



INSITU REMEDIATION OF MERCURY CONTAMINATED SITES

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Abstract: Indiscriminate disposals and spills of elemental mercury in terrestrial environments have become a common occurrence despite a number of stringent regulations against the usage of mercury. The objective of this study was to treat mercury contaminated soils insitu. This was possible by converting mercury to a more stable mercury sulphide HgS. Batch experiments were conducted to assess the feasibility for generation of the sparingly soluble solid HgS from elemental Hg and sodium polysulphide solution under various conditions. The results provided optimal design parameters like polysulphide dosage, pH and reaction time. With the optimal conditions known, it is feasible to create an environment at room temperature that leads to the generation of HgS from elemental Hg and liquid polysulphide. Concurrent HgS formation and HgS mobilization was achieved through micromodels. Micromodels are transparent tools employed with glass beads as representative porous media. They are effective in capturing HgS formation and mobilization which are predominantly pore scale processes. This approach would be novel, cost effective and has the potential for large scale in situ treatment of mercury that could substantially reduce the prohibitive cost of thermal desorption or excavation and disposal.

Keywords: mercury; mercury sulphide; micromodel; insitu.

INTRODUCTION

Mercury is often found in soils as “hot spots” located close to industrial facilities that either use mercury in their processes (e.g., chlor-alkali plants) or produce mercury related compounds. Indiscriminate disposals and accidental spills of liquid mercury in the soil is an alarming problem. Recently, Kodaikanal, a hill resort in Tamil Nadu, India has been subjected to mercury contamination originating from a thermometer factory. Land disposals in huge quantities make mercury drive deeper into the subsurface because of its high density. Mercury also gets entrapped in the void spaces and exists as a continuous source of contamination. In an effort to remediate the problem at contaminated sites, Hg-laden soils are excavated and undergo further treatment. However, this process is expensive, makes the problem much worse by resulting in Hg air emissions. Furthermore, disturbing the soils often causes the contamination to spread. An alternative approach to treat mercury contaminated sites is insitu stabilization. Because of the low solubility of mercuric sulfide (0.017 mg/L), less volatility and also HgS’s high mercury loading compared to other metals such as Zn, Sn, and Cu, HgS stabilization would be the best option to treat mercury contaminated wastes. It has also been reported that mercury stabilized as mercuric sulfide (HgS) emitted no mercury vapor (Hamilton and Bowers, 1997) and thus

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potentially less harmful.

Mercury has a strong affinity for sulphur and sulphur related compounds and infact this affinity outcompetes oxygen for bonding. Mercury reacts with powdered sulphur to form mercury sulphide and this is considered as the Best Demonstrated Available Technology (Gorin et al., 1994). However, simply placing elemental mercury in bed of sulphur does not yield the desired mercury sulphide formation. Sodium sulphide, though excellent for the removal of ionic mercury species does not adequately remove elemental mercury. Oji 1998, describes the formation of metacinnabar (at low shear of 1060 rpm and temperature of 50 C) and cinnabar (at high shear of 19000 rpm and temperature greater than 270 C). Svensson et al. 2006 assessed the feasibility of HgS formation from HgO and Hg by mixing individually with elemental sulphur, iron sulphide and synthetic troilite (FeS). Elemental sulphur gave best results under alkaline, anaerobic environment in a two year period of time. Findlay and Mclean (1981) proved that polysulphide salts (mixture of sodium sulphide and sulphur) are efficient in removal of elemental mercury from mercury cell chlor alkali plant wastewater. Moreover polysulphide treatment has been proved to reduce gas phase emissions from mine surfaces (Randall, 1943).

Polysulphide salts are more reactive and provide efficient and quick method of converting elemental mercury to mercury sulphide. Using polysulfide to treat mercury-containing wastes is a cost-effective pathway. However, due to the complexity of mercury sulfide chemistry, the process of polysulfide-induced stabilization of mercury containing wastes has not been sufficiently developed; further research is needed to optimize the process controlling parameters for treating elemental mercury containing wastes. This work was aimed at providing a set of optimized design parameters to effectively immobilize mercury from wastes and incorporate them in micromodels which are rational representations of these pore scale processes. The parameters include pH, sulfide dosage, sulfide/Hg ratio, and reaction time. The optimal conditions from the batch studies will be used in the micromodel to look at the process of HgS conversion very closely and also to simulate a typical saturated subsurface scenario.

EXPERIMENTAL PROCEDURES

Batch Studies

A mixture of aqueous sodium polysulphide was prepared by saturating sodium sulphide solution with sulphur. The stock solution was prepared by mixing Na₂S. 9H₂O, sulfur powder and water at room temperature. The mixture was dissolved and the reaction was completed in less than one hour. The reaction can be facilitated by stirring continuously. This gives the polysulphide solution. Upon completion of the reaction, a small amount of unreacted sulfur could settle out as yellow flakes. The powdered sulphur, sodium sulphide and elemental mercury were obtained from commercial sources. The conversion of elemental mercury to its sulphide was accomplished by blending mercury with liquid polysulphide. The reactions involved in the conversion of Hg to HgS are given below.



The ingredients of each sample corresponded to a Na₂S₅/Hg⁰ mole ratio of 3.4. Stoichiometric ratios of Na₂S₅ and Hg⁰ were varied by weight in order to determine the fixed ratio that provides

best conversion results. The constituents were transferred to 100 ml serum bottles and sealed. Samples were thoroughly and continuously mixed in a shaker.

Micromodel Studies

Micromodels are efficient flow visualization tools employed generally to investigate flow and transport in porous media. The fluid configurations and flow dynamics can be captured using high resolution camera and image analysis software. The experiment represents a scenario in which mercury is trapped in the interparticle void spaces and stay as residual mercury saturation. This residual elemental mercury is then treated with sodium polysulphide solution and gets converted to HgS. As and when it gets converted, the precipitate will be flushed out. The experimental set up comprises of a two-dimensional glass bead micromodel, Plenum SP syringe pump, tubing, digital camera, desk top computer, and associated image analysis software. The porous media, consisting of glass beads was procured from M/s Biospec Products, Inc. To avoid the effects of sorption of mercury onto the solid media the porous media consists of inert, spherical glass beads with a diameter of 1mm and porosity of 0.35. The porosity of the pack was calculated by the weight of beads added to the known internal volume of the micromodel (3 cm^3). The glass beads were cleaned by soaking overnight in concentrated nitric acid followed by repeated washes with acetone and distilled water and oven dried at 105°C .

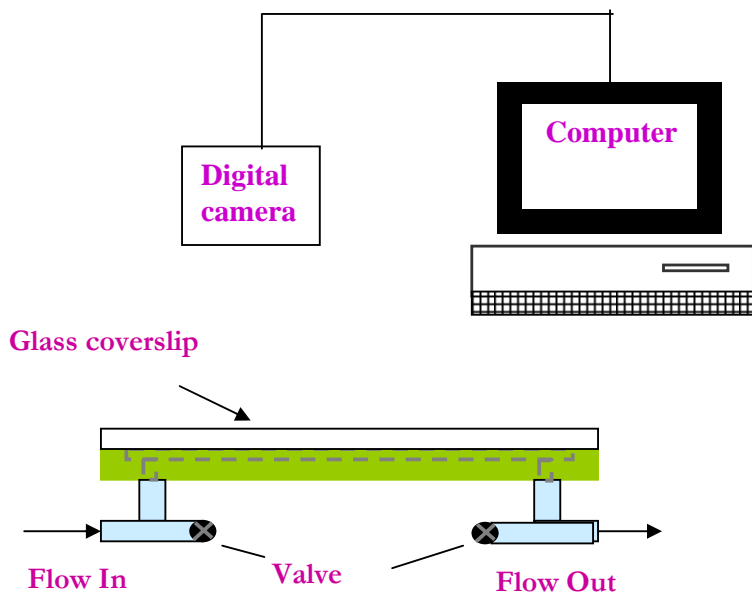


Fig. 1: Schematic of micromodel set up

Known quantity of mercury was physically placed as single blobs at predetermined locations in the pore spaces of the micromodel. Liquid polysulphide solution was passed continuously at the rate of 0.5 ml/hr and the formation of HgS was monitored over time. Image analysis will aid in quantifying the removal of elemental mercury over a period of time.

RESULTS

Batch Studies

Kinetic studies were done and the conversion efficiency of mercury to mercury sulphide was found to be 100% at the end of 96 hrs. The amount of mercury precipitated as HgS was found gravimetrically. Mass balance was done to ensure the formation of HgS precipitate and the simultaneous removal of elemental mercury. Similar mixing of Na_2S_5 and Hg was done, but the sample was left unshaken. The removal efficiency at the end of 96 hrs was only 5%. The results of kinetic studies in both the conditions are shown in Figure 2.

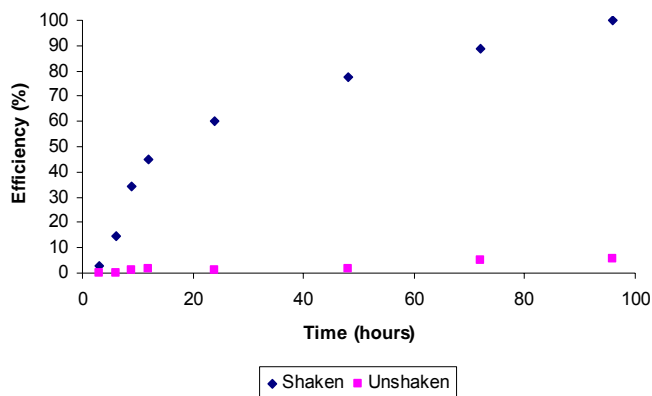


Fig. 2: Kinetic studies of mercury removal

Characterization of HgS

The product formed from batch studies were characterized by

1. Particle size distribution,
2. Scanning electron microscope (SEM) attached with EDAX and
3. X-ray diffraction (XRD) analysis.

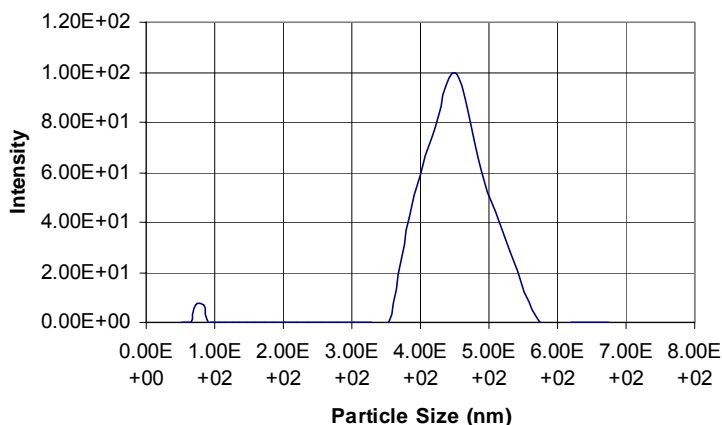


Fig. 3: Particle size distribution for HgS (Median Diameter = 425 nm)

Particle size distribution analysis for mercury sulphide was obtained using wet particle size analyzer as shown in Fig 3. The median diameter of the HgS particle was found to be 425nm. The various phases present in the samples were characterized by XRD. For powder XRD a Philips 1710 X-ray diffractometer with CuK α radiation ($\lambda= 1.5418 \text{ \AA}$) operating at 30 KV and 20 mA was used. Fig 3 is the X-ray diffraction pattern for the HgS. Mercury has two stable forms, metacinnabar and cinnabar. A major percentage of the product formed was black mercury sulphide (metacinnabar). Trace amounts of cinnabar was also detected. No extra diffraction peaks were observed (JCPDS) The formation on of HgS was thus confirmed by the XRD analysis and complete transformation of Hg to HgS was also known by the mass balance calculations.

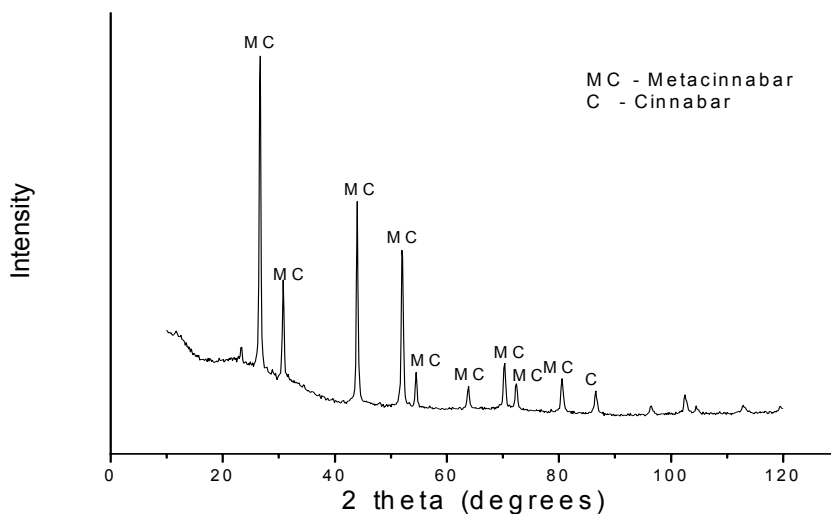


Fig. 4 XRD pattern of HgS

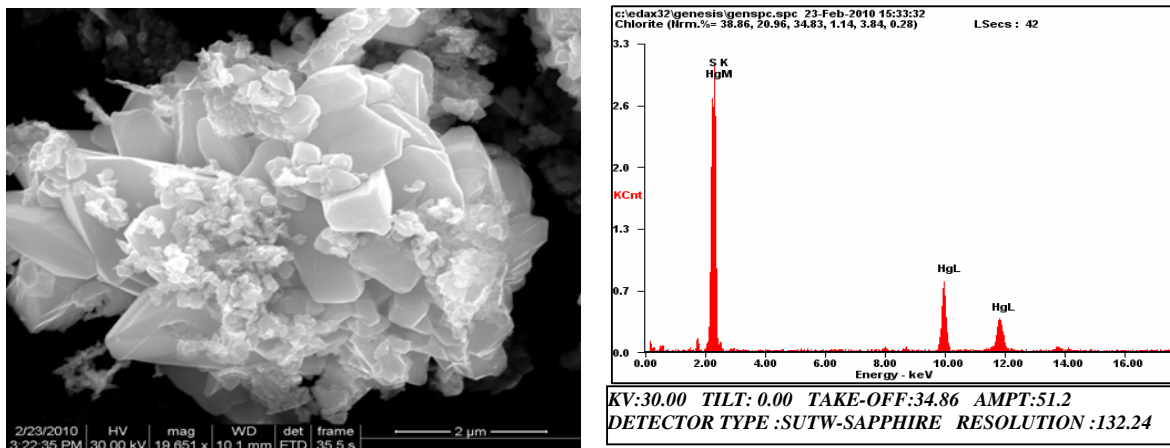


Fig. 5: SEM images and EDAX analysis of HgS

Figure 5 shows SEM image. The EDAX spectrum also confirms the formation of HgS.

RESULTS

Micromodel studies

Ongoing micromodel experiments are expected to produce results in a similar fashion depicted in the following figures. Figure 6a shows the residual mercury which was entrapped at predetermined locations. Figure 6b shows that flushing with polysulphide solution gradually adheres to the surface of mercury. As and when HgS coats Hg, it is being flushed out. This is shown in Figure 6c. Figure 6d shows the final HgS product left behind. And which is expected to be flushed out over a period of time.

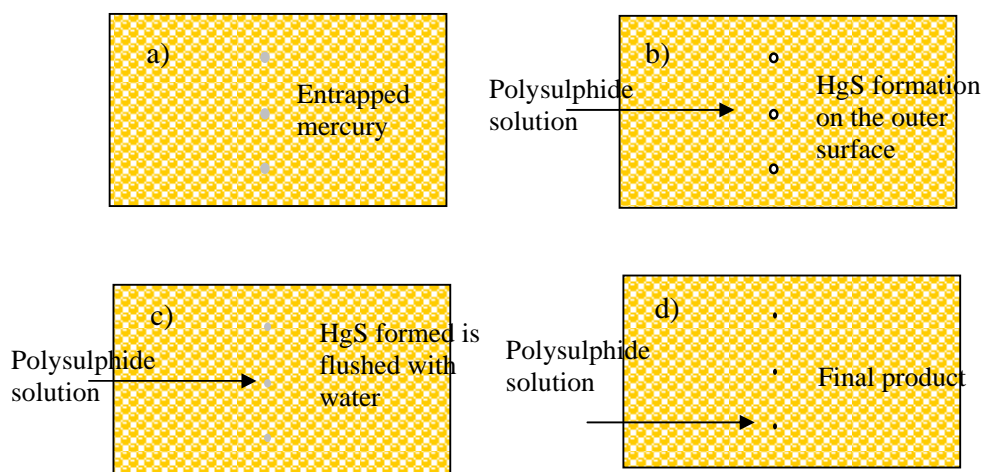


Fig. 6a: Trapped Hg Fig. 6b: Passing Na_2S_5 solution Fig. 6c: HgS precipitate is flushed out. Fig. 6d: Final HgS product

DISCUSSIONS

The preliminary batch studies were done to get a set of optimized design parameters to effectively immobilize mercury from wastes. Aqueous polysulphide in an alkaline anaerobic environment with a $\text{Na}_2\text{S}_5/\text{Hg}$ mole ratio of 20 gave a yield of close to 100% mercury sulphide within 96 hours. However, the process needs vigorous shaking. Mercury has a high cohesive force which severely inhibits the mixing of Na_2S_5 and Hg. Vigorous shaking is therefore required to allow maximum interaction with Na_2S_5 . The theoretical feasibility of converting Hg to HgS using liquid polysulfide has to be investigated. The ΔG values of the reactions involved have to be checked for thermodynamics. Proper care should be taken to ensure there is no excess sulphur present and if present it leads to the formation of mercury disulphide, yet another toxic form of mercury.

The results from batch experiments and HgS characterization were quite promising. Micromodel studies, if proven successful, this study has the potential for large scale in situ treatment of mercury contaminated soils that could substantially reduce the prohibitive cost of thermal desorption or excavation and disposal.

CONCLUSIONS

The application of liquid polysulphide to stabilize elemental Hg as HgS was investigated. 100% conversion was possible at the end of 96 hours with continuous shaking at an rpm of 200. HgS formation was clearly confirmed by XRD and EDAX analysis. Ongoing micromodel work, if successful, it is feasible to use liquid polysulphide insitu in the field, not only to stabilize elemental mercury as HgS but also to mobilize the HgS formed. However, additional time will be required since micromodel experiments are done in a undisturbed mode.

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