



*In Situ Mercury Stabilization (ISMS)
Treatment Technology*

*Technology Maturation Project
Phase I Results*

P. D. Kalb and L. Milian

March 14, 2008

Prepared for:

BNL Office of Intellectual Property and Sponsored Research

Brookhaven National Laboratory

P.O. Box 5000

Upton, NY 11973-5000

www.bnl.gov

DISCLAIMER

This work was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or any third party's use or the results of such use of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Notice: This manuscript has been authored by employees of Brookhaven Science Associates, LLC under Contract No. DE-AC02-98CH10886 with the U.S. Department of Energy. The publisher by accepting the manuscript for publication acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes.

**In Situ Mercury Stabilization (ISMS) Treatment Technology
Technology Maturation Project
Phase I Results**

1. Background

Mercury (Hg) was used to separate lithium-6 isotope for weapons production at the Y-12 Plant in Oak Ridge in the 1950s and 1960s. As much as two million pounds of elemental mercury was “lost” or unaccounted for and a large portion of that material is believed to have entered the environment.¹ The DOE site office in Oak Ridge has identified Hg pollution in soils, sediments, and streams as the most significant environmental challenge currently faced.² In industry, large amounts of mercury have been used to manufacture products (e.g., fluorescent light bulbs, thermometers) and for chemical processing (e.g., production of chlorine and alkali via mercury electrochemical cells) and many of these industrial sites are now polluted with mercury contaminated soil as a result of previous releases and/or inadvertent leaks.

Remediation techniques for Hg contaminated soils are either based on thermal desorption and recovery of the mercury or excavation and shipping of large volumes of material to remote facilities for treatment and disposal. Both of these alternatives are extremely costly. The Brookhaven National Laboratory (BNL) Environmental Research & Technology Division (ERTD) has demonstrated, in laboratory-scale experiments, the viability of treating mercury contaminated soils by means of sulfide treatment rods inserted into the soil through a process known as In Situ Mercury Stabilization (ISMS). This approach is partly based on BNL’s patented and successfully licensed ex situ process for Hg treatment, Sulfur Polymer Stabilization/Solidification (SPSS) which converts Hg to the more stable sulfide form.³ The original experiments showed that Hg homogeneously distributed in soil rapidly migrates to form a high concentration zone of chemically stable mercuric sulfide near the treatment rods while concentrations of Hg in surrounding areas away from the treatment rods are depleted to acceptable levels.⁴

BSA has subsequently filed for patent protection on the ISMS technology.⁵ If further developed it has the potential for large-scale in-situ treatment of contaminated soils that could substantially reduce the prohibitive cost of thermal desorption and/or excavation and disposal. Licensing and spin-off technology development opportunities would then be viable. Depending on performance and regulatory acceptance, the treated mercury could either be excavated for disposal elsewhere or left in place as a stable alternative. Excavated spent treatment rods could be processed by the SPSS process to reduce the potential for dispersion and lower leachability even further.

The Phase I objectives of the In Situ Mercury Stabilization Treatment Process Technology Maturation Project were to: 1) replicate the original bench-scale results that formed the basis for BNL's patent application, i.e., mercury contamination in soil will migrate to and react with "rods" containing sulfur and/or sulfur compounds, 2) provide enough information to evaluate a decision to conduct further development, and 3) establish some of the critical parameters that require further technology maturation during Phase II. The information contained in this report summarizes the work conducted in Phase I to meet these objectives.

2. Description of Experiment

2.1 Preparation of Mercury Soil Surrogate

The simulated Hg contaminated soil was prepared by adding one gram of elemental Hg to two kilograms of clean sand (sold for recreational purposes) in one gallon containers to create a target concentration of 500 ppm Hg. Clean sand was used in place of actual soil as a model system to eliminate the potential for additional uncontrolled variables e.g., interaction with other constituents in actual soil. A Sartorius, Model MA30 Moisture Analyzer was used to measure the moisture content of the as-received sand, which contained a relatively small amount (0.1 wt%) of moisture. The preparation procedure was repeated in six one-gallon plastic containers for a total of 12 kg of surrogate soil. The one-gallon containers were then placed in a rotating (~30 rpm), end-over-end tumbler (Figure 1) where the mercury-sand was mixed/homogenized and sampled after 12 days. A total of 9 sub-samples of the Hg contaminated surrogates weighing ~5g each were randomly removed from the containers and analyzed for Hg using a Jordan Valley EX-6600 Energy Dispersive X-ray Fluorescence (XRF) Spectrometer to confirm homogeneity. A discussion of the Hg analysis methodology is provided in Section 2.6, Sample Analysis. Variability in Hg was $\pm 30.1\%$, so mixing was continued to promote improved homogeneity. This was repeated several times until the variability in Hg concentration was reduced to $\pm 19.4\%$ after the soil surrogate was mixed for nearly 23 days.



Figure 1. End-over-end mixer used to homogenize the surrogate Hg contaminated soil

2.2 Description of Treatment Rods

Treatment rods for both sets of tests consisted of permeable fine mesh polyester tubes measuring ~ 0.7 cm in diameter x ~ 6 cm in height. The treatment rods were then filled with the finely powdered reagents consisting of either a mixture of 95 wt% sulfur polymer cement (SPC) and 5 wt% Na_2S (original 2002 composition) or 100 wt% Na_2S , which was used in an attempt to accelerate the treatment process. Figure 2 is a photo of the treatment rods used in the testing.

2.3 Test Configurations

Two separate sets of parameters were examined during Phase I testing. For initial first round of testing, the test environment consisted of a sealed rectangular plastic container measuring approximately 20.5 cm wide x 27 cm long x 11 cm in height. This represented an increase in area of more than 21 times and an increase in soil volume of about 27 times compared with the initial 2002 experiments which were conducted in sealed 5.8 cm diameter 140 cm³ plastic containers. The follow up testing was done using the same test environment as the 2002 study, i.e., 140 cm³ plastic containers. In addition variations in the treatment rod composition and several other parameters were also examined in the second round, including moisture content and exposure to elevated temperature. Each test configuration is described along with the results in the following sections.



Figure 2. Treatment rod tubes with (right) and without reagents (left).

2.3.1 Configuration for First Round of Testing

Four-kilograms of Hg-sand surrogate were transferred to the rectangular plastic container and the surface of the sand was leveled in preparation for placement of the treatment rods. Twenty empty sulfide treatment rods were precisely placed in the Hg-sand surrogate by using a template and grid system with holes measuring 5.1 cm on-center (Figure 3). A hollow, open-ended plastic tube measuring 1.3 cm dia. x 6 cm ht. was hand-pressed into the Hg-sand to the bottom of the vessel at each treatment rod location. The sand was then removed from the tubes using a low-suction vacuum, and a small-diameter hose attachment (Figure 4). The reagent-filled treatment rods were placed inside the hollow plastic tubes and the tubes were then gently removed by vertically lifting allowing the surrounding sand to backfill around the treatment rods. The treatment rods following placement are shown in Figure 5. An airtight/watertight lid was placed on the rectangular container and the test was initiated. A control experiment using an identical plastic container was filled with the Hg-contaminated soil surrogate contents without treatment rods and was tested simultaneously.



Figure 3. The paper template and grid system used to place the 20 sulfide treatment rods in the rectangular container



Figure 4. The sand being removed from the hollow tube using a low-suction vacuum, and a small-diameter hose attachment



Figure 5. The final placement of the twenty sulfide treatment rods prior to covering with a lid and the start of the experiment

2.3.2 Configuration for Second Round of Testing

In order to provide the most flexibility and examine the effect of additional parameters (moisture, temperature, reagent composition) the second round of testing was conducted in individual 140 cm³ containers. The test parameters for the second set of tests are shown in Table 1. Treatment rod composition consisted of either 100% Na₂S or 95% Sulfur Polymer Cement (SPC) + 5% Na₂S. Two replicates were tested for each per parameter variation resulting in the preparation of sixteen separate test containers.

Table 1. Test parameters for the second set of tests conducted in 140 cm³ containers

| Treatment Rod Composition | Parameter | | | |
|-------------------------------|------------------------------|---------------------------|------------------------------|---------------------------|
| | 20°C | | 50°C | |
| | As-received Moisture Content | 5% by Wt Moisture Content | As-received Moisture Content | 5% by Wt Moisture Content |
| 100% Na ₂ S | ✓ | ✓ | ✓ | ✓ |
| 95% SPC+ 5% Na ₂ S | ✓ | ✓ | ✓ | ✓ |

The air-dried moisture content of the as-received sand was between 0.1-0.15 wt%. The 5 wt% moisture content Hg-sand was prepared by adding de-ionized (DI) water to the air-dried sand. The mass of Hg-sand surrogate used in each individual 140 cm³ plastic cup was ~240g. This initial quantity was used for both the as-received (air-dried sand) and 5 wt% moisture content sand samples. Table 2 shows the actual Hg-soil surrogate and

treatment rod mass used for each container. Placement of treatment rods in the air-dried Hg-sand within the 140 cm³ containers was straight forward. Sulfide filled treatment rods were placed vertically in the center of each empty container until contacting the bottom of the cup. Holding the top of the treatment rod, the Hg-sand was carefully added to the container until it was full (~240g). The Hg-sand was gently compacted by lightly tapping the container on a hard surface several times. The cover was placed on the container and the test was initiated.

The preparation of the 5 wt% moisture content Hg-sand surrogates involved transferring 228g of air-dried Hg-sand to a glass beaker followed by the addition of 12g of DI water. Following addition of the DI water, the mixture was quickly stirred until the Hg-sand was thoroughly wetted. The mixture was transferred to the container with the sulfide-filled treatment rod position in the center of the cup. The moist Hg-sand was added until the cup was approximately one-half filled and then a Teflon rod (1.3 cm diameter) was used to tamp and consolidate the moist Hg-sand surrounding the treatment rod. Compaction of the Hg-sand was done a second time when the cup was close to capacity. Table 2 shows the actual mass of 5 wt% moisture Hg-sand that could be reasonably compacted in the container (between 210 – 225g).

Table 2. The mass of SPC/sulfide and pure sulfide in the treatment rod and the actual mass of the Hg-sand in each 140 cm³ test container

| Sample Parameters | Replicate | Mass of Treatment Rod Reagent, g | Mass of Hg-Sand, g |
|---|-----------|----------------------------------|--------------------|
| 95% SPC + 5% Na ₂ S, 0.1 Wt% Moisture, 20 °C | 1 | 3.05 | 240.16 |
| | 2 | 2.89 | 240.38 |
| 95% SPC + 5% Na ₂ S, 0.1 Wt% Moisture, 50 °C | 1 | 2.74 | 240.40 |
| | 2 | 2.89 | 240.32 |
| 100% Na ₂ S, 0.1 Wt% Moisture, 20°C | 1 | 2.39 | 241.80 |
| | 2 | 2.54 | 243.08 |
| 100% Na ₂ S, 0.1 Wt% Moisture, 50°C | 1 | 2.49 | 242.65 |
| | 2 | 2.25 | 241.63 |
| | | | |
| 95% SPC + 5% Na ₂ S, 5 Wt% Moisture, 20°C | 1 | 2.88 | 222.92 |
| | 2 | 2.65 | 225.13 |
| 95% SPC + 5% Na ₂ S, 5 Wt% Moisture, 50°C | 1 | 2.71 | 220.10 |
| | 2 | 2.60 | 219.19 |
| 100% Na ₂ S, 5 Wt% Moisture, 20°C | 1 | 2.52 | 209.77 |
| | 2 | 2.58 | 211.69 |
| 100% Na ₂ S, 5 Wt% Moisture, 50°C | 1 | 2.41 | 210.98 |
| | 2 | 2.41 | 213.75 |

2.4 Sampling

2.4.1 First Round Sampling

Sand samples were removed from the rectangular container for mercury analysis following a period of 95 days. Sampling was conducted for five of the twenty treatment rods; two sand samples per treatment rod were taken, one adjacent to the rod (labeled near) and another at an approximate distance of 2.5 cm (labeled far). The 0.7 cm green coring tubes in Figure 6 indicate the actual location of the samples taken. The coring tubes were pushed into the sand to a depth of 3 cm (total depth of sand was 5 cm) and 0.25 mL of de-ionized water was added to facilitate removal. The sample contents (between 1.39g-1.76g) were immediately transferred to 2.5 cm diameter x 2.2 cm height round XRF analysis cells, gently compacted using a Teflon rod to ensure similar counting geometries, and sealed with a thin Mylar film.

2.4.2 Second Round Sampling

The testing containers were sampled after 42 or 47 days by taking 0.7 cm diameter cylindrical cores to a depth of 3 cm in the media (Figure 7) such that about 1 – 2 g were taken. Two cores were taken in each of the 8 sample containers – one directly adjacent to the treatment rod (identified as near) and a second approximately 2 cm away from the treatment rod (identified as far) for a total of 16 analyses. The cores were placed in the XRF sample cells, gently tamped to form a uniform surface, and covered with a Mylar seal (Figure 8).

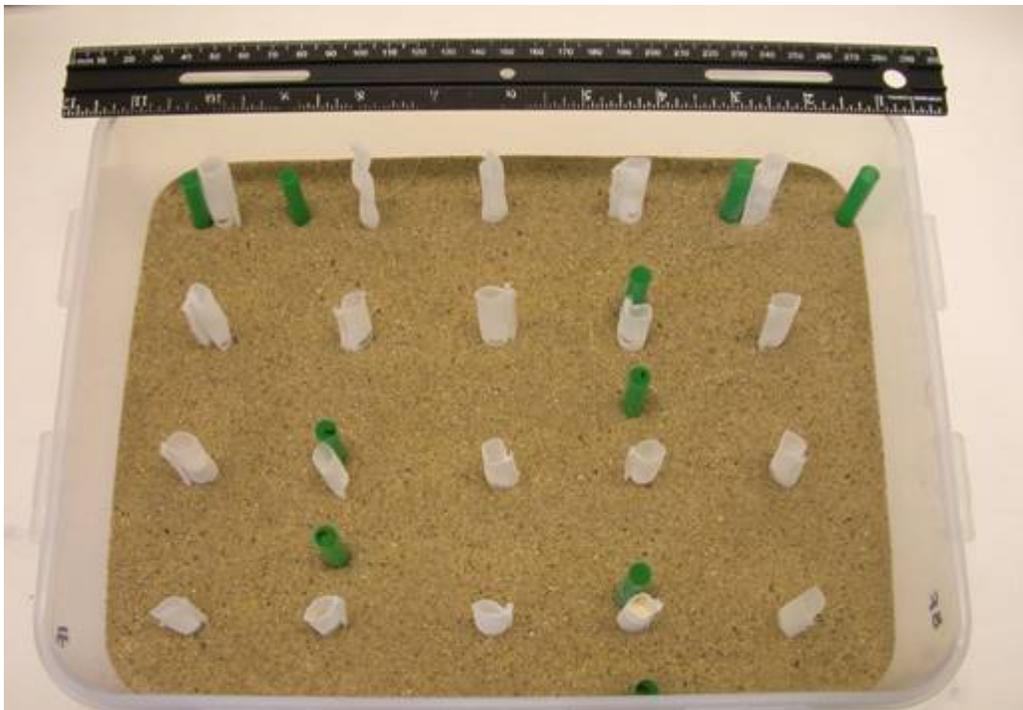


Figure 6. The first round rectangular container with top removed in preparation for coring samples (green tubes) for XRF analysis after 95 days.

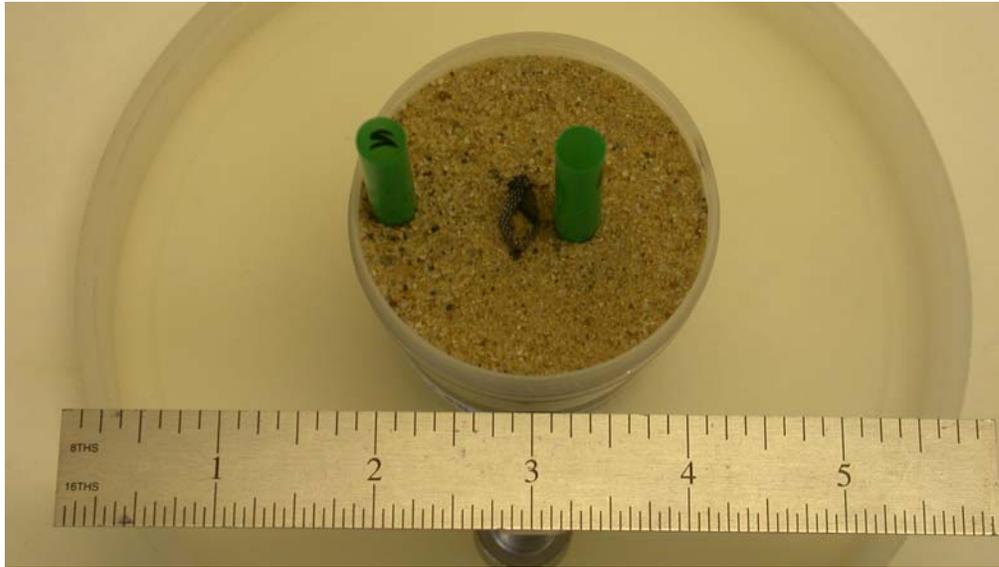


Figure 7. A reaction vessel with the lid removed and two plastic columns in place in preparation for soil column extraction (core)

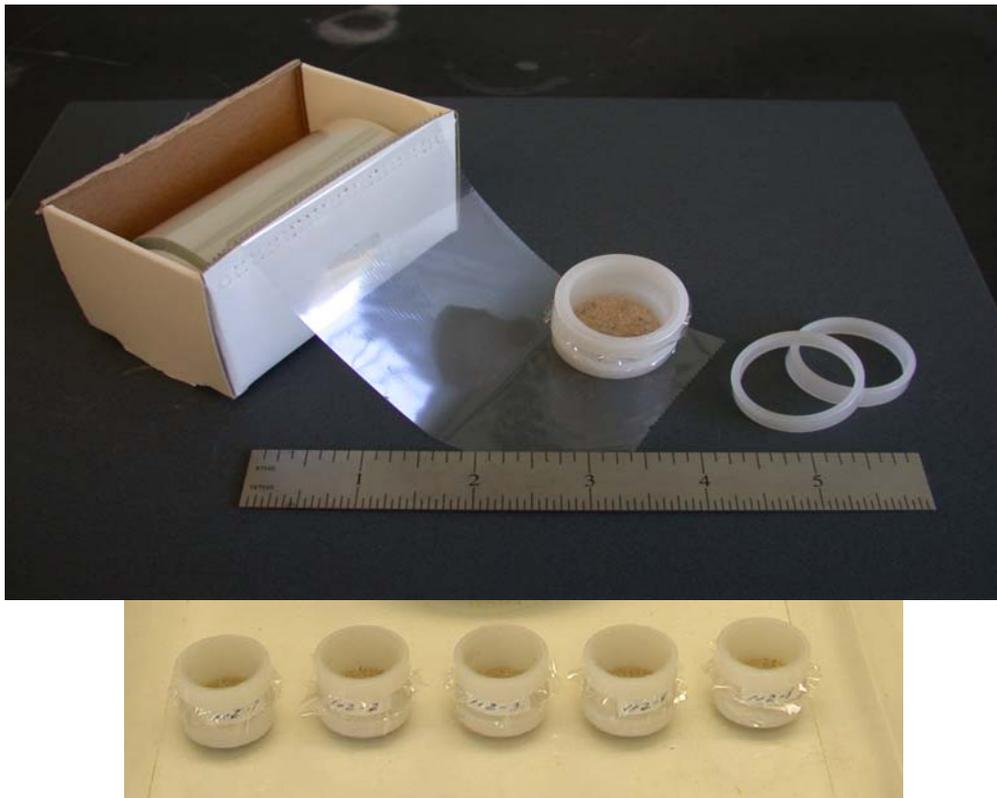


Figure 8. Top: Preparation of XRF sampling cell (25 mm diameter) sealed on the top and bottom with a thin Mylar film. Bottom: XRF sampling cells ready for analysis.

2.5 Sample Analysis

X-ray fluorescence measurements were made to provide qualitative analysis of Hg concentrations and determine the relative movement of Hg in the sand. Suitable Hg calibration standards were not available to provide accurate quantitative analysis of Hg concentrations, but qualitative analysis of Hg levels as a function of proximity to the treatment rods provides a good indicator of the effectiveness of the in situ process.

Samples were analyzed by means of the Jordan Valley EX-6600 Energy Dispersive X-ray Fluorescence (XRF) Spectrometer (Figure 9) for 5 minutes each. Sand with no added Hg was analyzed to quantify background counts, which were then subtracted from the gross sample counts to yield net counts. Mercury has two distinct characteristic XRF peaks (L_{α} and L_{β}) and the L_{β} peak was used for these analyses as it is more isolated from surrounding interference peaks and higher count rates were observed. The data were also normalized for soil mass by expressing results as counts/gram. Two identical replicate samples were run for each set of parameters and the reported data represents an average of the two.



Figure 9. Jordan Valley EX-6600 Energy Dispersive X-Ray Fluorescence Spectrometer used in mercury analyses

3. Results

The conversion of elemental Hg to HgS results in a color change to black (metacinnabar) or crimson red (cinnabar) so observation of the sample containers over time provides an indication of how the reaction is progressing. These color changes were observed, recorded and photographed as described in this section.

XRF counting data for Hg were then compared to provide a qualitative evaluation of the movement of mercury within the test soil environment. The ratio of net counts in samples taken close to and far from the treatment rods provides an indicator of the effectiveness of the process. For example, a “near/far” ratio of 1.0 indicates a homogeneous distribution of Hg, i.e., no change in Hg distribution while a ratio of 2.0 indicates Hg redistribution in the soil with twice as much Hg concentrated near the treatment rod compared with the concentration of samples taken far from the treatment rod. Results from each round of testing are discussed below in terms of this relative distribution and specific test conditions.

3.1 Results of First Round of Testing

The sand in the large rectangular container was examined daily for color changes indicative of the reaction to HgS. However, after four weeks no color changes were observed indicating that the sulfide treatment rods may not be demonstrating the same level of reactivity with mercury that was observed in the 2002 experiments. The condition of the first round test sand before and after 95 days of testing can be seen in Figures 5 and 6. At this point the decision was made to conduct a second round of tests that considered additional parameters to determine their impact on the effectiveness of the ISMS process.

The XRF analytical data for the first round of testing are shown in Table 4. The ratios of samples taken near the treatment rods compared with those taken further from the treatment rods range from 0.77 to 1.09 with a mean ratio of 0.94. Because the near/far ratios are close to unity, these data corroborate the physical observation that no significant movement of Hg occurred.

3.2 Results of Second Round of Testing

Many of the 140 cm³ samples tested in the second round exhibited observable changes in color over the course of the experiment. For samples containing 95% Sulfur Polymer Cement (SPC) + 5% Na₂S, 0.1% moisture and held at 50 °C, a change in color from tan (color of sand) to black (color of metacinnabar) can be observed in the vicinity of the treatment rod. The color change after 16 days shown in Figure 10 is indicative of the increasing concentration of HgS in the region adjacent to the treatment rod. As shown in Table 4, when the treatment cups were sampled after 42 or 47 days and analyzed by XRF the Hg concentrations near the treatment rods were 59.58 and 23.87 times higher, respectively for an average of 41.72 times higher concentration in samples near the

treatment rods. This set of parameters yielded the most dramatic results of all those tested. The near/far ratio of 42 was equivalent to the best results obtained in the original 2002 study.

For samples containing 100% Na₂S, 5 wt% moisture and held at 50 °C, distinct color changes could be observed after 22 days at the outside of the container as shown in Figure 11. Although this represents a probable conversion of the Hg to more stable HgS, the fact that it occurred at the outside edge of the sample far from the treatment rod, indicates that the treatment rod was likely ineffective in redistributing the Hg in the sand at or near the treatment rod. In fact, examination of the XRD data for this set of replicate samples reveals near/far ratios of 0.15 and 0.06 for a mean of 0.11. The inverse ratio (i.e., far/near) indicates that the Hg is actually concentrating further from the treatment rod (i.e., far/near = 6.7 and 16.7) by a factor of about 9 times.

Additional observations from the second round testing:

- An increase in the near/far ratio from 2.94 to 41.72 (an increase of more than 14 times) was observed when comparing the results for ambient and 50°C tests for samples containing 95% Sulfur Polymer Cement (SPC) + 5% Na₂S and 0.1% moisture content.
- For the 100% sulfide samples at low moisture (0.1%) content:
 - The results were good for both ambient and elevated temperature (near/far ratios of an average of 2.91 for ambient and 12.30 for 50°C runs)
 - At ambient temperature the results were about the same for the treatment rods containing 95% SPC + 5wt% sulfide compared with the treatment rod containing 100% sulfide (2.94 vs. 2.91).
 - The enhanced affect of elevated temperature is easily seen for the 100% sulfide samples as the near/far ratio was more than four times higher for the elevated temperature samples compared with ambient (12.30 vs. 2.91 respectively)

Table 3. XRF Data for First Round Testing

| Sulfide Rod Composition | Hg-Sand, Wt % Moist. Content | Temp., °C | Treatment Rod | Distance From Rod Core | Net Counts/g, L _b | Ratio N/F Net Counts/g, L _b |
|-------------------------|------------------------------|-----------|---------------|------------------------|------------------------------|--|
| 100% Na ₂ S | 0.1 | 20 | 4 | Near | 11,758 | 1.09 |
| | | | | Far | 10,788 | |
| | | | 7 | Near | 8,726 | 0.77 |
| | | | | Far | 11,330 | |
| | | | 14 | Near | 8,549 | 0.83 |
| | | | | Far | 10,282 | |
| | | | 16 | Near | 8,150 | 1.09 |
| | | | | Far | 7,459 | |
| | | | 20 | Near | 8,906 | 0.91 |
| | | | | Far | 9,819 | |



Figure 10. Change in color in the vicinity of the treatment rod (center of sample) from tan to black is evidence of reaction to HgS for rod containing 95wt% SPC + 5 wt% Na₂S immersed in sand with 0.1 wt% moisture at 50°C for 16 days.



Figure 11. Comparison of color change for treatment rod containing 100% Na₂S, 5 wt% moisture, 50 °C before start of experiment (left) and after 22 days (right).

Table 4. XRF Data for Second Round Testing

| Treatment Rod Composition | Hg-Sand, Wt % Moisture Content | Temp., °C | Replicate | Hg-Sulfur Reaction Time, days | Distance From Rod Core | Hg Analysis Results - L _b | |
|--------------------------------|--------------------------------|-----------|-----------|-------------------------------|------------------------|--------------------------------------|-----------------------|
| | | | | | | N/F Ratio Cnts/g | Mean N/F Ratio Cnts/g |
| 95% SPC + 5% Na ₂ S | 0.1 | 20 | 1 | 42 | Near | 1.06 | 2.94 |
| | | | | 42 | Far | | |
| | 0.1 | | 2 | 47 | Near | 4.81 | |
| | | | | 47 | Far | | |
| 100% Na ₂ S | 0.1 | 20 | 1 | 42 | Near | 3.66 | 2.91 |
| | | | | 42 | Far | | |
| | 0.1 | | 2 | 47 | Near | 2.15 | |
| | | | | 47 | Far | | |
| 95% SPC + 5% Na ₂ S | 0.1 | 50 | 1 | 42 | Near | 59.58 | 41.72 |
| | | | | 42 | Far | | |
| | 0.1 | | 2 | 47 | Near | 23.87 | |
| | | | | 47 | Far | | |
| 100% Na ₂ S | 0.1 | 50 | 1 | 42 | Near | 15.38 | 12.30 |
| | | | | 42 | Far | | |
| | 0.1 | | 2 | 47 | Near | 9.21 | |
| | | | | 47 | Far | | |
| 95% SPC + 5% Na ₂ S | 5.0 | 20 | 1 | 42 | Near | 1.80 | 1.47 |
| | | | | 42 | Far | | |
| | 5.0 | | 2 | 47 | Near | 1.14 | |
| | | | | 47 | Far | | |
| 100% Na ₂ S | 5.0 | 20 | 1 | 42 | Near | 0.61 | 0.85 |
| | | | | 42 | Far | | |
| | 5.0 | | 2 | 47 | Near | 1.09 | |
| | | | | 47 | Far | | |
| 95% SPC + 5% Na ₂ S | 5.0 | 50 | 1 | 42 | Near | 1.09 | 1.10 |
| | | | | 42 | Far | | |
| | 5.0 | | 2 | 47 | Near | 1.11 | |
| | | | | 47 | Far | | |
| 100% Na ₂ S | 5.0 | 50 | 1 | 42 | Near | 0.15 | 0.11 |
| | | | | 42 | Far | | |
| | 5.0 | | 2 | 47 | Near | 0.06 | |
| | | | | 47 | Far | | |

Discussion/Conclusions:

- Clean silica sand was chosen as the media for this study as a model system to reduce potential variabilities introduced by specific artifacts associated with actual soil. However, difficulty was encountered in achieving a homogeneous Hg contaminated surrogate soil, despite the lengthy period of end-over-end mixing. In order to achieve homogeneity the elemental Hg which tends to agglomerate as a liquid must be broken down into much smaller particles that can be redistributed throughout the matrix to avoid “hot spots.” In most soils there is a broad range of particles including a significant fraction of fines with proportionally higher surface area that can adsorb contaminants like Hg and thus aid in homogenization. Since the surrogate media consisted of pure silica sand of relatively uniform size distribution (not many fine particles) it was not easily wetted by the Hg and thus probably made it more difficult to achieve thorough mixing. The presence of Hg in larger particles within the soil can also potentially impact the effectiveness of the ISMS process due to lower reactivity and volatility, which depend on particle size.
- The lack of change in Hg concentration after 95 days of the first round testing was unexpected. The equivalent parameters (100 wt% Na₂S, 0.1% moisture, ambient temperature) tested in the second round yielded positive results i.e., the concentrations near the treatment rod were nearly three times greater than those far from the treatment rod. Other than the shape of the container and depth of the sand (which should not impact the process) the one parameter that differed in the second round of testing was the head space i.e., area above the soil within the closed container. The head space volume in the first round of testing was two orders of magnitude larger (~ 5 cm height for a total volume of 3,044 cm³) than the second round of testing and the 2002 study (~1 cm height for a total volume of 26 cm³). The concentration of Hg and/or sulfur in the headspace was therefore considerably more dilute in the first round experiment. Assuming the reaction is driven by difference in gas concentrations it stands to reason that the larger headspace would result in a much lower total reaction. This could be one of the most significant findings of this preliminary work in that it now appears that the process requires a closed system or one in which the free zone above the soil is limited. In a field application this can easily be accomplished by installing a thin layer of gravel to allow vapor transport above the soil with an impermeable cap or cover placed above the gravel layer after treatment rods are installed.
- The in situ treatment process works at ambient temperatures for moisture contents ranging from 0.1 to 5 wt% over relatively modest time frames (42 - 47 days). All samples tested showed positive concentration gradients, i.e., higher concentrations closer to the treatment rods and most showed significantly higher concentrations near the treatment rod. The effect of longer exposure times (months vs. weeks) to determine whether the reaction continues over time and mercury concentration are

further concentrated in the vicinity of the treatment rods will be examined in Phase II of the Technology Maturation study.

- Elevated temperature has a measurable effect in accelerating the transfer of mercury in the geomeia. For samples containing 95 wt% SPC + 5 wt% sulfide under low moisture conditions, application of heat dramatically increased the mercury concentrations near the treatment rods. For samples containing 95 wt% SPC + 5 wt% sulfide under high moisture conditions, elevated temperature had a slightly negative effect. Although mercury levels were higher close to the treatment rods at all temperatures, they were relatively higher close to the treatment rods at ambient temperature than at elevated temperature. This may be related to the greater solubility and/or enhanced diffusion properties of the sulfide at elevated temperature and might be controlled by reduction in sulfide solubility and diffusion, which will be examined in Phase II.
- The use of pure sulfide reagent in the treatment rods was not as effective as the combination of 95 wt% SPC + 5 wt% sulfide. The 100 wt% sulfide is effective only when there is little moisture present in the system. Otherwise the reagent quickly solubilizes and forms a plume that can take Hg away from the treatment rod. If solubility of the pure Na_2S and transport of sulfide into the surrounding geomeia could be slowed or stopped either via microencapsulation, use of a membrane, or a permeable gel, performance similar to the 0.1% moisture samples could likely be achieved (the concentration of Hg was almost three times higher near the treatment rod than far away from it at ambient temperature and more than 12 times higher at elevated temperature). The potential for controlling sulfide solubility and its impact on system performance will be examined in Phase II.
- In all cases, samples with additional moisture (5 wt%) performed less well than equivalent samples with less moisture (0.1 wt%) and in two cases the high moisture content samples showed negative results, i.e., mercury levels were higher further away from the treatment rods. This is likely due to dissolution and dispersion of soluble sodium sulfide in the geomeia with transport of mercury sulfide within the plume. In field applications controlling the soil moisture at low levels will require a tight, non-porous cover.

In summary, the Phase I Technology Maturation research and development effort was successful in completing the defined objectives. Results from the 2002 study were confirmed, demonstrating that the ISMS approach can be effective in concentrating Hg around passive treatment rods installed in contaminated soil. Although the portion of the Phase I study related to scale-up did not yield positive results, valuable information about process mechanisms was revealed. For example, the effect of head space on the system appears to be a critical parameter that requires additional investigation in Phase II. If confirmed, engineering solutions, e.g., impermeable caps or covers that reduce the volume of the head space can be incorporated into the process. Other important scientific questions that arose as a result of the Phase I effort would be addressed in Phase II. For

example, how do parameters including soil particle size distribution, chemical form and homogeneity of Hg, longer exposure times (months vs. weeks), and solubility of sulfides impact process effectiveness and efficiency? The plans for Phase II of this Technology Maturation project will specifically address these issues and will further advance the viability of field-scale application for ISMS.

References

¹ U.S. Department of Energy, *Mercury at Y-12: A Study of Mercury Use at the Y-12 Plant, Accountability, and Impacts on Y-12 Workers and the Environment-1950-1983* (Y/EX-24).

² Phillips, Elizabeth, “Groundwater Remediation on the Oak Ridge Reservation”, presented to the DOE ERSP Annual Program Meeting, Oak Ridge, TN, Oct. 25, 2006.

³ Kalb; P.D., D. Melamed; B. Patel, M. Fuhrmann, “Treatment of mercury containing waste” U.S. Patent No.6,399,849 (June 4, 2002)

⁴ Fuhrmann, M., J.W. Adams, and P.D. Kalb, In Situ Mercury Stabilization Royalty Project Status Report (Internal BNL Report to BNL Office of Intellectual Property and Sponsored Research), 2002.

⁵ Fuhrmann, M., P. Kalb, and J. Heiser, Mercury Contamination Extraction, BNL Patent application, Docket BSA 04-04