Immobilization of Heavy Metals in Industrial Waste by Solidification/Stabilization Methods

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INTRODUCTION

Heavy metals are essential in many manufacturing processes such as production of automotive batteries, chloralkali, and fluorescent lights. As a result, industrial wastes containing heavy metals can create problems to the environment and human beings because of their indestructible nature. Heavy metals can easily enter the food chain and continue up ultimately affecting human beings (Valenti, 1992, Okrent and Xing, 1993). Many kinds of heavy metal can cause the development of different types of cancers. For example, arsenic, nickel, cadmium, chromium, and beryllium can increase the risk of lung cancer in humans. In addition, the ingestion of inorganic arsenic compounds has been shown to increase the risk of skin cancer in human beings. Furthermore, the exposure of humans to the oxide of cadmium has been shown to increase chances for development of prostate respiratory, and genito-urinary cancers (Okrent and Xing, 1993).

Unlike the preceding toxic metals, mercury will not cause cancer, but will induce the development of "Minamata disease", which occurred during the 1950s in Japan. Furthermore, mercury can cause central nervous system disorder, numbness, impaired speech, paralysis, oleformity, coma and death (Chang et al , 1993).

Because of the release of heavy metals into the environment, it has become necessary to develop and implement suitable procedures for the treatment of heavy metal-bearing wastes prior to disposal. There are many common processed for the treatment of heavy metal wastes such as cheating by the strong binding compound, trimercapto-s-triazine (Ayoub et al., 1995), acid-extraction treatment system (Kastanek et al., 1994), and solidification/stabilization (Chang et al., 1993 and Twidwell et al., 1994). The latter method is the most common one used to prevent heavy metals from leaching into the environment.

TYPES OF SOLIDIFICATION/STABILIZATION

Solidification/stabilization is the usual method for treatment of heavy metal-bearing wastes. Indeed, there are different details between solidification and stabilization. Solidification is the conversion of a liquid meterial into a non-liquid material in order to improve its handling characteristics or in order to make it acceptable for landfill disposal. Stabilization can be defined as the treatment of a waste which results in the decrease of the mobility of contaminants in a landfill environment and making waste constituents less reachable. In heavy metal-bearing industrial waste menagement, solidification/stabilization is a term normally used for methods which reduce the mobility of pollutants, thereby making the waste acceptable under current land disposal requirements (Barth, 1990 and Weitzman, 1990)

Solidification/stabilization can be divided into six categories:

1. Cement based

Cement based binders can be classification into three types:

1.1 Portland cement

1.2 Cement kiln dust

1.3 Fly-ash mixtures

The cement-based methods are indeed very effective. However, their uses may be pending on the cost of cement (Chang et al., 1993). Among three types o cement-based binders methods, portland cement with some additives is about the most common and has been widely used as noted by many investigators (Cartledge et al., 1990, Roy et al , 1991. Gilliam et al , 1990 Vipulanandan and Krishnan., 1990 and Daniali., 1990).

2. Lime based

Lime based binders can be categorized into three types:

2.1 Lime

2.2 Lime kiln dust

2.3 Mixtures of fly-ash and lime

Lime-based methods using lime with some additives, to form pozzolanic concrete, have been developed. Various reusable wastes have been used as additives in the lime-based methods. For example, Johannesmeyer and Ghosh added fly ash to stabilize cadmium and chromium bearing sludge and Liu added fly ash to stabilize mercury-bearing sludge. The waste by-product lime was also employed to substitute virgin lime in solidification. The application of industrial wastes, such as fly ash and by product lime, in solidification reduces the cost of raw materials (chang et al , 1993).

3. Absorbents

Absorbents are divided into two types:

3.1 Hydrophilic clays and wood chips, sawdust, rice hulls

3.2 Organophilic clays and wood chips, sawdust, rice hulls.

This method is not considered to be an acceptable method of solidifying liquids. While certain heavy metals and even, possibly, some organics may have their leach ability diminished by absorption on solids, this has generally been discarded in favor of other solidification and stabilization practices. Clearly, absorption will have little impact on the stabilization of solid materials, such as contaminated soil (Weitzman, 1990).

4. Thermoplastic

Thermoplastic materials are classified into two types:

4.1 Asphalt bitumen

4.2 Thermoplastic polymer

Thermosetting material has been used to encapsulate radioactive wastes. However, their use for the treatment of hazardous wastes including heavy metals has been limited and little data exist to support their use at this time (Weitzman, 1990).

5. Thermosetting polymers

Thermosetting polymers are used to encapsulate solidified radioactive wastes. Thermosetting polymers have been suggested as a possible binder for hazardous waste; however, except for the treatment of off-specification monomers by reacting them to form polymers, this method of stabilization has not been used beyond the experimental stage. Basically, both thermosetting and thermoplastic materials can be used to coat or encapsulate wastes that are solids or have been solidified by other means (Weitzman, 1990).

6. Vitrification

This method is a comparatively new method of stabilizing wastes containing large amounts of solid materials. Vitrification is the process that melts waste into a solid, rocklike material. This method is common for treatment of ash from a rotary kiln incinerator (Weitzman, 1990).

Among those six applications of solidification/stabilization methods which are used to reduce the leach ability and improve the stability of many heavy metal-bearing waster, only a few practical types can be used to treat these waste, that is cement and lime/fly-ash based binders. They are used commercially and have been successful in reducing the leach ability of metals for many types of wastes. Their process involves the chemical reaction with the free water in the waste to form a dry solid making the contaminants as immobile as possible, and then restricting their mobility by encapsulating them in the resultant matrix. This encapsulation can result in significant reductions in the leachabiligy of Resource Conservation and Recovery Act listed metals (Weitzman, 1990).

FACTORS FOR SELECTING APPROPRIATE SOLIDIFICATION AND STABILIZATION PROCESS

According to a variety of solidification/stabilization processes, many factors have to be considered for selecting appropriate processes of treatment. Broadly. There are three factors.

A. Consider whether the waste is located at a remediation site, where it will remain after fixation, or whether it will be sent to a landfill.

When solidification and stabilization is used for on-site remediation, a special lined and capped bunker or landfill may be constructed to store the waste. If the solidification/stabilization process reduces the mobile of the hazardous constituents adequately, then the waste may be left on-site with a minimum of site preparation. If not, it can be stored in an on-site bunker The time that is takes the waste to set up and for its leachabilty to be reduced is less critical if the mass can cure in and on-site bunker. As a result, lime/fly ash types of binders may be adequate. They are less expensive than the cement based materials and can reduce the leachabilty of many metals. If the heavy metal-bearing waste is going to a landfill, then the economics of a process dictates that it be solidified and stabilized as rapidly as possible, so that operating time can be minimized. (Weitzman , 1990 and Okrent and Xing, 1993)

B. The physical consistency of the waste and its toxic constituents, is the second factor which will determine whether the waste must be solidified and/or stabilized.

Generally, the waste must be compatible with the solidifying/stabilizing agent and must be hazardous based on toxicity only. Physical characteristics of the waste and the binder are also important. Particle size and shape in the waste and of the hardened binder can play an important role in the performance of treatment processes in the field. If the waste contains large amounts of water, then solidifying it will require large amounts of binder. Cement or cement kiln dust is usually more expensive than fly-ash with lime, limestone, or lime/kilndust addition However, the latter may not produce an acceptable product Impurities can affect the strength, durability, and permeability of portland cement and asphalt mixtures Even minor quantities of some waste compounds act as accelerators or retarders can cause poor performance in solidification and stabilization products Methanol, xylene, and benzene increase the concentrations of toxic constituents in leachate from the solidified and stabilized samples (Weitzman, 1990, Okrent D and Xing L, 1993)

C. The cost of solidification and stabilization has generally been considered low compared with those for other treatment techniques.

Requirements for transporting raw materials to the plant or site and transporting finished products to disposal will also affect costs. Cements, fly ash, and so forth, are cheaper raw materials than are polyolefins and similar materials Processing requirements for the latter may also make their use more expensive (Weitzman, 1990).

Experimental studies : solidification/stabilization methods

A. Stabilization of Mercury Containing Sludge by a Combined Process of Two Stage Pretreatment and Solidification. (Chang et al., 1993)

Chang et al. have experimented with stabilization of a mercury-bearing sludge from a chlor-alkali industry in the South of Taiwan by using a cement-fly ash solidification method after pretreatment with sodium sulfide and ferrous sulfate.

The sample of mercury-bearing sludge is pretreated by adding 5 to 25 ppb. fof Na_2S and 5 ppb.for $FeSO_4$ and followed by solidification treatment, using varied ratio of portland cement:fly ash:mercury bearing sludge. Tests of the setting time and of the curing time then proceed. The measurement of the compressive strength of the cylindrical solid sample and the standard US extraction procedure are conducted to evaluate the performance of the solidification product. Acetic acid is used for the leaching test and measurement of the total mercury as well as the organic mercury concentrations of the extraction leachates.

The mercury-bearing sludge in this experiment is considered as hazardous waste because of its contents of 0.66 ppm. total mercury in the mercury-bearing sludge, which exceeds the permissible value of 0.2 ppm. (a US regulation on Hg for characterization of hazardous waste), and 0.055 ppm. organic mercury in the extraction leachate.

A comparison of the results of three solidification processes, respectively, without pretreatment, with one-stage pretreatment with Na_2S, and with two-stage pretreatment with Na2S and $FeSO_4$, indicates that the two-stage process yields the best stabilization effciency. The two-stage pretreatment greatly enhances the stabilization efficiency of the solid matrix. From the results of the effects of the ratio of cement (C), fly ash (F), and sludge (S) on the compressive strength, a sufficient amount of binding materials is needed for solidification so as to provide sufficient binding strength.

There exists a tendency for the concentration of total mercury, in the extraction leachate of the solids matrix to incresas with curing time during time during solidification for the process without the two-stage pretreatment. All cases at curing time = 28 days meet the strict Japanese regulation. However, as curing time increases from 28 days to 126 days, the values of total mercury tend to increase and may exceed 5 ppb. in some cases with values of pretreatment molar ratios of Na_2S:Hg = 15 and $FeSO_4$:Hg = 5 , and a mixing ratio of cement:fly ash:sludge = 30:30:40, the compressive strength of the solid endproduct and the concentrations of the total and of the organic mercury in the extraction leachate of the solids matrix all meet the strict Japanese regulation for the in-land safety sanitary landfill.

This experiment indicates that the possible organic mercury pollution problem associated with mercury-bearing sludge can be effectively reduced or prevented by suitable solidification/stabilization, including two-stage pretreatment.

B. Stabilization of Arsenic Bearing Waste Materials (Twidwell et al., 1994)

Arsenic and arsenical compounds have been reported in waste stream from the metallurgical, glassware, wood preservation, ceramic, tannery, dye and petroleum refining industries. In addition, the manufacturing of herbicides, pesticides, organic, and inorganic chemicals also produce an appreciable quantity of arsenical waste

The storage and disposal of waste residues containing arsenic, the disposal of arsenic-containing waste solutions, and the disposal of acid mine waters containing arsenic are common industrial problems The problem of safely disposing of arsenic bearing aqueous solutions is significant and has to date not been solved Efforts at Montana College of Mineral Sciences and Technology have been directed toward studies that may produce an acceptable solution to the arsenic solution disposal problem, including stabilization of arsenic bearing waste solids. There are four experiments studying the stabilization of solid waste materials. One experiment is based on the vitrification technique and three experiments use cement/lime mixtures for stabilizing various arsenic bearing materials

B.1 Vitrification Method

Twidwell and Mehta (1985) use the vitrification method that converts arsenic to calcium arsenate for disposal of copper smelter flue dust Then calcium arsenate can be dissolved in copper smelter slag and be doped arsenic by dissolution of calcium arsenate with copper smelter slag. Therefore, arsenic release was minimal from the glassy slag test materials.

B.2 Cement of Cement/Lime Mixtures

Tang (1992) investigated the stabilization of copper smelter flue dust with cement/lime and the influence of stripping copper from flue dust (by a pyrometallurgical process) on the stability of the final arsenic bearing residue From testing the mixtures of the final arsenic bearing residue added with cement (25%) and lime (10%), they passed the TCLP test for arsenic, lead and cadmium

The second experiment conducted by Twidwell and Charwin (1989) determined that calcium and iron arsenate/arsenite contaminated soils were not stabilized by cement alone, but required the additional stabilization roast

The third study by Twidwell and McGrath (1989) evaluated whether organic arsenic (monosodium methylarsonate) could be stripped from a salt brine solution (containing approximately two grams per liter arsenic) and the product was stabilized by cement. From four precipitation and one solvent extraction techniques, precipitation is the most effective method for removal of arsenic

V. CONCLUSION

Toxic heavy metals are usually considered persistent in the environment because they do not decay. This raises a serious concern about whether and how this kind of waste can be treated. Stabilization/solidification is typically used to immobilize heavy metal-bearing wastes because this method reduces and/or prevents the release of toxic heavy metals into the environment, including surface and ground waters, which may lead to the development of human illness. There are six types of S/S, each type is suitable for the immobilization of different kinds or heavy metals and depends on the purpose of treatment and other factors as described in the section titled "Factors for selecting appropriate solidification and stabilization process."

The results from many studies indicate that solidification and stabilization methods are useful processes in order to immobilize heavy metals from industrial waste. For instance, Chang et al. (1993) developed the effective method of adding two-stage pretreatment stabilization methods for reduction of leachabiligy of mercury-bearing sludge. This method provides such a good reduction of mercury ot the low level of less than 1 ppb. while the Japanese safety regulation of mercury for the inland sanitary landfill is equal to 5 ppb. In addition, Twidwell et al. (1994) tried to develop an acceptable process in order to stabilize arsenic bearing waste solids by using the vitrification and cement/lime mixtures. Their experiments were successfull because the treatment decreased the release of arsenic which cnd pass a U.S. regulation.

The solidification/stabilization method is one of the most widely used heavy metal treatment process. This method has several advantages and only some disadvantages. It is hoped that additional S/S methods will be developed for better heavy metal-bearing wastes treatment in the future.

REFERENCE

Ayoub G.M., Koopman B., Bitton G., and Riedese K. (1995) Heavy metal detoxification by trimercapto-s-striazine (TMT) as evaluated by a bacterial enzyme assay. **Environmental Toxicology and Chemistry.** 14, 193-196

Barth E.F. (1990) An overview of the history, present status, and future direction of solidification/stabilization technologies for hazardous waste treatment. **Journal of Hazardous Materials.** 24, 103-109

Cartlege F.K. Butler L G., and Chalasani D (1990) Immobilization mechanisms in solidification/stabilization of Cd and Pb salts using portland cement fixing agents. Environmental Science and Technology. 24,867-873.

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

Chatwin T.D. and Twidwell L G (1989) Treatability study for the whitmoyer laboratories site, Jackson Township, PA.:Cement Casting Final Report, Final Report to NUS Corporation, Pittsburgh, PA, Ebasco REM III Program, EPA 68-01-7250 WA No 200-3LC9, Montana Enviromet, Butte, MT, July 106 pp.

Cocke D.L. (1990) The binding chemistry and leaching mechanisms of hazardous substances in cementitious solidi fication/stabilization systems **Journal of Hazardous Materials.** 24, 231-235.

Damiali S. (1990) Solidification/stabilization of heavy metals in latex modified portland cement matrices. **Journal of Hazardous Materials.** 24,225-230

Gilliam T.M., Spence R.D., and Bostick W D. (1990) Solidification/stabilization of technetium in cement-based grouts. **Journal of Hazardous Materials.** 24, 189-197.

Kastanek F., Bizek V., and Matejka M, (1994) Elimination of heavy metals from microbial cultures by chemical and biological leaching under decreased values of pH **Journal of Hazardous Materials**. 37, p 46-67

Okrent D. and Xing L. (1993) Future risk from a hypothesized RCRA site disposing of carcinogenic metals should a loss societal memeory occur **Journal of Harazdous Materials**. 38,363-384.

Roy A., Eaton H.C., and Cartledge F K (1991) Solidification/stabilization of a hravy metel sludge by a portland cement/fly ash binding mixture. **Journal of Hazardous Materials.** 8, 33-41.

Tang X. (1992) Recovery of copper from stabilized copper smelter flue dust. M S. Thesis, Montana College of Mineral Science and Technology, Butte, MT, May 85 p

Twidwell L.G. and McGrath S (1989) Survey of arsenic removal and/or stabilization techniques applied to fermenta waste solutions and solids, Final Report to Fermenta, ASC, Dec, 84 p

Twidwell L.G. and Mehta A K (1985) Disposal of arsenic bearing copper smelter flue dust Nuclear and Chemical Waste management. 5, p 297-303.

Twidwell L.G., Plessas K. O., Comba P.G., and Dahnke D.R. (1994) Removal of arsenic from wastewaters and stabilaztion of arsenic bearing waste solids:Summary of experimental studies. **Journal of Harazdous Materials**. 36, p. 69-80.

Valenti M. (1992) Recovering heavy metals. Mechanical Engineering. December, 54-58.

Vipulanandan C., and Krishnan S. (1990) Solidification/stabilization of phenolic waste with cementitious and poly meric materials. **Journal of Hazardous Materials**. 24 123-136.

Weitzman L. (1990) Factors for selecting appropriate solidification/stabilization methods. **Journal of Harazdous Materials**. 24, 157-168.