TREATMENT OF MERCURY CONTAMINATED OILS

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ABSTRACT

We have demonstrated the removal of mercury (and heavy metals) from tritiated organics and the stabilization of mercury (and heavy metals) in mixed-waste organics from U.S. Department of Energy sites including Sandia National Laboratory, the Miamisburg Environmental Management Project site, the Savannah River site, Los Alamos National Laboratory, and Oak Ridge National Laboratory. Some of this work was done on-site as large-scale demonstrations. We have also demonstrated the applicability of removing plutonium and uranium from Rocky Flats Environmental Technology site oils. The removal treatment technique differs depending on the mercury concentration in the oil and the disposition alternatives of the treated oil. In this paper we present results for the treatment of mercury contaminated oil where the mercury is in excess of 260 mg/kg.

The work investigated two treatment approaches:
1. Mixing of SAMMS (Self-Assembled Mercaptan on Mesoporous Silica) N990 Petrobond (by Nochar, Inc.) followed by stabilization of the oil using this new agent.
2. Mixing of contaminated oil and SAMMS for approximately 24 h followed by stabilization of the SAMMS-oil mixture using N990 Petrobond.

The results demonstrated that a stabilization agent containing SAMMS (4%) and Nochar N990 can stabilize the oil containing heavy metals at substantial concentrations. The stabilized oil met Land Disposal Restrictions for leachability of metals. The combination of SAMMS and Nochar N990 as a stabilization matrix is advantageous and the technology would be easily implemented on a larger scale with stabilization drums containing mixture of SAMMS and Nochar N990. Oil can be added to this container periodically until the full capacity is utilized.

INTRODUCTION

First Article Tests of a stabilization method for greater than 260 mg mercury/kg oil were performed under a treatability study. This alternative treatment technology addresses treatment of U.S. Department of Energy organics (mainly used pump oil) contaminated with mercury and other heavy metals. Some of the oil is also co-contaminated with tritium, other radionuclides, and hazardous materials.

The technology is based on contacting the oil with a sorbent powder (Self-Assembled Mercaptan on Mesoporous Support, SAMMS), proven to adsorb heavy metals, followed by stabilization of the oil/powder mixture using a stabilization agent (Nochar N990). Two variations of the treatment technology were included in the treatability study.

The SAMMS technology was developed by the Pacific Northwest National Laboratory for removal and stabilization of RCRA metals (i.e., lead, mercury, cadmium, silver, etc.) and for removal of mercury from organic solvents [1]. The SAMMS material is based on self-assembly of functionalized monolayers on mesoporous oxide surfaces. The unique mesoporous oxide supports provide a high surface area, thereby enhancing the metal-loading capacity.

The SAMMS material has high flexibility—it binds with different forms of mercury, including metallic, inorganic, organic, charged, and neutral compounds [1]. The material removes mercury from both organic wastes, such as pump oils, and from aqueous wastes. Mercury-loaded SAMMS not only passes TCLP tests but also has good long-term stability as a waste form because: 1) the covalent binding between mercury and SAMMS has good resistance to ion-exchange, oxidation, and hydrolysis over a wide pH range and 2) the uniform and small pore size of the mesoporous silica prevents bacteria from solubilizing the bound mercury.

Nochar's N990 Petrobond (Nochar, Inc., Indianapolis, IN) is an oil stabilization agent, specifically formulated for stabilizing vacuum pump oil, which has fewer volatile organics than many other oils. This material is a non-uniform granular powder that resembles ground Styrofoam plastics. This material has previously been used by itself and in combination with SAMMS to stabilize oil containing low levels of mercury ≤50 mg/kg in surrogate waste studies [2].

MATERIALS AND METHODS

Used vacuum pump oil was shipped in two containers from Sandia National Laboratory to Oak Ridge National Laboratory for First Article testing as part of a treatability study. The first container held approximately 872 g of oil from pump number S554976 and based on the analytical data provided by Sandia National Laboratory the waste oil contained 198 mg/kg Ba, 6.5 mg/kg Cd, 4 mg/kg Pb, 0.5 mg/kg Ag, and 540 mg/kg Hg. The other container contained approximately 29 g of oil from pump number 3A and based on the analytical data provided by Sandia National Laboratory the waste oil contained 4.13 mg/kg Hg and no other metals. The total tritium contained in the oil was 17 µCi. The contents from both containers were combined and mixed before treatment.

The SAMMS material used in this study was received from Pacific Northwest National Laboratory as a fine white powder. This material is hydrophobic and mixes very well with oil, but needs initial vigorous mixing. The N990 Petrobond material was received from Nochar, Inc., Indianapolis, IN. These materials were used as part of two approaches.

1. The first approach (Approach A) involved dry-mixing of SAMMS material and Nochar N990 (4% SAMMS by weight) using equipment similar to a drum roller. This mixture was placed in a container (1 liter glass jar). The oil was then directly added to the container and allowed to be absorbed. Equal weight of oil and Nochar N990 was used. Four percent SAMMS was chosen because in past experiments oil poured on top of (equal weight) Nochar N990 penetrated half-way. Thus, all the oil would be in contact with approximately half of the SAMMS added to the container.
2. The second approach (Approach B) involved mixing of SAMMS and oil for 24 hr. The amount of SAMMS used was 2% (w/w). After mixing, the mixture was poured over Nochar 990 (in 1-liter glass jars). Equal weight of Nochar N990 and oil was used.

Triplicate experiments were performed using each method, treating approximately 150 g oil with 3 to 6 g of SAMMS and 150 g of Nochar N990 in each batch. All three of the containers with the solidified oils using the first approach were sampled and two of the containers using the second approach were sampled extensively.

RESULTS AND DISCUSSION

Both of the two treatment approaches were easy to implement. Of the two methodologies, the first approach using a stabilization agent consisting of dry-mixed SAMMS and Nochar N990 would be easier to implement on a large scale. Some difficulty of mixing dry SAMMS and oil was noted, requiring initial vigorous mixing to prevent the SAMMS from clumping together. On a large scale, this could be implemented with for example an impeller-type drum mixer if the treatment was performed in drums or as an alternative the SAMMS material could be presoaked in a solvent. The oil soaked quickly into the Nochar N990. After 30 minutes the oil was absorbed to a large extent (Fig. 1) and reached a constant penetration depth in a few hours. The penetration depth was deeper than expected, penetrating approximately 75% of the total height (Fig. 1). The oil had been expected to penetrate only to 50% of the total height. This means that, in the case of the first approach, the oil (150 g) was contacted with 4.5 g of SAMMS (present within the top (75%) layer). The oil was contacted with 3 g of SAMMS in the second approach.

Fig. 1. Penetration depth of oil after 30 min and 24 h into mixture of SAMMS and Nochar N990. The amount of oil (150 g) in each container is shown in the container labeled B3 to the left.

During the second approach, a slight variation of the planned activities was tested based on the following scenario:

> *With a large-scale treatment method one may envision that the waste is contained in drums. The method for treatment would be to add SAMMS material directly to the drum through the bung. Then, the content would be mixed with a drum mixer for 24 h. The SAMMS/oil mixture would be pumped into a new drum ("a stabilization drum") containing Nochar N990. When the original drum was empty (some slight oil would remain in the heel) this drum may serve as the next stabilization drum receiving a charge of Nochar N990.*

Thus, this variation was tried by mixing SAMMS and oil in a container, emptying this container, adding Nochar N990 to the container, and finally returning the SAMMS oil mixture to this container. When performed, this methodology was perceived not to work well because the oil penetrated via wall-channeling to the bottom of the container. The Nochar N990 finally soaked the oil and no free oil was visually noted in the bottom of the container, but from a visual standpoint the method looked less efficient.

The sampling protocol called for removing the solidified oil by layer (4 layers per container), sampling each layer for total mercury and leachability (TCLP) of metals. Three samples per layer were removed for total mercury analysis and one sample was taken for TCLP testing. Unused stabilization agent at the bottom of each container was not sampled. It should be noted that the stabilized matrix was sampled two months after the stabilization. The results from the analyses are shown in Fig. 2–4.

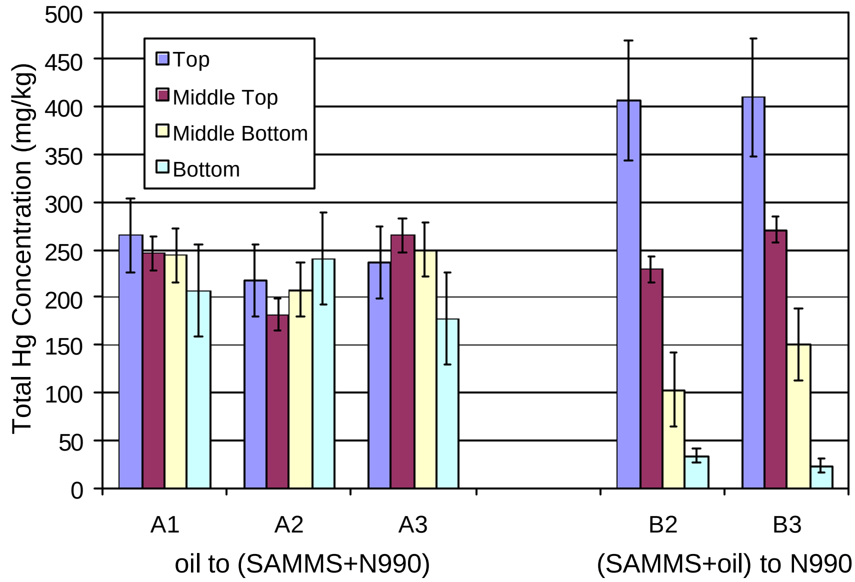

Fig. 2. Total concentration of mercury within each layer of the of the solidified oil matrix. For each layer, three samples were collected for total mercury analysis.

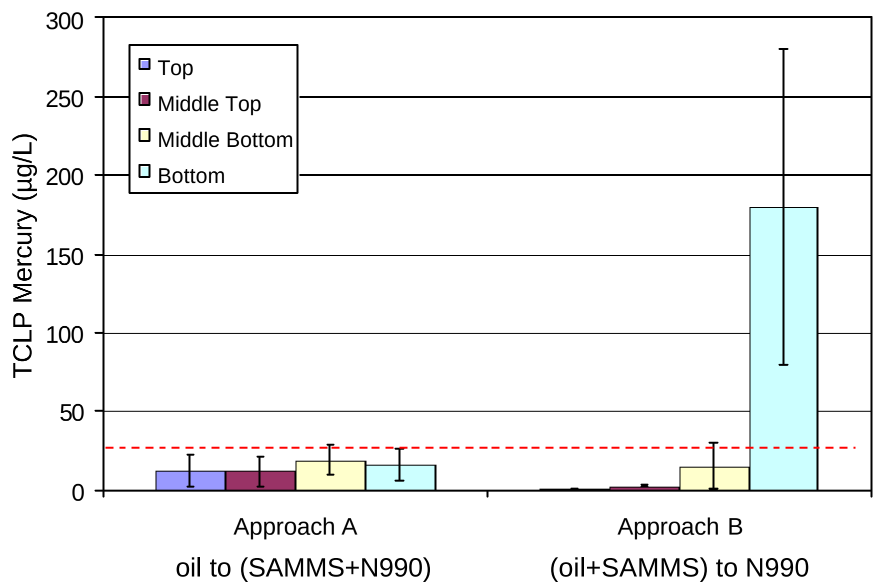

Fig. 3. Leachability of mercury in each layer of the solidified oil matrix. Dashed line indicates treatment goal.

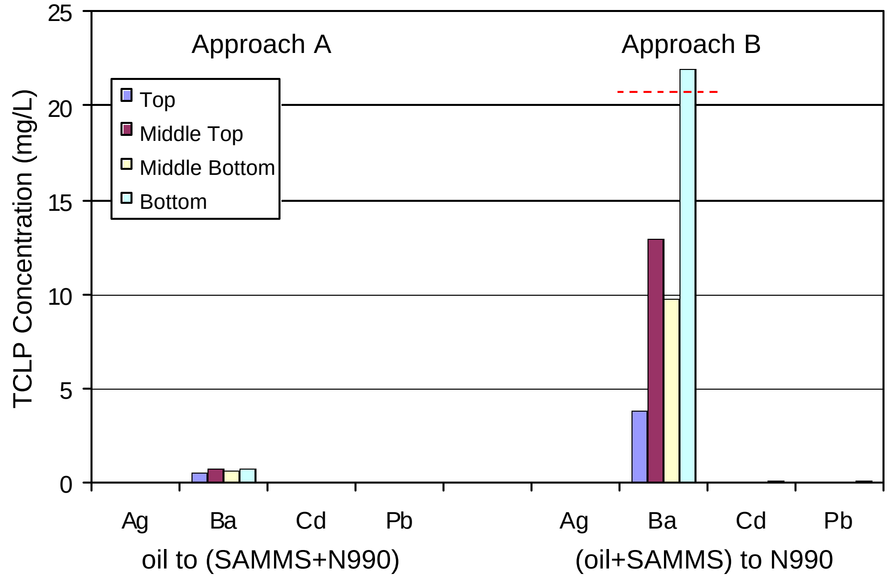

Fig. 4. Leachability of RCRA metals in each layer of the solidified oil matrix. Dashed line indicates treatment goal for barium. The other metals were below the treatment goals for all other cases.

The total mercury concentration measurements in the solidified matrix in Approach A show that this waste form was uniform (Fig. 2). The leachability of mercury in the solidified matrix in Approach A was very low at less than 0.025 mg/L, the Universal Treatment Standards (UTS) limit (Fig. 3).

This was not the case in Approach B where the Nochar N990 acted as a porous bed, filtering the oil as it penetrated and capturing the mercury-laden SAMMS in the upper portion of the matrix. This resulted in a distribution of both total and leachable mercury along the depth of the solidified matrix (Fig. 2 and 3).

In the case of Approach B, the leachability of mercury from the matrix was higher from the bottom layer, but still very low at 0.18 mg/L. We draw the following conclusions from the results:

1. In Approach B, the contaminated oil was only contacted with SAMMS for 24 h, before stabilization. However, in Approach A, the contact time was two months after stabilization; as the oil, SAMMS, and Nochar N990 formed a uniform medium. Mercury not yet adsorbed to SAMMS could easily diffuse the anticipated short distance to a SAMMS particle. This was not the case in Approach B as the SAMMS was captured in the upper portion of the matrix, leaving unadsorbed mercury in the lower portion of the bed. The distance for this mercury to a SAMMS particle was too great for diffusion. In the past we have shown that prolonged contact time improves removal efficiency [3]; 24 h was selected to anticipate a typical work schedule on a large-scale implementation. In retrospect, we should have allowed equal contact times for both approaches.
2. Nochar N990 should have stabilized the oil (and mercury) that penetrated the bed in Approach B. By design, the amount of SAMMS added to the oil would reduce the mercury level by about 90%; Nochar N990 would stabilize the remainder. As Nochar N990 has successfully been used to stabilize oil with 50 mg mercury/kg, we targeted this concentration by adding enough SAMMS (but not more) to reach this level after 24 h contact time. Even though the performance of the SAMMS material by itself was not measured directly, we can calculate from the data presented in Fig. 2 that the oil after being contacted with SAMMS contained approximately 46 mg Hg/kg oil [4], which is within range of the planned value. Based on previous results [2], Nochar N990 should have stabilized this mercury to

pass UTS limit. Low leachability (0.18 mg/L) was achieved in Approach B, but not low enough for Land Disposal Restrictions. We speculate the limitation of Nochar N990 to stabilize the mercury was due to difference in mercury speciation in our current experiment and the standards used to spike oil in surrogate studies at 50 mg/kg [2]. This finding would suggest the importance of detailed characterization of the various mercury species (which is not trivial) and knowledge of the selectivity and capacity for the SAMMS material toward these species (which we do not have at this point). As an alternative, one could implement a simple test protocol to demonstrate the effectiveness of the stabilization for each new waste stream.

3. Above, we discussed the limitation of Nochar N990 not to "completely" stabilize the mercury in the oil. The fact is that the Nochar N990 did very well. The matrix in the bottom layer of stabilized oil contained 28 mg Hg/kg matrix (Fig. 2). When submitted to the leaching procedure only a fraction (3.6 mg/kg) leached out, resulting in 0.18 mg/L in the leaching liquid. Very possibly, this is the same fraction that during long contact times with SAMMS in Approach A could be stabilized by SAMMS. This again suggests the importance of initial testing before final stabilization methodology is employed.

CONCLUSIONS

The results demonstrate that a stabilization agent containing SAMMS (4%) and Nochar N990 can stabilize the oil containing mercury at substantial concentrations. The stabilized oil meets Land Disposal Restrictions for leachability of metals. The combination of SAMMS and Nochar N990 as a stabilization matrix is advantageous and the technology would be easily implemented on a larger scale with stabilization drums containing mixture of SAMMS and Nochar N990. Oil can be added to this container periodically until the full capacity is utilized.

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4. In the two bottles used for Approach B, approximately 3.5 cm of unused Nochar N990 remained in the bottle. The initial height, corresponding to 150 g, was 10 cm. Thus, 97.5 g of Nochar N990 (= $150\times6.5\div10$) absorbed 150 g oil. The average total mercury concentration in the bottom layer in Approach B was 28 g/kg solidified oil (Fig. 2). This value can be used to back-calculate the mercury concentration in the oil as 46 g/kg oil {= $28\times(97.5+150)\div150$}, if the assumption is made that all the SAMMS material was retained in the top layers of the solidified matrix.