrier to the waste container are not covered by this report[1]. Moreover other waste treatment methods like thermal desorption, retorting or vitrification are not covered. Information on these approaches might be found elsewhere [73].

Given the constraints of the project an analysis, assessment or comparison of the different processes was not feasible. This would be subject of future work as well as recommendations for individual technical approaches. Nevertheless, after studying the range of available stabilization options, some information gaps could be identified that could serve as guidance for further investigations.

3.3   Methodology and sources of information

To fulfil the goal of the present project, a literature survey was conducted. Information was gathered from the following sources:

- Scientific literature databases (Chemical Abstracts Service, ScienceDirect.com) - query terms: mercury AND (stabilization OR immobilization OR solidification)

- Internet – google.de, query terms as before

- Patent databases (freepatentsonline.com), query terms as before

- Reports of US EPA, US DOE, UNEP

- Direct contacts to industry

- Monographs on hazardous waste management

The report does not claim to give an exhaustive overview on all available technologies. Nevertheless, after having investigated former reviews, available scientific literature

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[1] like waste encapsulation in polyethylene, asphalt, polyester

and patent databases the report is deemed to have covered at least the most important processes.

All technologies and methods that have been found in the literatures were shortly described; starting with some background information that gives an impression for what purpose the individual process has been developed. Following is a description of the process itself with information of the starting materials, the apparatus and the unit operations needed. Then the product of the process is characterized. Wherever available, facts are given on the type of the material, its leaching and its vaporization behaviour as well as on the maximum waste load. Information on the scale of industrial implementation (annual, daily throughput) is often scarce. Frequently it is unknown whether a particular process still is or ever was in industrial use. Due to lack of time no attempt was made to investigate the fate especially of the older processes. If available cost estimates were given that were found in recent reviews. These estimates should be treated with reserve, since they strongly depend on site-specific characteristics like waste type, expected throughput, total volume of waste and locality of operation (without exemption: US sites).

4   Description of stabilization technologies

4.1   Principle Stabilization approaches

In the past decades several approaches have been developed to stabilize mercury and mercury-containing waste. They might be grouped into three categories:

1. Stabilization as mercury sulphide or mercury selenide

2. Stabilization as amalgam

3. Stabilization with the components of an insoluble matrix (cement, phosphate ceramic, magnesia binder)

All processes described in this report are based on one or a combination of two of these approaches. In each case elemental mercury and/or oxidized forms of mercury are brought into reaction with certain chemical agents that convert mercury into a less soluble and less volatile chemical compound.

Sulphides and Selenides

The first approach mentioned in the list covers the formation of mercury sulphide. Processes that implement this approach often start with elemental mercury -$Hg_{(l)}$ that reacts with elemental sulphur or with other sulphur-containing substances like thiosulphate or pyrite (FeS_2) to mercury sulphide:

$$Hg(l) + S \rightarrow HgS$$

The conversion into mercury sulphide can be achieved by mixing solid sulphur with liquid mercury, by dissolving mercury in liquid sulphur or in a gas phase reaction between gaseous mercury and gaseous sulphur. At room temperature solid mercury sulphide exists on two kinetically stable modifications:

- α-HgS cinnabar (red) and

- β-HgS metacinnabar (black)

The latter is thermodynamically less stable but it is the principle product of reactions in a very broad temperature range. Both compounds are only very slightly soluble in water.

An also quite insoluble compound is mercury selenide that is formed from elemental mercury and selenium:

$$Hg_{(l)} + Se \rightarrow HgSe$$
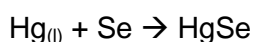
HgSe is also known under its mineral name Tiemannite[2]. Mercury selenide cannot be synthesized by mixing the elements at room temperature. Therefore, either a gas phase reaction is required or a reaction in aqueous media after oxidation of Hg(0) to Hg(II).

If mercury is present in its oxidized form Hg^{2+}, a sulphide-containing agent is needed for the reaction to mercury sulphide:

$$Hg^{2+} + HS^- \rightarrow HgS + H^+$$
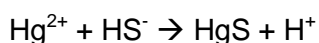
Agents might be hydrogen sulphide (H_2S), alkali sulphides (like Na_2S) or certain thiols (organic compounds with an -S-H group). In some processes elemental mercury is first oxidized by strong oxidizing acids like nitric acid (HNO_3) to aqueous Hg^{2+} and then precipitated as mercury sulphide.

A somehow similar approach was followed in the development of a new quite exotic looking sulphur-containing material: thiol functionalized zeolites. Zeolites are a group of porous silicate minerals. To functionalize them, chains of silanes[3] are chemically attached to the surface of the zeolite particles. At the end of each chain thiol-groups are placed that have an exceptionally high affinity towards any kind of mercury.

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[2] See http://webmineral.com/data/Tiemannite.shtml for some details.

[3] Silanes are molecules on the basis of silicon (Si) and hydrogen (H)

Amalgams

Mercury is the only metal that is liquid at ambient temperature and it is the only one that readily forms alloys just by bringing it into contact with other metals like lead, copper, zinc, nickel or cobalt (except iron which allows storing of mercury in iron flasks). Alloys with mercury are called amalgams. They are solid but sometimes quite soft or paste-like materials. In some processes amalgamation is used as a stabilization technique. Then mercury or the mercury-containing waste is mixed with a metal powder (mostly zinc or copper) to give the solid amalgam, e.g.:

x Hg(l) + y Cu → Cu_yHg_x
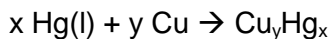
Stabilization in an insoluble matrix

Under this headline several processes are subsumed that don't convert mercury into a distinct compound or alloy but rather create a media in which mercury forms less soluble compounds. A quite commonly used method that is successfully applied for many types of hazardous wastes is stabilization/solidification with Portland cement based materials. They consist of chemical substances and minerals like Portlandit (calcium hydroxide, $Ca(OH)_2$), calcium silicates and aluminates that after mixing with water first form a slurry that hardens after a period of time due to the formation of a three-dimensional network of interlinked calcium silicate hydrates (CSH). At the same time, depending on the cement and the additives (fly ash, blast furnace slag) an alkaline or at least near neutral media is maintained in the remaining pore water. Most heavy metals form quite insoluble hydroxides under such conditions. Some metals are even incorporated into the CSH-matrix.

The same principle is utilized in Sorel cements (or "magnesia cement"). If magnesium oxide reacts with a magnesium chloride solution (or other soluble magnesium compounds) magnesium hydroxide chlorides are formed, e.g.:

$3MgO_{(s)}$ + $MgCl_{2(aq)}$ + $11H_2O$→ $Mg_4Cl_2(OH)_6(H_2O)_8$
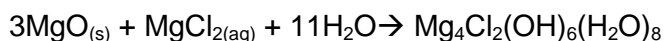
The resulting pore water has a near neutral pH and ensures a low solubility for many heavy metals.

Another type of stabilizing materials are phosphates. If magnesium oxide is mixed with an aqueous solution of hydrogen phosphates (or phosphoric acid), a solid magnesium phosphate is formed:

$$MgO + KH_2PO_4 + 5H_2O \rightarrow KMgPO_4 \cdot 6H_2O$$
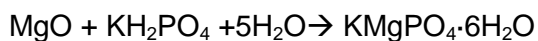
Heavy metals like lead Pb^{2+} or mercury Hg^{2+} form insoluble phosphates that are embedded in an impermeable matrix of magnesium phosphates.

4.2 Stabilization as mercury sulphide or mercury selenide

4.2.1 Process for stabilization of metallic mercury (DELA, Germany)

Short description

Elemental sulphur is vaporized in a heated vacuum mixer and reacts in the gas phase with added elemental mercury to mercury sulphide.

Motivation of the invention

The Swedish government follows a strict national strategy to phase-out the use of mercury in products and processes. Parts of this strategy are efforts to develop environmentally sound solutions for the disposal of elemental mercury, preferably in underground disposal facilities in stabilized forms [44]. The Swedish company SAKAB has partnered with the German DELA GmbH (Essen) in order to develop a process that is capable of converting elemental mercury that can be disposed without further treatment.

Process

The process utilizes a vacuum mixer, a device that is also being employed at DELA to treat different types of mercury-containing waste. First the vacuum mixer is flooded with nitrogen in order to replace any oxygen in the system that might oxidize mercury or sulphur. A vacuum (< 0.9 bar) is applied and the necessary amount of sulphur is added. The mixer is heated to a temperature higher than the boiling temperature of mercury (> 580 °C). Then mercury is added over a period of time. Unlike processes at lower temperature a nearly stoichiometric ratio between mercury and sulphur can be used. Due to the high temperature employed, within several seconds mercury

completely reacts with the gaseous sulphur to form mercury sulphide. Afterwards mixing is continued for a defined time and the still gaseous mercury sulphide can be condensed by cooling down the gas phase. The process can be operated in batch mode as well as in continuous mode [19].

Product

The final product is a mixture of black metacinnabar (β-HgS) and red cinnabar (α-HgS). Efforts are undertaken to produce red cinnabar only.

Leaching (German DEV S4/ DIN 38 414) showed mercury concentrations less than 0.05 mg/l (average: 0.009 mg/l). The mercury vapour pressure was below the detection limit of the instrument (< 0.003 mg/m^3). According to its characteristics DELA classified the product as a non-toxic, non hazardous waste (European Waste Catalogue EWC 19 03 05), that may in principle be finally disposed in landfills, but the final decision depends on national legislation that may define specific standards for subcategories of landfills. According to DELA the product fulfils the acceptance criteria for certain landfill categories, including above-ground landfills above the ground [32], [48].

Emissions

The process unit is gas tight and operated at a slight vacuum. The low exhaust gas flow (approx. 20 Nm^3/h) is directed into a multi-stage filter which reduces lowers the mercury content below regulatory standards. Under normal operation conditions no mercury is in the gas phase as it reacts with sulphur spontaneously and completely.

Scaling

A pilot plant has been operated batch-wise with a capacity of 500 kg per day [56]. It is planned to have an operational full scale unit at the beginning of 2010. The maximum treatment capacity will be in the range of 3 to 6 t per day [32].

4.2.2 Stabilization of metallic mercury using sulphur (STMI, Gif sur Yvettes, France)

Short description

Liquid mercury and elemental sulphur are brought to reaction in a glass apparatus by stirring the mixture at elevated temperature.

Background

The process has been developed with the aim of stabilizing radioactively contaminated elemental mercury with the purpose of later storage.

Process

The process employs a molar Hg/S ratio of 1:1 to 1:3 [55]. Both reactants are poured into the round-bottom flask of an apparatus consisting of a motor, an axial glass pipe and a rotatable axial flask[4]. Stirring is accomplished by rotating the flask, preferably at 50 rpm for 2 hours (higher speed gave slower reaction rates). Reaction already takes place at 20 °C but heating to 60 - 80 °C is preferred. If the mercury contains volatile contaminations these can be distilled off at 90 - 110 °C in the same apparatus. Application of even higher temperatures (e.g. 360 °C) enables the distillation and purification of mercury itself. Mercury is then collected in a receiver that subsequently can be employed to act as a reactor also.

Product

Finely grained black powder, identified as a mixture of metacinnabar and sulphur. After 2 - 24 h of stirring the mercury content of the gas phase was between 70 - 200 µg/m^3. Mercury concentration in the leachate (NF EN 12457-2) was found to be between 0.46-0.74 mg/l. The product meets French regulatory standards for acceptance to storage.

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[4] The apparatus has strong similarities with commercially available rotary evaporators.

Scaling

According to available information the method in its semi-pilot stage is limited to batches with 1 kg mercury.

4.2.3 Conversion to mercury sulphide by milling (CENIM, Spain)

Short description

Conversion of elemental mercury to mercury sulphide by milling at room temperature.

Background

After the adoption of the EU mercury strategy in 2005 it became evident that within the EU the supply of mercury will soon exceed the demand. Spain had a long experience in mining, managing and trading mercury and therefore looks for ways to treat mercury after the European export ban enters into force in 2012. The project MERSADE[5] (funded through the European LIFE programme [40]) aims at the design and construction of a safe storage installation prototype for mercury metal. One part of this project were investigations of stabilizing methods for mercury [36].

Process

Equal weight amounts of mercury and sulphur (according to a stoichiometric excess of 45 wt %) were brought to reaction in a planetary ball mill containing stainless steel balls. Milling was done at 400 rpm for 15 minutes to 3 hours.

Product

The process yielded a black product consisting mainly of black HgS (metacinnabar) and sulphur. Depending on milling time different phases were found in the product. Up to 60 minutes milling time the concentration of mercury in the leachate decreased, indicating a decline of free mercury. Longer milling times than 120 min yielded higher amounts of soluble mercury that were attributed to the formation of mercury oxide. Mercury concentrations in leachates (TCLP) were found to be at 0.002 mg/l whereas the original mercury caused concentrations around 8960 mg/l.

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[5] Mercury Safety Deposit.

4.2.4   Mercury stabilization as mercury sulphide (Bethlehem Apparatus)

Short description

A process that converts liquid mercury into mercury sulphide and encapsulates them in a polymer matrix.

Process

Bethlehem Apparatus Co., Inc. (Hellertown, PA, USA) is currently developing a process to convert mercury into a high purity mercury sulphide. In a second step the sulphide is blended with a proprietary mix of polymers and is finally formed into pellets of the size 7 x 7 mm [6]. Because the process is still under development definite information on the process details are not available.

Product

The material is said to be equal in its physical and chemical properties to naturally occurring cinnabar. According to company information the produced mercury sulphide did not show any trace of elemental mercury and headspace analyses also confirmed the absence of mercury in the gas phase [7]. It meets Canadian regulatory standards for land disposal [6].

Scaling

When brought to full-scale the process is planned to have an annual conversion capacity of 1.000 t [7]. The current scaling is unknown.

4.2.5   Wet process to synthesize mercury sulphide

Short description

Mercury is dissolved in a strong acid and precipitated as mercury sulphide in the aqueous phase.

Background

A classical route to synthesize mercury sulphide. May be found in any textbook on inorganic chemistry and is mentioned here only for the sake of completeness.

Process

Mercury is dissolved in a strong acid. The acid must be oxidizing (like concentrated nitric acid, HNO_3) or contain a strongly complexing agent like chloride (hydrochloric acid, HCl) in order to overcome the noble character of liquid mercury. Addition of an aqueous solution of a sulphide like sodium or potassium sulphide (Na_2S, K_2S) leads to the precipitation of black metacinnabar.

Product

Black metacinnabar.

Emissions

The process produces large volumes of a secondary waste stream – an acidic, mercury contaminated process water [25]. Gaseous hydrogen sulphide may be released during the process.

4.2.6   Synthesis of mercury sulphide by shaking

Short description

Powdered sulphur is mixed with elemental mercury at ambient temperature to give mercury sulphide.

Background

Several methods were investigated to stabilize radioactive mixed waste that contains mercury.

Process

Finely powdered sulphur (< 60 mesh) is beaten in a paint shaker with stainless steel milling balls for 1 h [25]. Elemental mercury is added (50 % wt % excess of sulphur). Then the mixture is shaken longitudinal for 1 h and subsequently transversely for another hour [25].

Product

The product of this process was identified by XRD as mercury sulphide. Leaching experiments showed a solubility of mercury of less than 0.0008 mg/l (TCLP), far below the limits of the US Resource Conservation and Recovery Act (RCRA 0.2 mg/l). In the final product about 300 ppm elemental mercury where found which equals to a reaction yield of > 99.96 %. In the headspace about 0.006 to 0.0012 mg/m^3 Hg were found (72 h equilibration time), one order of magnitude lower than the threshold limit value of 0.05 mg/m^3 (NIOSH). Commercially produced mercury sulphide resulted in an even lower pressure showing that in the product some elemental mercury is still present in occluded pores. Some methods were discussed that could lead to higher conversion rates, but they were not further investigated. The maximum waste load in the final product was 86 wt %.

Scaling

The method was demonstrated in 1 kg batches. As far as known no scale-up to larger dimensions was made.

4.2.7   Stabilization of radioactive mercury as sulphide or selenide (FZJ)

Short description

Mercury is dissolved in nitric acid and then precipitated as mercury sulphide by adding ammonium sulphide.

Background

Mercury is used as a target in spallation sources, research devices in nuclear physics to produce neutrons and neutron beams. It is estimated that during the lifetime of a spallation target facility (40 y) about 30 - 40 t of radioactively contaminated and activated mercury are produced. Different from mercury-containing mixed waste from nuclear facilities, waste mercury form spallation targets also contains radioactive mercury isotopes so that a complete separation of radionuclides from liquid mercury is not feasible. Since the mercury is highly radioactive, the waste can only be handled in "hot cells" [14], [15].

Process

It has been shown that under hot cell conditions it was not possible to achieve a complete conversion of elemental mercury to mercury sulphide using a dry process on the basis of powdered sulphur. Therefore a wet process in a closed glass apparatus was developed, in which mercury was first dissolved in concentrated nitric acid (HNO_3). Then aqueous ammonium sulphide (and hydrogen sulphide if necessary) was added to precipitate mercury as mercury sulphide. Reactions took place in a 2000 cm^3 glass reactor with external temperature control (circulating water). Maximum load per batch was 1000 cm^3. In a later stage it was investigated whether embedding of mercury sulphide in a polysiloxane matrix would further reduce the leachability of mercury.

Product

The product is metacinnabar: If embedded into a polysiloxane matrix the leachate concentration was found to be below 0.02 mg/l [16].

Scaling

At the moment the process was only demonstrated with inactive mercury in an experimental setup with 2 litre capacity. Up-scaling for a process that is able to handle tons of irradiated mercury under hot-cell conditions was considered as a challenging task[6].

Emissions

The described wet process produces considerable amounts of aqueous radioactively contaminated solutions that must be disposed separately.

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[6] Chiriki, S. Personal communication

4.2.8 Sulphur Polymer Cement (Brookhaven National Laboratory)

Short description

Mercury, powdered sulphur and polymerizing additives are mixed at room temperature and then heated until the mixture melts. The product is mercury sulphide encapsulated in a sulphur polymer matrix.

Background

The method was originally developed to treat mercury-containing radioactive mixed waste, where a separation of mercury by heating/ thermolysis was not desirable or feasible. But the technology is applicable to all types of mercury-containing waste including pure elemental mercury [31].

Process

Mercury containing waste (or liquid mercury) is mixed with powdered sulphur polymer cement (SPC, consisting of 95 % sulphur, 5 % organic modifiers) under an inert atmosphere (mixing ratio typically between 0.2 and 3.0) [30], [29], [41]. Mixing takes place at elevated temperature and should be continued for 4 - 8 hours. A chemical stabilizer (like sodium sulphide or triisobutyl phosphine sulphide, 0.5 - 20 wt %) may be added to convert soluble mercury compounds like mercury chloride.

The mixture is then heated to 120 - 150 °C to form a molten product. Additional SPC may be added to improve viscosity and to ensure complete conversion of mercury into mercury sulphide. Waste loads depend on the waste type. In case of less mercury containing waste the load may range from 25 - 80 wt %, while in the case of elemental mercury the waste content will stay at 10 - 50 wt % (33 wt % in case of elemental mercury [42]). The system could be operated under vacuum or under inert atmosphere.

The molten product can be cast in any desirable form, preferably in containers ready for final disposal.

The process was successfully tested for elemental mercury [24], mercury compounds, debris, sludges (moisture must be removed prior to treatment), mine tailings, mixed oxides [53], mercury containing gold mining residues [10]. It is incompatible with high nitrate content [31].

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Product

After cooling down the final product shows considerably lower mercury solubility and vapour pressure. In the product mercury sulphides (cinnabar, metacinnabar) were found by XRD [30]. The inventors stress that by encapsulating mercury sulphide into a sulphur polymer matrix an additional barrier against leaching is created. Moreover, the polymer is chemically stable against a broad variety of common reagents, among them acids, concentrated brines and reducing agents.

Investigations in the mid-1990s showed that the process as performed at that time was inferior to direct reaction with sulphur (TCLP test showed failure of the product to meet regulatory standards) [25]. Leachate concentrations were even higher than previously for elemental mercury, possibly due to the formation of soluble mercury oxides. But improvements introduced by Brookhaven National Laboratory (e.g. reaction under inert atmosphere) drastically improved the performance of the product.

The stabilized product performed well in constant pH leaching tests between pH 2 and 10. At pH 12 the mercury concentration in the leachate exceeded the target concentration of 25 ppb [28]. TCLP analysis showed leachate concentration of less than 0.025 mg/l [2].

In one test case radioactively contaminated mercury was stabilized using the BNL process. Mercury concentrations in the gas phase could be reduced to an average of 0.6 mg/m^3. This is still considerably higher than the recommended threshold limit value of 0.05 mg/m$_3$ [24].

In another test case mercury contaminated soil (4500 ppm) was treated in the same way. Volatility of mercury was then investigated at 2, 20 - 22, and 60 °C. While the untreated soil produced mercury concentrations around 18 mg/m^3, after the stabilization only 0.02 to 0.033 mg/m^3 were found [39].

Scaling

Pilot-scale (55-gal drums of mixed-waste soil) [41]. 62 kg (approximately 137 lb) of radioactively contaminated elemental mercury were successfully treated.

Costs

The SPC material costs around 0.12 USD/lb (0,27 USD/kg). For mixed mercury-containing waste the life cycle treatment costs for a 1000 lb/h operation unit was estimated to be in the order of 2.30 USD/kg (without transportation) 89 % of which is for disposal [41].

In another study the costs for the treatment of 5000 t liquid mercury (annual throughput: 1000 t) were estimated to be around 15 USD/kg including disposal in a new monofill landfill. It was not possible to separate the treatment cost from the calculation.

Similar processes

A similar process (SULKO) has been developed in the 1990 by the Austrian Forschungszentrum Seibersdorf (ÖFZS, now part of the Austrian Institute of Technology) for the treatment of hazardous waste (e.g. sludges), but not specifically for mercury-containing waste [43].

Pildysh Technologies Inc. (Calgary, Alberta, Canada) has developed a technology named TerraBond[TM], which is based on mixing waste with molten sulphur without the addition of polymerizing agents but with suitable stabilizers and fillers. Waste load is reported to be around 65 %. After cooling the material is pelletized and eventually coated with a hydrophobic sealing [52], [53].

4.2.9   Process for stabilization of mercury (ADA Technologies)

Short description

Mercury and powdered sulphur as well as polysulphides and sand are vigorously mixed.

Background

The stabilization process of ADA Technologies was developed for treating radioactive mixed mercury waste [1], [35]. The purpose of the method is to stabilize both elemental mercury as well as mercury compounds. Therefore in the process several agents are added that react with both types of mercury in waste.

Process

Elemental mercury

Powdered sulphur (10 - 500 micrometers) is added to an (open) pug mill with a set of counter-rotating blades [35]. After starting the mixing blades mercury is then poured in. Mixing is continued for 5 - 10 minutes when a bulking material (typically sand) is added to the mixture and mixing pursued for additional 10 - 30 minutes. Then a polysulphide (calcium, sodium or any other alkali or earth alkali compounds) is added that acts as an activator for the reaction between mercury compounds and the sulphur reagent. Further agitation typically from 60 to 120 minutes. The end of the reaction is signalled by an end of heat generation as the reaction between mercury and sulphur is exotherm. All operations do not require heating.

Mercury-containing waste

The process to treat particulate mercury-containing waste (> 260 ppm Hg, > 50 wt % solid content) delivers a similar product but consists of more distinct steps [8], [9]. In the first step the waste is pre-treated in a way that oxidized forms of mercury are reduced to elemental mercury. This is been done by adding a powdered metal (like zinc, tin or copper 0.4 - 2 wt %) and agitating the mixture vigorously for 20 minutes to several hours under an oxygen-containing atmosphere. After that a sulphide or polysulphide is added, approximately in a range of 1 to 3 moles per mol of mercury and the mixture agitated again up to several hours. The amount of sulphide is often higher than needed to transform mercury into mercury sulphide. Since free sulphides are often regulated, an iron-containing compound like metallic iron or solutions of ferric/ferrous

salts are introduced in order to bind sulphide as insoluble iron sulphides. If the waste contains water insoluble liquids like oils or PCBs a dispersion agent may be added to obtain a homogenous phase. Another option is the activation of the metal reagent by adding an acid or salts of an acid that are able to remove/dissolve slowly reacting oxide layers form the surface of the metal particles.

The process is said to be applicable to mercury-containing waste or elemental mercury with a mercury content between 0.01 to 100 wt % [35]. The waste load in the product is around 50 - 60 wt % [68].

Product

Mercury

In the case of elemental mercury the product achieve a granular state. In order to prevent the formation of dust, up to 30 wt % water may be added. The final product contained about 600 ppm free elemental mercury, leachable mercury was below 0.1 mg/l (TCLP test, limit: 0.2 mg/l). Omission of sand and calcium polysulphide resulted in large amounts of unreacted metallic mercury.

In the case of mercury-containing waste the method proved to be effective not only in stabilizing mercury but also other heavy metals that were present in the waste under investigation. Leaching tests (TCLP) showed that the metal concentrations in the leachate were below US regulatory standards (RCRA).

Scaling

The process was up-scaled after licensing it to Perma-Fix Environmental Services. It could handle batches up to 100 kg, including a mixer that was purged with a nitrogen gas stream in order to prevent the formation of mercury oxides. Perma-Fix was licensed to treat 235 t of a mercury-containing waste from one US nuclear complex [8]. The throughput is > 100kg in 8 hours. The process may be deployed as a mobile unit [68]. It was estimated that in future implementations up to 375 kg mercury could be treated in one batch [58].

Costs

<u>Mercury</u>

Process costs to treat 1.500 kg of mercury were estimated to be in the order of 300 USD/kg (1999) [67]. In another study (2005) costs for annually stabilizing 1000 t mercury (5000 t in total) were estimated to be in the order of 4.9 to 8.2 USD/kg including disposal in a new monofill landfill. It was not possible to separate the treatment cost from the calculation.

Emissions

The secondary waste stream amounts to 5 wt % of the final product: Sand, PPE, decontamination materials, filters [68].

4.2.10   Mercury sulphide by shearing (Westinghouse Savannah River Co.)

Short description

Mercury is brought to reaction with sulphur by a high-shear mixer [47].

Process

Mercury and powdered sulphur (weight ratio 5:1) are blended in a high-shear mixer with a rotating speed up to 19000 rpm. Devices were operated under an inert atmosphere to prevent oxidizing of sulphur. Cooling was necessary to prevent overheating of the mixer. At low mixing speed black mercury sulphide is produced, while at > 5000 rpm red sulphide is observed, but a lower speed is recommended to prevent overheating and danger of ignition.

Product

Black powdered metacinnabar or red cinnabar. The products passed the leaching tests (TCLP: 0.2 mg/l) only in case that the weight ratio S/Hg was larger than 0.24. Mercury in the vapour phase was below the detection limit (10 mg/m^3).

4.2.11 Stabilization of mercury as mercury selenide (Boliden Mineral, Sweden)

Short description

Mercury is thermally extracted from waste and allowed to react with gaseous selenium to react to solid mercury selenide.

Background

The procedure was developed to extract and stabilize mercury from mercury-containing button cells.

Process

Mercury-containing waste is heated and agitated in a furnace (e.g. a rotary furnace) at a temperature that allows all mercury to evaporate. Selenium is added in adequate amount to bind all mercury in the waste. In an example a ratio of batteries to selenium of 10:1 was mentioned (average mercury content: 2 %). The temperature in the furnace is chosen high enough to prevent the immediate formation of mercury selenide (600 - 850 °C). On the other hand, the oxygen content of the gas phase has to be maintained low enough to prevent any selenium to be oxidised to selenium oxide (e.g. by flooding with an inert gas or adding a reducing gas like SO_2). The mercury-free waste is separated from the gas phase which is subsequently cooled down so that mercury selenide can precipitate. The whole process is operated in a closed system.

Scaling

The process has been demonstrated in a furnace of 1 m length. The throughput per hour was 100 g batteries. It is unknown whether the process has been up-scaled.

Costs

The process costs are unknown. But it may be mentioned that in the case of treated batteries 10g/h Selenium were needed to bind 2 g/h mercury in 100 g/h batteries (weight ratio 5:1, molar ratio 12.5:1). With respect to current metal prices (selenium: 40 - 60 USD/kg) the costs for selenium alone would amount to 200 - 300 USD/ kg Hg.

4.3   Amalgamation of mercury

4.3.1   Mercury Amalgamation (Ecoflo, Greensboro, NC, USA)

Short description

Mercury reacts with powdered metals to form solid amalgams.

Process

Liquid mercury is mixed in a disposable bottle or container with a powdered amalgamating agent in ratio of 1:1 to 1:3, but preferably 1:3. Proposed agents are copper, nickel, zinc or sulphur powder. Shaking is performed by means of a paint mixer for at least 5 - 15 minutes, but 40 minutes (metals powders) and 20 minutes (sulphur) are recommended, respectively [75].

Product

Both reaction types resulted in the formation of solid powders, both of which were said to meet US EPA standards (1989). Reaction with sulphur produced a "mercury sulphide gas", so that the inventors didn't know whether standards for the emission of fumes were met.

4.3.2   Stabilization of liquid mercury (Institute of Gas Technology, Des Plaines, IL, USA)

Short description

Mercury is stabilized as copper amalgam [54].

Process

Powdered copper is cleaned from oxides and other compounds by immersing it into diluted hydrochloric acid/ammonium chloride or by heating it at 500 - 700°C in hydrogen gas. Mercury is added (50 - 80 wt % in the final mixture) and the resulting mixture agitated. A slurry develops that hardens at ambient temperature within a day or two.

Product

The obtained product is a hard metallic alloy. There is no information about leaching results or volatility. In comparison with the Ecoflo process the amalgams produced by this method contain more than 50 wt % mercury.

4.3.3 Amalgamation with zinc or copper

Background

Decontamination and decommissioning of certain nuclear facilities result in the production of radioactive mercury and mercury containing waste. In the USA amalgamation is one of the standard procedures to treat such residues[7].

Process

Copper amalgam

Fine copper powder (325 mesh) is washed with nitric acid and then milled in a laboratory shaker with stainless steel balls [25]. Elemental mercury is added so that the mixture contains 65 wt % mercury. The mixture is milled for 45 minutes, the resulting paste stirred and, milled for 45 minutes. It is then allowed to harden and later crushed into a powder, if necessary.

Zinc amalgam

Fine zinc powder (325 mesh) is washed with nitric acid and then milled in a laboratory shaker with stainless steel balls [25]. Elemental mercury is added so that the mixture contains 45 wt % mercury. The mixture is milled for 2 h.

Product

TLCP test resulted in mercury concentrations between 0.02 to 0.1 mg/l (copper amalgam) and 0.09 to 6.3 mg/l for zinc amalgam. The latter failed to meet the regulatory limit of 0.2 mg/l, which was confirmed by a later investigation [57].

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[7] By definition in some regulations reaction with sulfur is also called amalgamation. In this chapter only the metallic alloys of mercury are denoted as amalgams.

Headspace analysis showed that the vapour pressures of mercury above zinc and copper amalgams were nearly the same as those above pure elemental mercury. This result was also confirmed later [38].

The maximum waste load was 73 wt % for copper amalgam and 50.6 wt % for zinc amalgam.

4.3.4 Two-stage stabilization/solidification with copper powder and Portland cement (British Nuclear Fuels)

Short Description

Amalgamation with copper powder and subsequent solidification with Portland cement and blast furnace slag [11].

Background

The process was developed with the aim of stabilisation and disposal of radioactively contaminated waste.

Process

Mercury is mixed with an amalgamating powdered metal, preferably copper using a weight ratio (Hg/metal) of 1:1 to 1:4, preferably 2:3. Then a diluted (0.01 to 1 M, pref. 0.1 M) mineral acid like nitric acid (HNO_3) is added (weight of amalgamating metal to acid volume 1:2 to 2:1, pref. 1:1). The mixture is agitated for 5 - 15 minutes until the reaction is complete which is signalled by the disappearance of liquid mercury droplets. The resulting amalgam sludge is the mixed with ordinary Portland cement (OPC) (ratio of 2:1 to 1:4 (w/w), preferably 1:1) and optionally with additional fillers like blast furnace slag, lime, silica or fuel ash in a ratio of 5:1 to 1:1, pref. 3:1 (fillers to amalgam). The resulting product is allowed to cure for 48 h, after which it is ready for disposal.

Product

The product is a concrete-like homogenous monolith. No further information is available.

Similar Processes

A similar approach has been proposed an successfully tested by Oak Ridge National Laboratory [60].

4.4   Other treatment methods for mercury-containing waste

4.4.1   DeHg^{TM}- Process - Nuclear Fuel Services, Inc. (NFS)

Short description

Mercury is amalgamated with a proprietary mixture of reagents. Oxidized species are solidified by another group of unspecified agents.

Background

The process was originally developed to treat over 50 cubic meters of mercury mixed waste from production operations at NFS. It is capable of treating wastes containing elemental mercury and/or oxidized forms of mercury.

Process

The DeHg process is operated at ambient temperature in a ventilated hood. Reactions take place in a reactor. It consists of two parts. In the first one (amalgamation) elemental mercury content is reacted with amalgamating agents (unspecified), in the second part (stabilization, if necessary) oxidized mercury species and complexes are broken up using a proprietary reagent and removed from the waste as an insoluble precipitate [68], [42]. Further details about this process have not been disclosed. The process is applicable to various waste types like contaminated bulk elemental mercury, debris, ion-exchange resin, soils, sludges and solutions containing various chemical forms of mercury.

The achievable waste load is reported to be in the range of 20 - 25 wt % if elemental mercury is treated. It was estimated that the secondary waste stream amounted to 15 wt % (solutions, bottles, other laboratory expendables) [68].

Product

The final product is a press cake. If the material passes TCLP tests it is ready for disposal, otherwise it will be reprocessed. This implies that in some cases the process fails to meet regulatory standards.

Scaling

The process has been used at several US sites (among them Oak Ridge) [45]. The only documented daily throughput was 80 kg in 8 hours [68]. The process may be deployed as a mobile unit [68].

Costs

About 300 USD/kg if planned for a treatment of 1500 kg radioactively contaminated mercury (1999). Disposal of primary and secondary waste is not included in this figure [68].

For the treatment of soil, sludges and shredded debris under 5 wt % Hg the costs were estimated to be around 5.35 to 6.93 USD/kg at 1000 lb/h or 33 - 37 USD/kg at 100 lb/h. Disposal costs are estimated to be 1.89 USD/kg (2002) [41].

4.4.2 ATG Stabilization process (waste > 260 ppm)

Short description

Mercury waste is stabilized by addition of sulphur-containing compounds and then further solidified by mixing with clay or Portland cement.

Process

The process consists of mixing the waste with an immobilizing agent – that converts mercury species in an insoluble form – and clay [49] or Portland cement [41] to solidify the waste. Several formulations for the immobilizing agent are described, among them a proprietary dithiocarbamate, sodium tetrathiocarbamate or sodium hydrogen sulphide [62]. Small-scale tests have to be performed in order to find suitable formulations for individual wastes. The stabilization system is transportable and can handle solid and liquid wastes. The waste load in the final product is up to 70 wt % [41].

Product

Treatment of liquid waste resulted in a damp paste, with no free standing water [69]. TCLP tests showed that mercury concentrations were below regulatory standards. Treatment of soil with reagents and Portland cement resulted in a concrete-like material that was easily granulated. The volume increase was reported to be between 7 and 20 %, depending on the reagent formulation used for a specific waste. Test showed that the volume increase could be even lower when Portland cement was omitted [41]. The leaching behaviour (TCLP) of several products met regulatory standards. In the course of the operations secondary waste is produced in the form of treated waste samples that were produced for testing purposes.

Scaling

Full-scale operation is performed with a commercially available mobile mortar mixer, e.g. 7 - 9 ft^3. The full-scale system is portable and capable of processing liquid and solid waste as well as sludges [41].

Costs

For the stabilization of mercury mixed waste costs were estimated to be around 0.4 USD/kg at 1200 lb/h or 2.40 USD/kg at 100 lb/h. Disposal costs were assumed to be 1.91 USD/kg (2002) [41].

4.4.3 Stepwise solidification with hydraulic cement and sulphur-polymer-cement (Southwest Research Institute, San Antonio, TX, USA)

Short description

Waste is being mixed with a pozzolana, lime and other components to give a cured material, heated to 180 °C, ground to an aggregate and then mixed with a molten sulphur polymer cement.

Background

The process was developed to immobilize and stabilize a broad range of waste types including radioactive and mixed wastes. Not specifically aimed at mercury-containing wastes it shares some characteristics with the later BNL process and is therefore mentioned here.

Process

The waste in form of a slurry (< 50 wt % solids) is mixed with a pozzolana (e.g. fly ash), lime, kiln dust, a hydraulic cement and other additives, and allows to cure at room temperature. The material is then heated to 180 °C for 8 hours to complete curing. After that the material is ground to an aggregate with a particle size between ¼ and ½ inch. At the same time a sulphur polymer cement is prepared by mixing sulphur with 10 wt % of polymerizing agent like cyclopentadiene or vinyl toluene, and melting the mixture. Now the sulphur cement and the aggregate are admixed, eventually after adding further amounts of pozzolana and siliceous material like sand. The new material is allowed to cure [37].

Product

Concrete-like material with high compressible strength. Can be shaped in any form needed. Leaching tests (TCLP) confirmed that regulatory standards were met.

Emissions

There is no information about emissions during the first and the second heating.

4.4.4   Stabilization of high mercury wastes with reactivated carbon (University of Cincinnati)

Short description

Mercury-contaminated waste is stabilized by adding reactivated carbon and subsequent solidification with Portland cement.

Background

Activated carbon is a well known and effective agent to control mercury in gas streams. High costs prevented its application in stabilizing mercury in solid waste. The motivation of the research was to find a cost-effective way to use the outstanding properties of this material by employing reactivated carbon that is available at much lower prices.

Process

Thermally reactivated carbon (BET 966 m^2/g) was used that has previously been used for other purposes. To improve its adsorption capacity it was soaked in CS_2 (or aqueous Na_2S) for 48 h and then dried. Experiments were conducted with mercury-doped test sand with a total Hg load between 100 and 1000 mg/kg. Surrogate samples were mixed with water (waste/water: 10:1) and reactivated carbon in a weight ratio of 100:1 to 5:1, whereas the pH was manually adjusted at 5.5. Adsorption equilibrium was reached within 24 hours. Type I Portland cement (waste/cement: 1:1, water/cement 1:2) was used to solidify the samples [76], [77]. In another test mercury-contaminated soil (2300 ppm) from a chlor-alkali plant was treated in the same way [78]. The process has been tested with mercury containing waste with up to 2230 mg /kg Hg.

Product

After addition of Portland cement a concrete is formed. Leaching tests (TCLP) confirmed that the product passes regulatory standards. Moreover, it could be shown that the material resisted constant pH leaching at pH 4 - 12 (0.17 M chloride present). However, strong mercury release was observed at pH 2 [78].

Scaling

Information was only found on lab-scale experiments.

4.4.5 Stabilization of mercury-containing wastes using sulphide (University of Cincinnati)

Short description

Mercury-containing waste is treated with sulphide solutions.

Process

Mercury-containing waste is treated with an aqueous solution of sodium sulphide at pH 6 for 168 h. The amount of added sulphide was adjusted to the mercury content of the waste so that the molar ratio of S/Hg was exactly 1 [50], [51].

Products

The efficiency of the stabilization was calculated to be approximately 98 %. The product leachability (TCLP) met regulatory standards (0.2 mg/l).

4.4.6   Solidification/ stabilization with Portland cement based materials

Background

Stabilization of wastes with Portland cement based materials is common practice in waste management.

Process

Details on this method may be found elsewhere [18], [61] but basically it consists of mixing Portland cement based materials with the waste, a necessary amount of water, and sometimes additives. The mixture is allowed to cure for a certain period of time. The procedure has proved to be effective in solidification/stabilization of many waste types [59]. Several vendors offer special cement mixtures that can be utilized for this purpose, among them HeidelbergCement (Depocrete™), Silicate Technology Corporation (SOILSORB™), Waste Services NSW (EcoFix™).

In one study it was investigated whether solidification with Portland cement was sufficient to stabilize mercury-containing wastes [26]. It was found that Portland cement that has been doped with either HgO or elemental mercury released gaseous mercury. In the case of added liquid mercury, the headspace above the cured phase reached 20 % of mercury saturation within 2 h. On the other hand no mercury was found in the gas phase if HgS was added. Another study compared the retardation efficiency of several cement based formulations and found that with many high-mercury wastes (> 260 ppm) mercury was too soluble and TCLP tests failed [57]. In some cases the mercury leachability was even increased.

Other investigators found that wastes up to 1000 mg/l Hg could be treated by applying blast furnace cement that contains a considerable amount of sulphides. Leachate concentrations rose when waste samples contained a higher mercury concentration (2000 - 4000 mg/kg) [5].

Another study showed that mercury-containing sludges from the chlor-alkali industry (1200 mg/kg Hg) could be stabilized by addition of a cement-fly ash mixture, if waste was pre-treated with sodium sulphide and ferrous sulphate. The cured product released very little mercury when subjected to leaching tests (< 1 ppb Hg) and met Japanese Standards (< 5 ppb) [12].

In a Swedish study elemental mercury and mercury oxide (1 - 5 wt %) were mixed with either Portland cement or slag cement (Portland cement and blast furnace slag), quartz sand, sulphur or troilite (FeS) and water and allowed to set and cure. The resulting monoliths were aged for 14 months. Leaching behaviour was investigated by applying the Dutch tank-leaching test for up to 11 months. Monoliths that initially contained HgO released up to 0.7 % of the initial mercury amount. The situation was significantly better with samples that started with elemental mercury and sulphur (or FeS). Very little mercury was released if it has been added as HgS [64].

4.4.7   Stabilization/solidification of mercury-containing waste in magnesia binder (Dolomatrix)

Short description

Waste is stabilized and solidified in a magnesium hydroxide matrix.

Background

The process has been developed by Dolomatrix (North Sydney, NSW, Australia) for general application for a broad range of wastes, not specifically targeted at mercury [20], [21], [22].

Process

The treatment involves the initial homogenisation of the waste with water, then adding the Dolocrete® reagents (magnesium oxide, proprietary mix of additives) at a ratio appropriate to the chemistry and concentration of the waste being treated. After complete mixing, the resultant slurry is cast into a suitable vessel for curing. The pH of the mixture is governed by the Dolocrete components and remains at 9.5 - 10.

The process has been demonstrated for high-level mercury wastes (filter cake, mercury iodide waste) from zinc smelter operations [20]. It also works under saline conditions. The volume of the waste is increased by about 25 %.

Product

The product is a solid material. Leachate concentrations (TCLP: < 0.01 mg/l) were far below regulatory standards (0.2 mg/l).

4.4.8 Stabilization of mercury-containing waste (Chemical Waste Management, Oak Brook, IL, USA)

Short description

Waste is mixed with sulphur in an alkaline medium and solidified by adding cement kiln dust.

Process

Sulphur (0.5 - 3 wt %, preferably 1 wt % of the waste) is added to the waste. This is done in presence of a strong base like sodium or potassium hydroxide (0.3 to 10 wt % of the waste, pref. 3 wt %). After 5 - 10 minutes of stirring cement kiln dust (CKD) is added in a ratio of 0.1 to 0.5 parts by weight CKD to 1 part waste. After mixing for 5 - 10 minutes the waste is allowed to cure for at least several hours but practically for several days. The process was demonstrated for sludges form the chlor-alkali industry with high salt content (up to 60 wt % NaCl or KCl).

Product

The product is a solidified waste. For a distinct waste with 94000 ppb mercury the leachate concentrations (TCLP) could be lowered to 2 - 8 ppb.

4.4.9   Fixation of mercury in desiccants (Mobil Oil)

Short Description

A mercury-containing desiccant is treated with dilute aqueous solutions that either sodium sulphide, sodium thiosulfate or potassium peroxomonosulphate. In the first case, mercury sulphide is formed in the second mercury oxide.

Background

The process has been developed to treat mercury-contaminated desiccants (molecular sieves).

Process

In order to carry out the process, first the quantity of mercury in the waste is determined. The waste is then treated with sodium thiosulphate ($Na_2S_2O_3$) an hydrochloric acid, causing a reaction in which elemental sulphur and sulphurous acid (H_2SO_3) are released. The former will react with mercury to give mercury sulphide (HgS) that will precipitate within the desiccant. In an alternative approach sodium polysulphide is added that reacts with hydrochloric acid to hydrogen sulphide (H_2S) and sulphur. H_2S will then corrode mercury to form mercury sulphide and hydrogen.

For the third described method potassium peroxomonosulphate is used. It oxidizes elemental mercury to mercury oxide (HgO) [3].

Product

Desiccants with entrapped insoluble mercury compounds. Leaching characteristics are unknown.

4.4.10   Mercury stabilization in chemically bonded phosphate ceramics (CBPCs) (Argonne National Laboratory, Argonne, IL, USA)

Short description

Stabilization of mercury as sulphide and subsequent solidification in a phosphate matrix.

Background

The process was developed to treat mercury-containing mixed radioactive waste.

Process

Powdered calcined magnesium oxide (MgO) and potassium dihydrogen phosphate (KH_2PO_4) are blended in equal molar amounts. Additional ingredients like fly ash or potassium (sodium sulphide (0.5 wt %) are added and all components together with water mixed with the waste for approx. 30 minutes. MgO and KH_2PO_4 react to form solid and insoluble $MgKPO_4 \cdot 6H_2O$. Afterwards the mixture is allowed to set. Setting occurs in approximately 2 h while curing needs about two weeks [74]. The process has been tested for a wide range of wastes including evaporator residues, contaminated soils, various salts, wastes, small homogenous debris wastes, wastewater residues, sludges from uranium ore processing operations, incinerator ash, and spent incinerator scrub solutions, including elemental mercury. The waste load in the final product is up to 70 wt % depending on the type of waste [13], [71].

Product

The product is a ceramic waste form of high strength and low open porosity. After 2 weeks curing, mercury leachability (TCLP: 0.04 - 0.05 µg/l) for several surrogates and a waste were far below EPA standards (0.025 mg/l) [53].

Scaling

The process has been successfully demonstrated in 55-gallon disposal drums with a planetary type mixer (batch mode). It can be deployed on a continuous basis after determination of the individual process parameters for each waste type.

Costs

Process costs have been calculated for a daily throughput of approx. 1.8 cubic meters or 3.4 t mixed radioactive waste form US DOE sites per day. Excluding disposal the costs would amount to 11.76 USD/kg (1999) [71]. In another study costs were estimated to range between 2.49 and 4.62 USD/kg, depending on the achievable waste load [13].

Similar processes

A process that is also based on the retarding properties of phosphate is marketed under the trade name Xtaltite® (Greg Eaton & Associates, Rhyll, Victoria, Australia).

Mercury can be incorporated in a phosphate structure by mixing it as mercury oxide with calcium fluoride and dilute phosphoric acid to form a kind of mercury apatite. The precipitate is filtered, dried and heated to 600 °C for up to 12 h. Slow heating prevents volatilization of mercury [57].

4.4.11 Stabilizing mercury-containing waste by adding thiol-modified zeolites (Steward Advanced Materials)

Short description

Treatment of mercury-containing liquid waste with thiol functionalized zeolithes and subsequent solidification with a commercial polymer [63], [65].

Process

The reagent in this method is a thiol-modified zeolite, more specifically a material with self-assembled monolayers on mesoporous supports (SAMMS), consisting of zeolite as a substratum and a packed monolayer of vertically stretched thiol-functionalized silane molecules. In a case study this material was added to a mercury-containing (1.5 wt %) liquid waste. The resulting sludge was mixed for 48 h. Afterwards solidification was accomplished by adding 10 wt % of an aqueous liquid absorbent (WaterWorks SP-400, a polyacrylate[8]). The method has been designed for liquid waste that may contain organic substances also.

Product

The product is a solid mass. TCLP-test showed that the mercury contents of the leachates (around 0.03 mg/l) were well below regulatory standards (0.2 mg/l).

Similar processes

Another group of investigators developed a process also based on thiol-functionalized zeolites and applied it to a solid waste surrogate (mercury-doped sand: up to 1000 mg/kg) and a real waste (contaminated sediment near a zinc smelter. Hg: 1.600 mg/l).

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[8] It may be noted that similar products on the basis of polyacrylate are available from other vendors also, like Stergo © or Aquadox ©.

The dosage of zeolite was 5 to 10 wt %. Portland cement was used for solidification (surrogate / waste ratio 0.5 - 2.0; water / cement ratio 1.0). All leachate concentrations (TCLP) passed US regulatory standards (0.2 mg/l) [79].

5 Potential advantages of elemental mercury stabilization from a thermodynamic point of view

The physical and chemical properties of elemental mercury pose some challenges for storage. Unlike all other metals it is liquid and could be spilled if a mercury-containing flask, container or other packaging is damaged accidently or by corrosion. Upon spillage mercury tends to form many, often very tiny droplets because of its high surface tension. Standard cleaning procedures are often not sufficient remove this finely dispersed mercury from the surfaces, cracks and corners of a contaminated area. Moreover, if done improperly cleaning may cause secondary contamination of other areas, tools and equipment.

Vapour pressure

One central problem of liquid mercury is its vapour pressure. At 20 °C it amounts to 13.2 mg/m^3, at 30 °C to 29.5 mg/m^3 and at 40 °C 62.5 mg/m^3 [34]. In Germany the maximum allowable concentration at workplace is 0.1 mg/m^3 [4], while in the USA a value of 0,05 mg/m^3 has been defined [46]. It is obvious that these limit concentrations may be easily exceeded if liquid mercury is not contained entirely.

In contrast with liquid mercury, most mercury compounds have a negligible vapour pressure at ambient temperature. A complete conversion of mercury into a solid compound would add an inherent protection against vaporization of mercury. Another feature of solid mercury compounds is their presumably lower physical mobility in case of a leakage. While mercury droplets may roll far away from the original place of leakage the heavy powders or granulates of mercury compounds are likely to stay close by so that the area of contamination might be significantly smaller, and the clean-up more easy.

Whether or not a conversion technology really can benefit from lower the vapour pressures of mercury compounds depends on the achievable conversion rate. If there remain unreacted mercury droplets in a product with a porous structure, they will control the mercury pressure – that can be as high as over pure elemental mercury.

Mercury alloys, the amalgams, are no compounds, but should be discussed here, too. They form easily when mercury is brought into contact with suitable metals like zinc,

copper or nickel. Amalgams are solids and therefore fulfil the criteria of safer handling. On the other hand it could be shown by experiment that copper or zinc amalgams do not have a lower mercury vapour pressure [39].

Aqueous solubility

If contact between water and mercury cannot be excluded in a storage facility, the leaching behaviour of the stored waste must be taken into account.

At 25 °C the solubility[9] of pure elemental mercury in pure water is approximately 0,06 mg/l [17]. That is less than the regulatory limit of 0.2 mg/l that is stated in the US Resource Conservation and Recovery Act (RCRA). Unfortunately neither mercury-containing waste nor waste mercury consist of pure mercury alone, but always contain mercury compounds to some extend. Potential impurities could be mercury oxide (HgO) or mercury chloride ($HgCl_2$). Their aqueous solubility is higher by several orders of magnitude and may further increase if ions like chloride or hydroxide are present in the solution.

A conversion of elemental mercury and mercury compounds to mercury sulphide (HgS) or selenide (HgSe) results in products of very low solubility. The minimum solubility of mercury sulphide is estimated at 10^{-10} mol/l or $2 \cdot 10^{-5}$ mg/l, while that of mercury selenide amounts to $10^{-7.8}$ mol/l or $3.2 \cdot 10^{-3}$ mg/l [23].

Thus, leaching of stabilized products should give lower concentrations of mercury than observed for elemental mercury. In practice, however, often much higher concentrations have been found. Reasons for this behaviour could be incomplete conversion (leaving some elemental mercury or mercury compounds unreacted) and the formation of by-products like mercury oxide that have a much higher solubility.

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[9] Most thermodynamic data have been determined at 25 °C. Temperature in landfills might be higher or lower. The resulting temperature effects cannot be foreseen in every detail at the moment, but within a margin of 15 - 35 °C it is not expected that they exceed one order of magnitude.

6   Conclusions

On the basis of the literature survey a number of technologies were identified that have been proven successful in stabilizing/solidifying elemental mercury and mercury-containing waste. Most of them, but not all, aim to convert mercury and mercury compounds into mercury sulphide or similar sulphide-containing compounds. Some of them have been demonstrated in full-scale or are expected to reach full-scale in short-time allowing them to treat up to 1000 metric tons per year.

Only one method was found that is based on the formation of mercury selenide. It is restricted to one special waste type and might not be applicable to others.

Several methods have been described that solidify elemental mercury as an amalgam either with copper or with zinc. Although the product is a solid, strong doubts were raised whether its solubility and vaporization characteristics show any advantage in comparison with liquid elemental mercury.

In many cases important information about emissions, possible exposition to workers, secondary waste streams and total volume and types of waste products is fragmentary. Facts on these issues will be needed to assess whether a specific process achieves a sufficient level of environmental and occupational safety.

Cost estimates are available for some technologies, but the calculations are based on assumptions made for specific US project parameters that cannot be easily applied to other settings.

In order to compare the cost-effectiveness of different stabilization/solidification options scenarios would have to be developed that take into account the expected throughput, the total amount and type of mercury-containing material to be treated, the necessary investments and the local operational costs.

Moreover there is a lack of appropriate experimental data on the long-term chemical behaviour of stabilized mercury, especially if the waste is or in the future could be in contact with aqueous solution. Activities in this direction may be accompanied with geochemical modelling.

References

Remark: if not noted otherwise all internet addresses have been checked in September 2009.

[1]   ADA Technologies (undated) Technologies for mercury control and stabilization.
         http://geco.mineroartesanal.com/tiki-download_wiki_attachment.php?attId=479

[2]   Adams, J.W.; Bowerman, B.S.; Kalb, P.D. (2002) Sulphur polymer stabilization/solidification (SPSS) treatability of simulated mixed-waste mercury contaminated sludge. WM'02 Conference, February 24- 28, 2002, Tucson, AZ.
         http://www.wmsym.org/archives/2002/Proceedings/11/511.pdf

[3]   Audeh, C. A. (1992) Fixation of elemental mercury present in spent molecular sieve desiccant for disposal. US Patent 5173286.

[4]   Bundesanstalt für Arbeitsschutz und Arbeitsmedizin (2009) Technische Regeln für Gefahrstoffe: Arbeitsplatzgrenzwerte. TRGS 900.
         http://www.baua.de/nn_16806/de/Themen-von-A-Z/Gefahrstoffe/TRGS/pdf/TRGS-900.pdf?

[5]   Baustoff-Service GmbH (undated) Immobilisierung von Quecksilber-verbindungen durch Verfestigung mit Zementen und industriellen Anfallstoffen - Immobilisierung von Quecksilberverbindungen durch Verfestigung -.
         http://www.baustoff-service.de/Fo_Text1/Fo-Text1.htm

[6]   Bethlehem Apparatus (undated). Mercury Retirement / Stabilization.
         http://www.bethlehemapparatus.com/mercury-retirement.html

[7]   Bethlehem Apparatus (2009). John M. Boyle. Personal communication 17 September 2009.

[8]   Broderick, T. E.; Grondin, R. (2003) Industrial-scale processes for stabilizing radioactively contaminated mercury wastes. WM'03 Conference, February 23-27, 2003 Tucson, AZ.
         http://www.osti.gov/servlets/purl/827608-I092Kt/native/

[9] Broderick, T. E.; Roth, R. L.; Carlson, A. (2002) Method for fixating sludges and soils contaminated with mercury and other heavy metals. US Patent 2002/0106317.

[10] Bowerman, B.; Adams, J.; Kalb, P.; Wan, R. Y.; LeVier, M. (2003) Using the sulphur polymer stabilization/solidification process to treat residual mercury wastes from gold mining operations. Presented at the Society of Mining Engineers Conference Cincinnati, OH February 24-26, 2003. http://www.pubs.bnl.gov/documents/25533.pdf

[11] Chan, H. B.; Hall, R. (2008) Treatment of elemental mercury. US Patent 2008/0234529.

[12] Chang, C.-Y.; Hsu, C. P.; Jann, J. S.; Chen, Y. W.; Shih, Y. C.; Mao, C. F.; Lin, W. Y.; Yin, K. L.; Wu, Y. M (1993) Stabilization of mercury containing sludge by a combined process of two-stage pretreatment and solidification. J. Hazard. Mat. 35, 73-88.

[13] Chattopadhyay, S. (2003) Evaluation of chemically bonded phosphate ceramics for mercury stabilization of a mixed synthetic waste. http://www.epa.gov/nrmrl/pubs/600r03113/600r03113.pdf

[14] Chiriki, S. (2006) Disposal strategy for proton irradiated mercury. Joint meeting of SAFERIB and EURISOL-DS (Task 5) on Oct 12/13, 2006. http://eurisol.wp5.free.fr/WP5/Documents/5th_meeting_Munchen_2006/chiriki-presentationon12-10-2006s.pdf

[15] Chiriki, S. (2007) Disposal strategy for proton irradiated mercury. 6th progress meeting of SAFERIB and EURISOL-DS (Task 5) May 11/12, 2007(FZ Jülich, Germany). http://www.eurisol.org/site02/secure.php?operation2=download&file=146----talk-397-S. Chiriki-Disposal strategy for proton irradiated mercury target .pdf&id_meeting=146&type=talk-S. Chiriki-Disposal strategy for proton irradiated mercury target

[16] Chiriki, S. (2009) PhD thesis (in preparation).

[17]   Clever, H. L. (1987) Mercury in liquids, compressed gases, molten salts and other ele-ments. Solubility Data Series 29. Pergamon Press, Oxford.

[18]   Conner, J. R. (1990) Chemical fixation and solidification of hazardous wastes, Van Nostrand Reinhold, New York.

[19]   DELA GmbH (2009) Verfahren und Vorrichtung zur Herstellung von Queck-silberfluid zur anschließenden Entsorgung, German Patent DE 102008006246.

[20]   Dolomatrix (undated) Treatment of mercury compounds with Dolocrete. http://www.dolomatrix.com/images/case_studies/treatment%20of%20mercury%20compounds%20with%20dolocrete.pdf

[21]   Dolomatrix (undated) Immobilization method. http://www.dolomatrix.com/index2.php?option=com_content&do_pdf=1&id=18

[22]   Doumbos, J.; Garman, D. (2005) Hazardous waste treatment technology by chemical fixation and stabilisation. 2005 International Conference for Hazardous Waste Management, Policy and Treatment/Disposal Technologies Beijing 31st May – 1st June, 2005. http://www.bcrc.cn/gb/backup/meetings/2005h-waste/6-1%200945-1030%20Hazardous%20Waste%20Treatment-cfs%20%20Bejing.pdf

[23]   Dyrssen, D.; Wedborg, M. (1991) The sulphur-mercury(II) system in natural waters. Water, Air, Soil Poll. 56, 507-519.

[24]   Fuhrmann, M.; Melamed, D.; Kalb, P. D.; Adams, J.W.; Milian, L. W. (2002) Sulphur Polymer Solidification/Stabilization of elemental mercury waste. Waste Man. 22 (2002) 327–333.

[25]   Gorin, A. H.; Leckey, J. H.; Nilf, L. E. (1994) Final disposal options for mercury/ uranium mixed wastes from the oak ridge reservation. Oak Ridge Y-12 Plant, TN (United States), Report Y/DZ-1106. http://www.osti.gov/bridge/servlets/purl/290905-stQxjA/webviewable/290905.pdf

[26]   Hamilton, W. P.; Bowers, A. R. (1997) Determination of acute Hg emissions from solidified/stabilized cement waste forms. Waste Man. 17, 35-32.

[27] Kaczur, J. J.; Taylor Jr., J. C.; Simmons, J. J. (1982) Stabilization of mercury in mercury-containing materials. US Patent 4 354 942.

[28] Kalb, P. D. (2002) Sulphur Polymer Stabilization/Solidification of Elemental Hg and Hg Contaminated Soil,Sludge and Debris. Presented at: Breaking the Mercury Cycle: Long Term Management of Surplus & Recycled Mercury & Mercury-Bearing Waste Boston, May 1 –3, 2002.

[29] Kalb, P. D.; Adams, J. W.; Milian, L. W. (2001) Sulphur Polymer Stabilization/ Solidification (SPSS) Treatment of Mixed-Waste Mercury Recovered from Environmental Restoration Activities at BNL. BNL Report 52614. http://www.pubs.bnl.gov/documents/22164.pdf

[30] Kalb, P. D.; Melamed, D.; Patel, B. R.; Fuhrmann, M. (2002) Treatment of mercury containing waste. US Patent 6 399 849.

[31] Kalb, P. D. (2005) Sulphur polymer cement (SPC), in: Spence, R. D; Shi, C. (2005) Stabilization and solidification of hazardous, radioactive, and mixed wastes. CRC Press, Boca Raton, 121-130.

[32] Kummel, S. (DELA, SAKAB) Personal communication 19 September 2009.

[33] Langton, C. A.; Iversen, G. M. (2002) Aqueous zinc bromide waste solidification. Westinghouse Savannah River Company, Report WSRC-TR-2002-00189. http://sti.srs.gov/fulltext/tr2002189/tr2002189.pdf

[34] Lide, D. R. (Ed.) (1996) Handbook of chemistry and physics, 77. ed. CRS press, Boca Raton.

[35] Litz, J. E.; Broderick, T.; Steward, R. M. (2002) Method and apparatus for stabilizing liquid elemental mercury. US Patent 6 403 044.a

[36] López, F. A.; Alguacil, F. J.; Roman, C. P. ; Tayibi, H., López-Delgado, A. (2008) Disposal of elemental mercury via sulphur reaction by milling. http://digital.csic.es/bitstream/10261/7692/1/DISPOSAL%20ELEMENTALHg.pdf

[37]   Mallow, W. A..; Young, R. D. (1996) Method of immobilizing toxic waste
        materials and resultant products US Patent 5 569 153.

[38]   Mattus, C. H. (1999) Measurements of mercury released from amalgams and
        sulfide compounds. ORNLITM-13728.

[39]   Mattus, C. H. (2001) Measurements of mercury released from solidified/
        stabilized waste forms. ORNLITM-2001/17.
        http://www.ornl.gov/~webworks/cpr/v823/rpt/109832.pdf

[40]   MAYASA (undated) Mersade –Life. http://www.mayasa.es/ing/mersade.as

[41]   Morris, M. I.; Osborne-Lee, I. W.; Hulet, G. A. (2002) Demonstration of new
        technologies required for the treatment of mixed waste contaminated with ≥260
        ppm mercury. ORNL/TM-2001/147.
        http://www.ornl.gov/~webworks/cppr/y2002/rpt/111527.pdf

[42]   Morris, M. I.; Hulet, G. A. (2003) Development and selection of technologies for
        mercury management on U.S. Department of Energy sites: the mer01–mer04
        and mercury speciation demonstrations. WM'03 Conference, February 23–27,
        2003, Tucson, AZ. http://www.ornl.gov/~webworks/cppr/y2001/pres/115882.pdf

[43]   Mostbauer, P.; Ziegler, C.; Lechner, P. (1994) Möglichkeiten und Grenzen der
        Immobilisierung von Abfällen.
        http://www.wien.gv.at/umweltschutz/pool/pdf/grenzen.pdf

[44]   Naturvårdsverket (2003) A Safe Mercury Repository. A translation of the Official
        Report SOU 2001:58 (Kvicksilver i säkert förvar).
        http://www.naturvardsverket.se/Documents/publikationer/620-8105-5.pdf

[45]   NFS (undated) DeHg - More Information.
        http://www.nuclearfuelservices.com/DeHg_More.htm

[46]   NIOSH (2005) Pocket guide to chemical hazards. Appendices. NIOSH
        Publication 2005-149. http://www.cdc.gov/niosh/npg/nengapdx.html

[47]   Oji, L. N. (1998) Mercury disposal via sulphur reactions. J Env. Eng. 124, 945-
        952.

[48]   Ortheil, M. (2009) Mercury stabilization - A new option for final disposal (presentation provided by DELA GmbH).

[49]   Osborne-Lee, I.W.; Conley, T. B.; Hulet, G. A.; Morris, M. I. (1999) Demonstration results on the effects of mercury speciation on the stabilization of wastes. ORNL/TM-1999/120.

[50]   Piao, H. (2003) Stabilization of mercury-containing wastes using sulphide. PhD Thesis. University of Cincinnati. http://etd.ohiolink.edu/send-pdf.cgi/PIAO%20HAISHAN.pdf?acc_num=ucin1059751247

[51]   Piao, H.; Bishop, P. L. (2006) Stabilization of mercury-containg wastes using sulphide. Env. Pollution 139, 498-506.

[52]   Pildysh, M. (2002) Synthetic aggregate and process for the production thereof. US Patent 6 416 691.

[53]   Randall, P.; Chattopadhyay, S. (2004) Advances in encapsulation technologies for the management of mercury-contaminated hazardous wastes. J. Hazard. Mat. B114 , 211-223.

[54]   Rehmat, A. G.; Goyal, A.; Laird, D. H. (2000) Method for stabilization of liquid mercury. US Patent 6 312 499, 6 Nov. 2001.

[55]   Riviere-Huc, C.; Huc, V.; Bosse, E. (2008) Method for stabilization of metallic mercury using sulphur. US Patent 2008/0019900.

[56]   SAKAB (2008) Fact Sheet - Stabilization of metallic mercury. http://www.sakab.se/upload/dokument/pdf/Laddningsbara%20filer/Produktblad/StabMerc_in_english_.pdf (retrieved 19 March 2009, no longer retrievable from this address).

[57]   Science Applications International Corporation (1998) Technologies for immobilizing high mercury subcategory wastes. http://www.epa.gov/waste/hazard/tsd/ldr/mercury/imoblzn2.pdf

[58]   Science Applications International Corporation (2005) Economic and environmental analysis of technologies to treat mercury and dispose in a waste containment facility. EPA/600/R-05/157.
http://www.epa.gov/nrmrl/pubs/600r05157/600r05157appf.pdf

[59]   Sollars, P. J.; Perry, R. (1988) Cement-based stabilization of wastes: practical and theoretical considerations. Water Env. Man. 3B, 125-134.

[60]   Spence, R. D. (undated) MASS: Mercury Amalgamation Stabilization/Solidification.
http://www.ornl.gov/~webworks/cppr/y2001/pres/114122.pdf

[61]   Spence, R. D; Shi, C. (2005) Stabilization and solidification of hazardous, radioactive, and mixed wastes. CRC Press, Boca Raton 378 p.

[62]   Smith, W. J.; Feizollahi, F.; Brimley, R. (2002) Stabilization of a mixed waste sludge surrogate containing more than 260 ppm mercury. WM'02 Conference, February 24-28, 2002, Tucson, AZ.
http://www.wmsym.org/archives/2002/Proceedings/11/355.pdf

[63]   Steward Materials (undated) Use of SAMMS® for Highly Radioactive, High Level Mercury Wastes.
http://sammsadsorbents.com/page/resource-center/case-studies/case-4

[64]   Svensson, M.; Allard, B. (2008) Leaching of mercury-containing cement monoliths aged for one year. Waste Man. 28, 597-603.

[65]   Tyson, D. R. (2008) Meeting the Mercury Target.
http://www.pollutionengineering.com/Articles/Article_Rotation/BNP_GUID_9-5-2006_A_10000000000000460372

[66]   UNEP (2008) Report on the current supply of and demand for mercury, including the possible phase out of primary mercury mining. UNEP(DTIE)/Hg/OEWG.2/6/Add.1.
http://www.chem.unep.ch/mercury/OEWG2/documents/f6)/English/OEWG_2_6.doc

[67]   US DOE (1999) Mercury contamination – amalgamate (contract with NFS and
        ADA) Stabilize elemental mercury wastes. DOE/EM-0472.
        http://www.p2pays.org/ref/13/12725.pdf

[68]   US DOE (1999) Mercury contamination – amalgamate (contract with NFS and
        ADA) Demonstration of DeHg^{SM} process. DOE/EM-0471.
        http://www.p2pays.org/ref/13/12725.pdf

[69]   US DOE (1999) Demonstration of ATG Process for Stabilizing Mercury (<260
        ppm) Contaminated Mixed Waste. DOE/EM0479.
        http://www.p2pays.org/ref/26/25268.pdf

[70]   US DOE (1999) Demonstration of GTS Duratek Process for Stabilizing Mercury
        Contaminated (< 260 ppm) Mixed Wastes. DOE/EM0487.
        http://www.p2pays.org/ref/26/25269.pdf

[71]   US DOE (1999) Stabilization using phosphate bonded ceramics salt containing
        mixed waste treatment. DOE/EM0487.
        http://www.p2pays.org/ref/13/12699.pdf

[72]   US EPA (2003) Land disposal restrictions: treatment standards for mercury-
        bearing hazardous waste; notice of data availability. Federal Register: January
        29, 2003 (Volume 68, Number 19)].
        http://www.epa.gov/EPA-PEST/2003/January/Day-29/p2035.htm

[73]   US EPA (2007) Treatment technologies for mercury in soil, waste, and water.
        EPA-542-R-07-003.
        http://www.epa.gov/tio/download/remed/542r07003.pdf

[74]   Wagh, A. S.; Singh, D.; Jeong, S. Y. (2000) Chemically bonded phosphate
        ceramics for stabilization and solidification of mixed waste. Environmental
        Protection Agency's Workshop on Mercury Products, Processes, Waste, and
        the Environment: Eliminating, Reducing and Managing Risks, Baltimore, MD,
        March 22-23, 2000.
        http://www.anl.gov/techtransfer/Available_Technologies/Material_Science/Cera
        micrete/wagh-mercury.pdf

[75]   Woodward, J. C. (1991) Process for treating mercury in preparation for disposal. US Patent 5 034 054.

[76]   Zhang, J. (2002) Stabilization/Solidification Treatment of Mercury Containing Wastes Using Reactivated Carbon and Cement. PhD Thesis. http://etd.ohiolink.edu/send-pdf.cgi/ZHANG%20JIAN.pdf?acc_num=ucin1035207019

[77]   Zhang, J.; Bishop, P. L. (2002) Stabilization/solidification (S/S) of mercury-containing wastes using reactivated carbon and Portland cement. J. Hazard. Mat. B92, 199-212.

[78]   Zhang, J.; Bishop, P. L. (2003) Stabilization/ solidification of high mercury wastes with reactivated carbon. Pract. Period. Hazard. Tox. Radioact. Waste Man., 7 (1), 31-36.

[79]   Zhang, X.-Y.; Wang, Q.-C.; Zhang, S.Q.; Sun, X.-J.; Zhang, Z.-S. (2009) Stabilization/solidification (S/S) of mercury-contaminated hazardous wastes using thiol-functionalized zeolite and Portland cement. J. Hazard. Mat. 168, 1575–1580.