

Treatment and Disposal of Mercury Contaminated Waste from Oil and Gas Exploration Facilities.

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Abstract

Mercury is one of the major toxic elements found in waste from oil and gas industries. It is available in all forms. Due to its abundant availability, it has a wide range of environmental and health impacts. Once disposed into atmosphere, it starts transforming continuously into various other forms. It also moves upward in food chain causing various health hazards. After having suffered from various episodes such as Minamata resulting from mercury poisoning, various techniques are suggested to separate and treat the mercury from wastewater and solid wastes. Solidification and thermal treatment are considered as best among other physical, chemical and biological processes. Although technically viable, these technologies are quite costly at present situation. Combination of thermal and solidification process could be one of the feasible methods through which the cost could be reduced. This paper summarizes the selection of treatment and disposal systems for mercury-contaminated wastes from and oil and gas exploration facilities, and experimental results on solidification conducted at AIT.

Introduction

Hazardous waste is classified based on four fundamental properties of the waste: *corrositivity, flammability, reactivity and toxicity* (La Grega and Buckingham, 1994). Based on these properties, hazardous waste can be divided into three different categories, namely Category A, B, and C.

Category A comprises of wastes for which principle hazard is flammability and is physically threatening the human beings. Asbestos, fluorescent tubes, hypodermic needles fall in this category. Category B consists of the less toxic heavy metal, compounds and non-toxic reaction products from chemical treatment category C wastes. Salts of irons, copper, manganese and barium fall in this category. Category C consists of salts of toxic inorganic cations like chromium, *mercury*, cadmium, arsenic etc.

Mercury is naturally occurring metal, which has several forms. Under normal condition of temperature and pressure, it exists in liquid form, When heated it can be transferred to gaseous state. In combination with other elements it is available in inorganic and organic form. Organic mercury (methylmercury) is most dangerous compound that is of great concern for the present situation. Mercury is used in various industrial processes/applications, consumer products and fossil fuels.

Mercury is emitted through human activities and natural sources such as volcanic eruption and degassing or vaporization from earth crust. Anthropogenic emissions have increased related to natural sources since the onset of industrial period. Basically, there are two different sources of

mercury from industrial activities namely, *Intentional use* and *Incidental release* (URL: epa.gov). Intentional use consists of production or supply of mercury, use in manufacturing, waste disposal. Mercury from manufacturing process and energy production falls under Incidental release. Incinerators and coal-fired boilers emit mercury to the atmosphere than all other point source combined.

The most important factor to be considered is that it can be re-emitted into atmosphere once it is deposited in earth surface. When mercury enters into the atmosphere, it starts to get transformed into another form. Metallic mercury once deposited in bottom of water bodies can be remobilized and introduced into aquatic cycle through physical, chemical process, and largely through microbial process. When uptake of a toxic metal occurs, microorganisms are frequently able to perform detoxification, yielding a product that can be more toxic to higher organisms. This is particularly true in the bacterial production of methyl mercury, a compound 1000 times more toxic to man than metallic mercury.

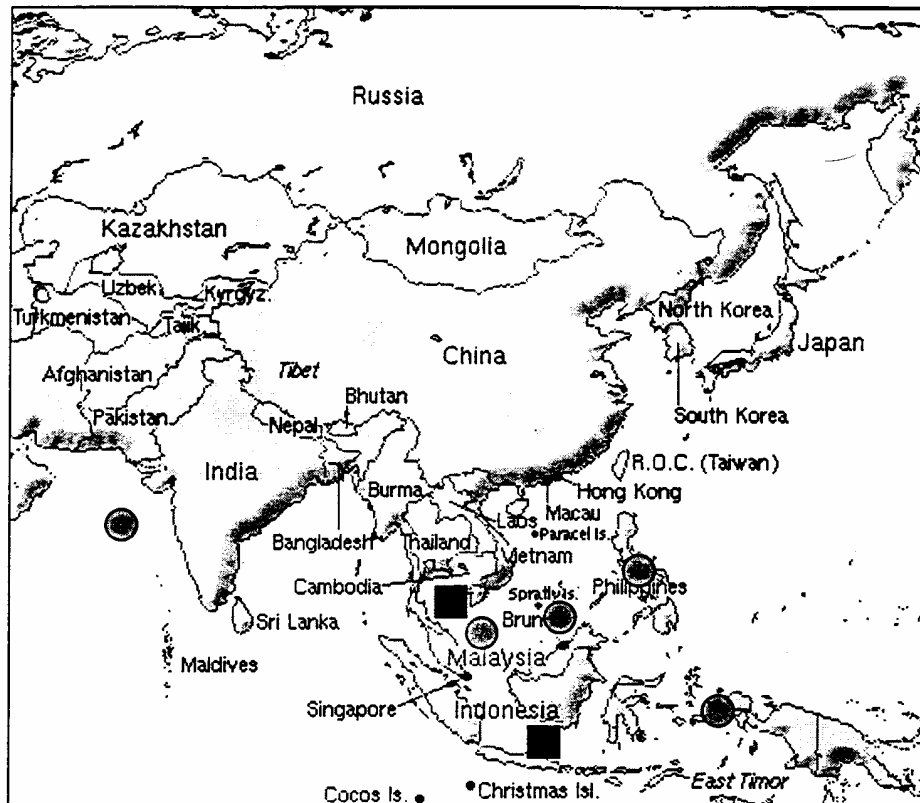
Methyl mercury easily gets into tissues of the plants and animals. For decade, large amounts of mercury were directly discharged into lakes and rivers. Local discharges led to high mercury concentrations in fish. Compared to mercury, methyl-mercury is more easily absorbed by fish and other aquatic fauna, either directly through the gills or by ingesting of contaminated aquatic plants and animals. This could further move to human and other animals through food chain causing various physical and disorder. Several end points, including late walking, late talking, nervous system dysfunctioning, and delayed mental development can be seen in children who are exposed to high level of methyl mercury. Impact on central nervous system, reproduction system, immune system, genotoxic effects are some of the impacts of methyl mercury toxicity. Minamata Bay disaster in Japan is one of the examples of long term mercury poisoning caused by uncontrolled disposal of mercury in to sea. The neurological damage, known as Minamata disease, caused thousands of people to suffer during 1960s. This was observed during 1960 as a result of disposal of tons of mercury from 1930 to 1960 into Minimata Bay in Japan.

Oil and Gas Industry: A major Source of Mercury

Mercury is a prevalent contaminant to hydrocarbon reservoir in Asia as shown in Figure 1. *Oil and gas* falls in category *Incidental release-manufacturing processes*. The solubility of mercury in petroleum liquids and its volatility in gaseous state, means that mercury and mercury compounds contaminate essentially the entirety of production, processing and petrochemical manufacturing systems. The range of mercury in SE Asian gas and gas liquid is about three orders of magnitude, from approximately 1 to 1000 $\mu\text{g}/\text{m}^3$ in gas and 1 to 1000 ppb in liquids. And too all the segments of production, processing and chemical manufacturing complex that utilize hydrocarbons in Asia are affected by the complications caused by the presence of mercury in process fluids. Mercury was found to produce several impacts on gas processing operations. They include;

- Mercury deposits in cryogenic fractionation equipment causing cracking of welds in the headers of aluminum exchangers.
- Mercury contaminates gas treatment processes such as molecular sieve and glycol dehydration units, chloride removal systems, and acid gas removal systems,

- Mercury sorbent materials, when spent, constitute a generated hazardous waste that plant operators must store or process for disposal.
- Mercury poisons catalysts in ethylene, aromatics and olefins manufacture.
- Mercury contamination of equipment poses a health and safety risk for workers involved in maintenance or inspection activities



- $< 100 \text{ ug/m}^3 \text{ (gas)} ; < 100 \text{ ppb (liquids)}$
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Figure 1. Mercury contents of Asian gas and gas liquid

The most important concern for production operations apart from market image and economic / treatment liabilities, are the toxic nature of sludge that accumulates in separators and heat exchangers; water discharge, especially from offshore platforms; and mercury accumulation in transportation systems such as tankers and pipelines.

The principal method to prevent mercury contamination of equipment and to eliminate mercury from plant products is to remove mercury from various feeds to the plant. At present, mercury removal beds are employed in which the removal material is specially designed for the particular application. Some commercial mercury removal systems are targeted at gas phase treatment and some are targeted at liquids. Gas phase treatment systems primarily consists of sulfur impregnated carbon or alumina, metal sulfide on carbon or alumina, and regenerative molecular sieve (zeolite) onto which is bonded a metal that amalgamates with mercury. Liquid removal processes consists of iodide impregnated carbon, metal sulfide on carbon or alumina, silver on zeolite mol-sieve and a two step process consisting of a hydrogenation catalyst followed by metal sulfide caption.

Removal of mercury from the gas and oil processing units can be done by various methods. Although the removal of mercury is done at various streams (gas drier, condensate stripper overhead treater, condensate drier, propane/butane treaters, depropanizer and debutanizer), it is recommended to remove mercury from the main feed to the plant, which eliminates the complications caused by mercury contamination of downstream plant equipment and eliminates the mercury in the products. One of the important factors to be considered in the transport and fate of elemental mercury from gas industry site is the particle size distribution of mercury droplets, because the rate of transport of the metal, directly or through secondary chemical reactions or transformations, will be largely controlled by its surface area. The dispersion of mercury in small droplets could result in a more rapid oxidation due to greater available surface area, resulting in an increased transport potential of the resultant mercuric compounds.

Mercury Waste Treatment and Recovery Methods

Mercury waste, once identified, must be treated prior to disposal of residue or debris to avoid the long-term liabilities of burial or storage. Hydrocarbon sludge is normally higher in mercury content than the process fluid from which it was deposited. The reason is that elemental and organic mercury has higher molecular weight organic compounds. Moreover one technology is not sufficient to completely treat mercury waste. Often a combination of physical, chemical, immobilization, thermal, electrolytic and in situ vitrification treatment methods need to be used. Due to the presence hydrocarbon matrix in sludge, the sludge is one of the more difficult waste materials to process for treatment and disposal.

Mercury waste can be treated and disposed by,

1. Recovery / recycle / reuse
2. Physical / chemical treatment
3. Incineration

Recycling methods can be gravity separation, filtration, distillation, solvent, chemical regeneration etc. Physical methods could be neutralization, precipitation / separation and detoxification (chemical). In incineration, the waste is burnt at medium / high temperatures. Various researchers have conducted researches on treatment of mercury laden waste and have found some success to reduce and recovery mercury from the waste. Some of the research works are summerised in Table 1.

Table 1: Summary of research on mercury waste treatment, recovery and disposal methods

Origin of waste	Treatment methods/chemical employed	Reference
Discarded and spent products from thermameter etc.	Crushing, Separation and Oxidation (550 ⁰ C and Nitric acid), Stabilization (Sodium sulfide), storage.	
Gas processing facilities	Cleanup and disposal of mercury waste.	Wilhelm & McArthur (1994)
Contaminated sludge by methyl mercury in Minamata Bay	Sediment disposal by revetment and dredging.	Yoshinaga (1995)
Municipal wastewater	Incineration of 238 g/day out of 248g/day mercury with remaining 10g/day is discharged into river.	Balog & Liang (1995).
sludge	Ion exchange method to separate solid phase heavy metal using composite ion exchange membrane.	Sengupta & Sengupta (1996)
Wastewater	Use of Duolite GT-73 ion exchange resin.	Ritter & Bibler (1992)
Removal of gas phase mercury	Use of impregnated granular activated carbon.	Mc Laughnin & Vidic (1995)
Mercury from fluorescent and other lamps etc.	Dry crushing and heating technology and fluidized bed process.	AERC, USA
Chloride solution	By contact deposition on iron felt.	Grau & Bisang (1995)

From the tabulation above, it can be seen that the major treatment and recovery process applied were revetment, ion exchange, adsorption, crushing and heating, and incineration. Failure on revetment can cause sever damage to the surrounding environment, where as ion exchange and adsorption can be hindered by presence of other contaminants. Heating and incineration can release the mercury vapor into atmosphere causing atmospheric pollution. The process of solidification and disposal into secured landfill, gas phase recovery of mercury, and thermal treatment is gaining interest in mercury treatment and recovery field by various researchers and industries.

Solidification

Solidification is the physical stabilization process that is designed to improve the engineering properties of the materials, such as compressive strength, bearing capacity, resistance to wear and erosion, and permeability so that the chance of release of contaminants from solidified blocks in a disposal site can be reduced. Binders such as cement, pozzlonas, and thermoplastics are used to immobilize contaminants in sludge. The effectiveness of stabilization is tested using leachability analysis. Some of the research works published on stabilization of hazardous waste is summerised in Table 2.

Table 2: Summary of research on mercury waste treatment and recovery using solidification.

Origin & characteristics of waste	Treatment Methods	Results	Reference
Mercury containing waste of gold mines	Dressing and methods of selective stabilization of pulp.	Could be effectively stabilized	Khanturgaeva et al 1994.
Leachate produced from integrated sludge treatment facilities.	Cementation of mercury in a chloride medium using metallic zinc, iron and aluminum as reducing agents.	Efficiency of removal is dependent upon the type of metal used and pH and surface area of sacrificial metal.	Anacleto & Carvalho 1996
Hazardous waste (comparison of cost)	Stabilized and landfilled	Cost can be reduced (130 to 150 US \$ per ton).	GENCO 1997
Hazardous waste mixed	Pozzolanic materials used to react with polyvalent metal ions and other waste components.	Formation of inert and stable solid materials.	ARM Inc.

Experimental Study at AIT Research Station

An experimental study was conducted at AIT Research Laboratory for effectiveness of solidification in mercury contaminated sludge produced from an oil and gas exploration facility. The ratio for cement, sand, sludge and water were fixed based on the earlier study made at AIT for solidification of COD heavy metal sludge. Table 3 presents the mix ratio and other parameters for the experiments.

Table 3. Experimental Parameters and selected values, and test methods

Description	Selected value / Methods	Remarks
Number of batches based on sludge to cement ratio	4 (0.15, 0.10, 0.01, 0.005)	
Sand to cement ratio	1:1	
Water to cement ratio	1:1	Sometime modified based on workability
Assumed mercury concentration at beginning of experiment	30% by weight	Based on preliminary results
Reaction time for pretreatment with sodium sulfide	30 min	From Chang (1993)
Assumed sodium sulfide to Mercury molar ratio	15:1	From Chang (1993)
Sludge to sodium sulfide ratio	1:0 to 1:10	

Test methods used

Compressive strength	ASTM C 109-86 UTM machine	
Density	Weight per unit volume of waste	
Leachability Test	IWD, Thailand-Extraction Procedure	
Heavy Metal detection	AAS or equivalent standard method	

The experimental procedure for the solidification experiment of the sludge is shown in Figure 2.

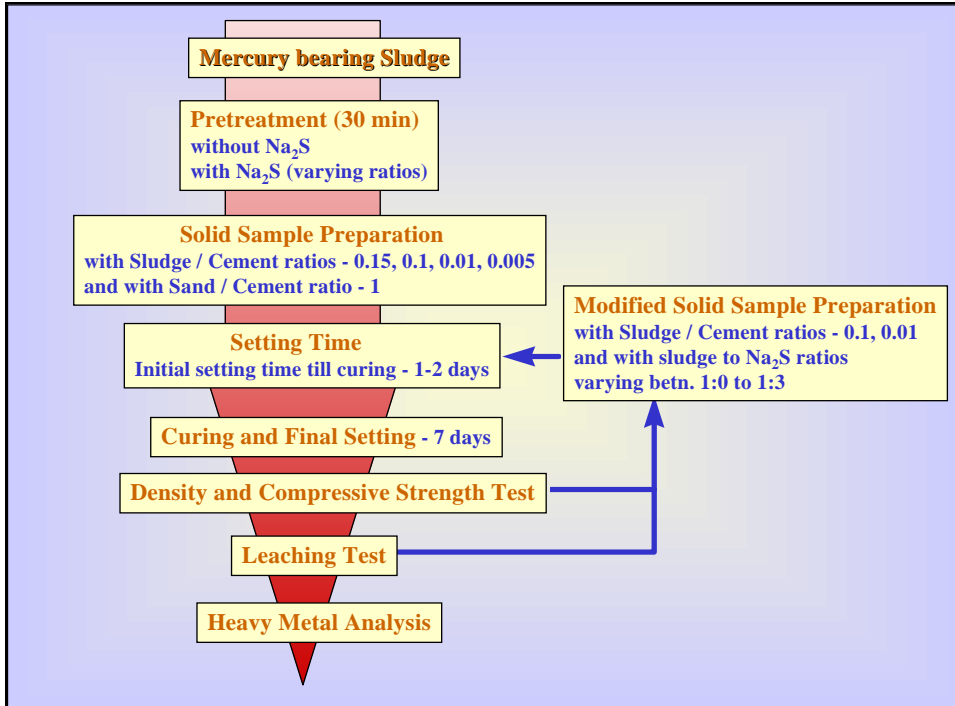


Figure 2: Experimental methods

Here, it was noted that, the higher percentages of sodium sulfide have caused the improper solidification and setting. From the density and compressibility test it was found that the blocks with low sulfide percentages have high density and compressive strengths. Also increase in sludge volume has resulted in increase in volume of solidification volume beyond sludge cement ratio of 0.01 (Figure 3).

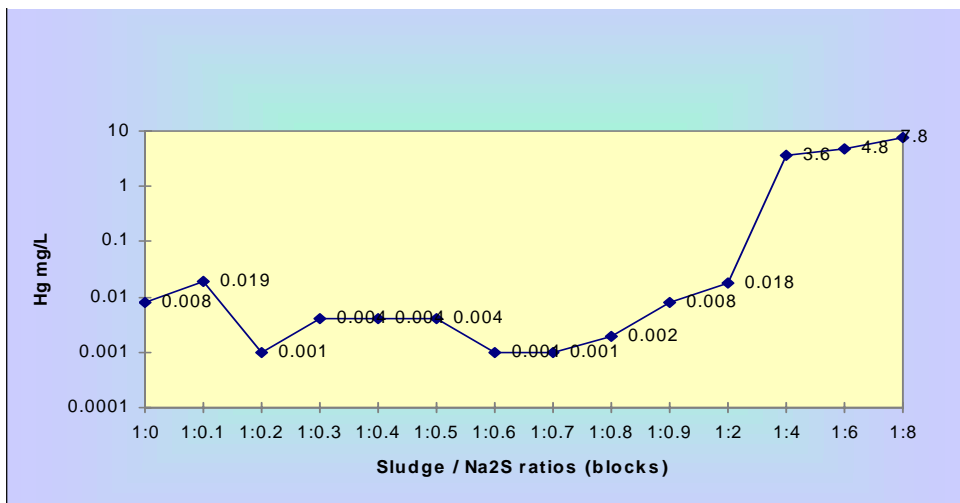


Figure 3. Leachability analysis for different sludge to sodium sulfide ratio.

Similarly, the leachability test presented an interesting result. From the results it was found that the increase in mercury concentration for a sludge sodium sulfide ratio was more than 1:0.2, where as it was minimum for sludge sodium sulfide ratio less than 1:0.2. The value is still less than Thailand Standard (0.2 mg/L) for sludge sodium sulfide ratio of 1:1.

Economic Evaluations

Based on the results obtained from the Laboratory scale experimental studies, the optimum values were found to be, sludge to cement ratio as 0.01, sludge to sodium sulfide ratio as 1:0.02, volume in cum per kg of sludge as 0.08. From cost calculation it was found that the solidification cost quite high (= US \$ 6,000 per ton of sludge excluding labor cost). This could imply that although effective for stabilization of sludge, it is quite costly for the industries to implement.

Thermal treatment

Thermal process is considered as an alternative technology for the treatment of mercury contaminated waste. Thermal treatment is viewed as a distillation process at controlled temperature and reactor conditions, in which mercury vapor is condensed and collected in relatively pure form. The normal practice for thermal treatment is incineration and pyrolysis.

Table 4: Summary of mercury waste treatment and recovery by thermal treatment method.

Origin and characteristics of waste	Treatment methods	Results	References
Soil contaminated with high level of mercury such as in metering of natural gas sites.	Prototype thermal treatment process, chemical leaching process, combination of physical separation / chemical leaching process.	Chemical treatment combined with physical separation process is most effective.	GRI
Hazardous waste of organic nature	Use of moderate temperature for thermal treatment.	The method can handle soils and dewatered sludge.	Hsieh YU, Chang & Burn (1994)
Mercury contaminated waste	Pretreatment, volume reduction and high temperature oxidation (1000 ⁰ c)	Good recovery with decomposition of all mercury compounds.	Bohm & Mussig 1996
Mercury contaminated sludge.	Components: furnace, heat exchanger, gas purifier carbon, and vacuum pump.	99% pure mercury received.	MRS Inc.

There are various organizations working on mercury recovery systems using thermal treatment. Some of the disadvantages of thermal treatment are requirement of additional fuel, maintenance of combustion temperature, regular monitoring requirement, possibilities of distillation of other volatile contaminants in distillates requiring subsequent treatment for recovery, High cost per unit recovery if used for soil/sludge with low percentage of mercury contaminants. Ultimately, the requirement of a secured landfill can not be ignored since the ash left after incineration should be landfilled.

But from the data available for thermal treatment and recovery system, the cost could be considerable and can have a larger mobile unit with a capacity of 4 cubic yards per day (\$ 1,300,000).

Conclusion

Laboratory scale studies on solidification indicate that although the strength and leachability criteria can be satisfied, volume of solidified waste and the cost of solidification per ton of sludge are not practically viable. The probable reasons could be requirement of high quantity of binder and stabilising chemical. Also, all the mercury (after solidifying) is lost to the disposal site without any avenue for recovery and reuse/sale. In conclusion, solidification would not be the best economically viable option for treatment of the sludge.

Moreover, presence of 90% of the mercury in the elemental form, defeats the necessity to stabilise the metal in solidification, because removal of elemental mercury could be better achieved by certain technologies like thermal treatment or physical separation. As discussed earlier, recovery of mercury in high percentages could be achieved by employing thermal treatment. Detailed technical feasibility studies including trial runs will have to be conducted to finalize the exact configuration and components of the thermal unit. It would be necessary to know what type of thermal process (vacuum, inert, gas recycle, low pressure oxidative) would be best suited for decomposing and condensing the mercury complex present in the sludge.

The thermal treatment option could be materialised either by having an onsite (onshore) mobile treatment unit or by exporting the waste to a waste treatment company either within the nation or outside the country. Exporting outside the country would require an assessment of the hazardous waste transport legalities and regulations (Basel convention).

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