

MUCH ADO ABOUT MERCURY: EVALUATION OF TREATMENT OPTIONS FOR MERCURY CONTAMINATED SOIL AT BNL

Paul K. Boyce, P.E., Kris E. Almskog
P.W. Grosser Consulting Engineer & Hydrogeologist, P.C.
630 Johnson Avenue, Suite 7, Bohemia, New York 11716

INTRODUCTION

Various mercury treatment technologies were reviewed, evaluated and compared to determine the most viable alternative to treat mercury contaminated soil at Brookhaven National Laboratory (BNL). The technologies included; acid leaching, amalgamation, soil washing, retorting and stabilization. The alternatives were evaluated and compared based on cost, treatment efficiency, availability, process operating parameters and the potential for the generation of secondary waste streams such as wastewaters and off-gases. Due to the total and leachable mercury concentrations of the soil, the material is classified as a D009 USEPA regulated hazardous waste low mercury subcategory (i.e., total mercury concentration < 260 mg/kg). As such, the soil is required to be rendered non-hazardous (i.e., TCLP mercury concentration reduced to < 0.2 mg/l) prior to final disposal. Stabilization was the treatment technique found to be the most viable option primarily due to a relatively low cost, likelihood of having the optimal treatment efficiency (i.e., not requiring secondary treatment) and minimal production of secondary waste streams. Stabilization can be accomplished on site as well as off site and involves a relatively simple operating procedure mixing the contaminated material with a stabilizing agent.

The BNL remedial excavation of the Animal/Chemical Pits and Glass Holes during the summer of 1997 produced over 12,000 cubic yards of potentially contaminated soil and debris material from 55 separate waste pits. Characterization and disposal of the material is currently on going. Segregated and processed soils were staged in as many as 18 individual stockpiles ranging in size from 100 to 1,800 cubic yards. Stockpiled soils were initially segregated based on the results of field screening during the excavation and processing phases of the remedial effort. After subsequent sampling and characterization of the stockpiled soils was performed, three (3) separate classifications were generated; non-hazardous/non-radioactive, non-hazardous/low level radioactive and hazardous/low level radioactive. Only one (1) of the 18 soil stockpiles was designated hazardous based on mercury and at the same time is also characterized as containing residual radioactive contents. DOE policy currently considers this a mixed waste and therefore the 440 cubic yards of soil contained in the stockpile must be properly disposed of and treated.

BNL is a 5,265 acre site located in central eastern Long Island, New York. The facility is a federally owned and funded international research and learning center managed by Brookhaven Science Associates (BSA), under contract with the United States Department of Energy (DOE). As of December 21, 1989, the site was placed on the U.S. Environmental Protection Agency (USEPA) National Priorities List (NPL), which is a federal ranking of hazardous waste sites as part of the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA). The placing of BNL on the NPL resulted in establishing a remediation task list for seven (7) separate remedial areas known as Operable Units. Part of OU I's remedial activities included the Animal/Chemical Pits and Glass Holes Remedial Action, which was the excavation of buried laboratory wastes, debris and associated contaminated materials. The excavation took place in a secluded wooded zone in the south central portion of OU I that was formerly used for waste disposal.

Most of the excavated materials from the remedial action are currently stored on site. Higher hazard materials such as biological wastes, cylinders, liquids and solid chemicals were segregated, inventoried, bulked, staged and either secured on site or disposed of off site. Excavated and processed soils, and large debris are stockpiled in the excavation areas. These stockpiled materials currently consist of 13 soil piles and four (4) waste debris piles. The soil stockpiles were sampled and characterized and are currently awaiting off site disposal. Characterization of the waste debris piles is currently being coordinated.

Of the soil stockpiles currently staged on site, only one is characterized as hazardous with residual radioactive contents requiring disposal as a mixed waste. The hazardous characterization was established based on TCLP mercury concentrations in excess of the USEPA criteria of 0.2 mg/l. The residual radioactive contents classification is based on radiological parameters exceeding BNL's site specific values that indicate the presence of radiation above site background levels. Radiological activities that exceeded BNL site specific background levels included gross alpha radiation, americium-241, neptunium-237, plutonium-239/240, thorium-232, uranium-234 and uranium-235.

Several treatment technologies exist for mercury contaminated soil and applicability varies based on the form and concentrations of mercury present in the soil medium. In some instances one specific technology is often required by federal regulations based on the types of mercury present as well as other co-contaminants such as organics or radiological parameters. A few of the more applicable technologies for treating mercury contaminated soil include acid leaching, amalgamation, soil washing, retorting and stabilization. Each of these technologies are described and evaluated based on feasibility and costs for this project. Table No. 1 presents an overview and comparison of the aforementioned treatment alternatives.

Acid Leaching - Overview

Acid leaching or soil leaching, is a chemical process used to extract mercury from contaminated soil. The soil is leached with a strong acid such as sulfuric or hydrochloric

Acid Leaching	6 - 8 tons/hr	< 0.2 mg/l TCLP	1 hr.	batch & continuous	ambient	off site	acid, water, GAC
Amalgamation	100 lbs/day	< 0.2 mg/l TCLP	4 hrs.	batch	ambient	off site	N/A
Soil Washing	200 tons/day	< 0.2 mg/l TCLP	N/A	batch & continuous	ambient	on site & off site	wash water
Retorting	3 - 12 tons/day	< 0.2 mg/l TCLP	4 - 6 hrs.	batch	500-1000°F vacuum	on site & off site	off-gases cooling water
Stabilization	40 tons/day	< 0.2 mg/l TCLP	N/A	batch & continuous	ambient BNL SPC - 20-100°C atmospheric to negative press	on site & off site	little to none BNL SPC - off-gases

N/A = not available

SPC = sulfur polymer cement

Amalgamation is primarily conducted on elemental mercury in order to render it non-hazardous based on leachable concentrations. Soil contaminated with mercury would typically first have to be treated using another technology to remove and recover the mercury. The current technology is essentially limited to off site treatment and has a maximum processing rate of around 100 lbs/day (8 hr shift) at a batch processing cycle of 4 hours. The process itself is fairly simple and involves mixing elemental mercury with an amalgamating material in a batch reactor such as a paint shaker at ambient temperatures and pressures. Much is still unknown about how to optimize the process such as the amalgamating particle size, moisture content, pH, mixing speeds and processing cycle durations, effects of impurities, etc., and therefore the technology has yet to achieve large-scale industrial application.

Soil Washing - Overview

Soil Washing is a technology where by liquids such as water (sometimes combined with chemical additives) and a mechanical process are used to "scrub" soils. The scrubbing removes the bulk of the hazardous contaminants from the larger coarser soils and concentrates them into a smaller volume. Hazardous contaminants tend to bind physically or chemically to silt and clay. Silt and clay in turn naturally bind to sand and gravel particles. Soil washing is important for its separation of contaminated fine soil (silt and clay) from the coarse soil (sand and gravel). When the process is completed, the smaller volume of soil which contains mainly fine silt and clay particles, can be further treated by

other methods (incineration or retorting) or disposed of according to state and federal regulations. The larger volume of soil if non-hazardous can be used as backfill.

An advantage of soil washing is that the equipment is transportable so the process can be conducted on site. The larger scale soil washing equipment presently in use can process over 100 cubic yards of soil per day. The first step of the process is to excavate the contaminated soil and to move it to a staging area where it will undergo treatment. The soil is then sifted for the removal of rocks, debris, and other large objects. The remainder of the material is then passed through a soil scrubbing unit where the soil is mixed with a washing solution to remove contaminants. The washing solution may simply be water or contain additives such as detergent, cultured bacteria or flocculating agents. The soil is rinsed with clean water after the wash water is drained out of the scrubbing unit. The heavier sand and gravel particles that settle out of the processed soil are tested for contamination. If the material still contains contaminants it may be run through the soil washer again or collected for alternate treatment or off site disposal. If clean, the material can be used on site or taken elsewhere for backfill. If the silt and clay that settle out of the wash water are not contaminated, they can also be taken elsewhere and used as backfill. If still contaminated, the material may be run through the soil washing process again, or collected for alternate treatment or off site disposal in a permitted RCRA (Resource Conservation and Recovery Act) or TSCA (Toxic Substances Control Act) landfill. The contaminated wash water is then treated with a wastewater treatment process so it can be recycled for further use.

Soil washing is available for both on site and off site treatment and has been widely used in the United States to successfully remove a variety of contaminants from soils, including mercury.

Retorting - Overview

The retorting process is a thermal heating and distillation technique used to extract mercury from contaminated materials such as soils, debris, metals and glass. Materials that were prepared for retorting (crushed and shredded to a uniform size) are placed in metal trays and placed in the retorting furnace (a heating oven that operates under vacuum). Mercury contaminated materials placed in the retort unit are heated to 500 - 1000°F for a period of 4 to 6 hours. During this time mercury is vaporized, cooled and condensed into liquid mercury. The recovered liquid mercury can then be distilled for purification and resold as product or treated further if radiological contamination is present (amalgamated). Once retorted, the remaining material is tested to ensure that the hazardous characteristic for mercury has been reduced below TCLP limits (efficiency typically > 99%). The retorted material is then disposed of or further treated depending on remaining hazardous or radiological characteristics.

Retorting is required for USEPA D009 regulated hazardous waste high mercury-inorganic subcategory (total mercury > 260 mg/kg). Retorting can be performed on or off site and currently has a process throughput of 3 to 12 tons/day depending on the material to be processed and the retorter's equipment and facility capabilities. Process by-products

or waste streams generally involve off-gases which are treated using granular activated carbon adsorption columns and cooling water used in the condensing process.

Stabilization - Overview

Stabilization involves physically and/or chemically binding mercury to the contaminated medium to reduce leachable concentrations below the 0.2 mg/l TCLP hazardous criteria. This treatment is acceptable for low mercury subcategory wastes (total mercury < 260 mg/kg) and applicable to residues of high mercury subcategory wastes from other treatment technologies such as retorting, incineration and amalgamation. Stabilization can be applied to non-wastewaters that contain less than 260 mg/kg total mercury such as non-aqueous sludge, soil, debris, and partially or fully stabilized sludges containing mercury or mercury compounds. Stabilization is not suitable for direct treatment of mercury concentrations greater than 260 mg/kg (high mercury subcategory) or wastes containing elemental mercury contaminated with radioactive materials.

Typical stabilization processes involve dry mixing the contaminated medium in a pug mill (batch reactor) with a stabilizing agent such as sulfur, fly ash, pozzolan, Portland cement or kiln dust. Pilot testing determines the most suitable or effective stabilizing agent. Pug mill mixers are generally best suited for clean sand materials with little to no debris or large stones. The unprocessed or unscreened material, meaning non-uniform materials containing solids greater than 2" in diameter, are generally not appropriate for pug mill mixers. Materials of this nature are often dry mixed in open roll off containers or lined pits using a backhoe. Most dry mix stabilization processes usually have little to no secondary waste associated with them. Common processing rates are as high as 40 tons/day and the procedure can be conducted on or off site. Stabilization efficiencies of <0.2 mg/l leachable mercury are achievable and operating temperatures and pressures are ambient.

More advanced stabilization procedures involve mixing, heating, cooling and solidifying the waste using polymers. These processes often produce an off-gas waste stream as a result of the heating. A bench scale two-stage mercury stabilization process was developed at BNL's Environmental & Waste Technology Center (EWTC). The process essentially involves a sulfur polymer cement (SPC) that is mixed and heated with the mercury contaminated material to form mercuric sulfide. The mixture is allowed to cool and solidify. Once stabilized, the solidified waste mass can then be disposed of as non-hazardous. Off-gases are treated using granular activated carbon. Depleted carbon can be solidified into the waste mass and disposed of with the stabilized mercury waste thus minimizing secondary waste streams. Operating temperatures are said to range between 20 to 100°C and the system is operated at either atmospheric pressure or a slight vacuum to capture off-gases.

Acid Leaching - Evaluation

Acid leaching costs were found to range between \$450 to \$2,000 per ton to treat mercury contaminated soil (see No. Table 2). The technology is performed primarily off site,

however, small plants can be built on site. For the relatively small soil quantity at BNL (approx. 440 cubic yards) requiring

Table No. 2
Brookhaven National Laboratory
Mercury Contaminated Soil Treatment Alternatives Evaluation
Chemical Holes Stockpile 6B

TREATMENT ALTERNATIVES SUMMARY AND COMPARISON

Technology	Cost (\$/ton)	Processing Rate (tons/day)	Availability	Treatment Efficiency	Waste Streams
Acid Leaching	\$450 - \$2,000	50 - 60	off site	< 0.2 mg/l TCLP may require multiple processings and secondary treatment	acid water GAC
Amalgamation		0.05	off site	< 0.2 mg/l TCLP requires primary treat	
Soil Washing	\$150	200	on site off site	< 0.2 mg/l TCLP may require secondary treatment	water
Retorting	\$500 - \$2,500	3 - 12	on site off site	< 0.2 mg/l TCLP may require secondary treatment	off-gases water
Stabilization	\$40 - \$2,000	40	on site off site	< 0.2 mg/l TCLP	none off-gases

Shading indicates best rating under column heading.

Amalgamation omitted from comparison, not a primary treatment alternative for soil.

processing, construction of an on site treatment plant would not be cost effective (package plants can cost over \$500,000 to construct). Therefore, from the standpoint of transportability, the technology is not a mobile one, and thus, for this study, the process availability is essentially limited to off site treatment only. Acid leaching can yield treated soils with leachable concentrations of mercury less than the USEPA hazardous criteria of 0.2 mg/l TCLP. Heavily contaminated soils may require multiple processings to achieve a TCLP concentration below 0.2 mg/l. The low total mercury concentration of

10.25 mg/kg for 440 cubic yards of contaminated soil at BNL would most likely require a single processing.

One of the biggest draw backs to acid leaching is the production of additional waste streams and the DOE's concern for waste minimization made this alternative unappealing. Waste streams that are generated as a result of the soil leaching process include wastewater, spent leaching solution and depleted granular activated carbon, and all would require treatment and disposal. The process can be carried out in either batch or continuous fashion and requires about one hour to complete. Approximately 50 to 60 tons/day of soil can be treated at ambient temperatures and pressures. An additional concern is that the material would have to be transported off site as a hazardous low level radioactive waste to a processing facility and then either returned to BNL or shipped as a radioactive material directly to a low level waste facility for disposal. Based on the production of additional waste streams and costs associated with processing, handling and shipping, acid leaching though potentially effective, was not a preferred treatment alternative for the soil at BNL.

Additional concerns with the acid leaching process include the possibility of leaching the radioactive constituents from the soil into the acid solution and generating a potentially hazardous/radioactive or mixed liquid waste. The benefit of this possibility is that the soil may be rendered non-hazardous and non-radioactive. The concern with this possibility is the generation of a separate mixed waste that would require proper disposal. Pilot testing is recommended prior to implementation to determine the likelihood of radioactive parameters leaching from the soil.

Amalgamation - Evaluation

Amalgamation was eliminated immediately as the primary mercury treatment alternative since it is currently only performed off site at very small scale (i.e. 100 lbs/day) and principally on elemental mercury. Should a mercury extraction or recovery technology be applied such as acid leaching or retorting, the recovered mercury may be radioactive and then would require amalgamation as per federal regulations. Since approximately 600 tons of material require treatment, amalgamation would take too long to be acceptable and should only be considered as a secondary treatment for mercury recovered from the contaminated soil.

Soil Washing - Evaluation

Soil washing costs were quoted at around \$150 per ton to treat mercury contaminated soil (see Table No. 2). The technology can be performed either on or off site and is available from numerous environmental and remediation contracting companies from around the country. Soil washing has the greatest processing rate of the technologies investigated at around 25 tons/hr, which means once the process is mobilized the soil requiring treatment could be processed in less than a working week. Soil washing neither removes nor stabilizes the contaminating mercury but rather removes the smaller, finer contaminated soil particles such as the clays and silts from the bulk of the soil medium and thus tends

to concentrate the hazardous mercury into a smaller waste volume. The coarser larger sands and gravels that are separated may or may not require additional treatment for mercury and/or radiological parameters. Thus, soil washing is often best applied as a technology in combination with other treatment technologies. The resulting smaller concentrated waste volume will often have higher total and TCLP mercury concentrations and will therefore require additional treatment such as retorting or stabilization.

The benefit of soil washing is that the amount of material requiring either mercury recovery or stabilization will be drastically reduced. The draw backs include secondary treatment of the concentrated waste volume and the generation of a wastewater volume that may require treatment prior to discharge. Without additional soil testing such as grain size distribution and determination of percent organics applicability of soil washing is difficult to determine. Soils with large amounts of fines and organics are less susceptible to soil washing because of the strong chemical and physical attractions between smaller soil particles and contaminants. Based on the total and TCLP mercury concentrations for the soil and visual observation of the soil media (a medium to coarse sand) it appears that soil washing would have a high likelihood of success in reducing the bulk of the soil medium to below USEPA hazardous leachable mercury concentrations. However, the quantity of the smaller concentrated waste stream requiring further treatment is at this time unknown. Therefore, if soil washing is wished to be pursued further additional soil testing and a field pilot test are recommended prior to full scale implementation. A secondary mercury treatment for the washed soils may also be warranted based on the results of field pilot testing, or, if the expected quantity is small enough, direct disposal as a hazardous low level radioactive material may be cost effective. Additionally, the smaller or washed soil particles may contain radiological parameters and the resulting reduced waste mass may be classified as a mixed waste. Again, pilot testing is recommended prior to implementation to determine to what degree radiological parameters can be expected in the washed soil residues.

Retorting - Evaluation

Retorting costs were reported to vary from \$500 to \$2,500 per ton to treat mercury contaminated soil (see Table No. 2). The retorting process is available for either on or off site treatment from multiple firms located in the northeastern United States. Processing rates were found to vary between 3 to 12 tons per day. The rate varied based on the waste management facilities' equipment and capabilities and the degree and type of mercury contamination present. The retorting process would extract mercury from the soil medium and, depending on the presence of radiological contamination, the extracted mercury may require amalgamation. Utilizing a total mercury concentration of 10.25 mg/kg and an estimated 600 tons of soil requiring treatment and assuming 100% recovery of the mercury this would yield approximately 12.3 lbs of liquid mercury potentially requiring amalgamation. The retorting process is carried out at elevated temperatures between 500 and 1000°F in order to thoroughly vaporize the mercury. The process is also carried out under a vacuum to capture and condense the vaporized mercury.

Process waste streams include off-gases which can be treated using either granular activated carbon or scrubbers, and the cooling water used in the condensing process. Often the off-gases are of such low concentrations no off-gas treatment is required, however thorough investigation and review of local air discharge requirements should be conducted prior to on site treatment utilizing retorting. Based on the analytical data pertaining to the contaminated soil no significant off-gases would be anticipated other than possibly water vapor. The cooling water used in the condensing process can be recycled and reused. Mercury concentrations in the retorted soil would be below the USEPA hazardous criteria of 0.2 mg/l TCLP.

Retorting of the soil appears to be a viable and cost competitive option. Potential drawbacks include the possibility of having to amalgamate the recovered mercury and the generation of off-gases that may require treatment. Additionally a fuel source is required in some retorting operations for heating and vaporization. Typical fuel sources are natural gas, propane, diesel fuel and electricity.

Stabilization - Evaluation

Stabilization can be performed on or off site for mercury contaminated soils and costs were found to vary from \$40 to over \$2,000 per ton (see Table No. 2). Numerous environmental and remediation firms across the country can provide this service. Many of the off site stabilization procedures investigated at waste management facilities are proprietary and therefore most of the process information is unavailable except for pricing. Processing rates of up to 40 tons/day are attainable and a stabilized waste mass TCLP mercury concentration of less than 0.2 mg/l is achievable as well. Stabilization has the potential to be one of the most cost effective treatment alternatives as well as one with the smallest secondary waste streams associated with it. Typical procedures simply involve dry mixing the contaminated medium with readily available stabilizing agents at ambient temperatures and pressures. Very little secondary waste or process by-products are associated with the procedure.

Summary

Each of the treatment technologies reviewed have some merit with regard to the mercury contaminated soil stockpile at BNL. However, the optimal or most preferred alternative will stand out from among the rest by having the highest rating in multiple categories of concern. Table No. 2 presents the five (5) reviewed treatment technologies and indicates the most desirable rating in each category of concern.

Stabilization was found to be the most preferred alternative specifically because of the relatively low cost, the treatment efficiency (i.e. stabilization does not require secondary treatment) and the least likelihood for the production of significant secondary waste streams. Soil washing also ranked high because of the low cost and high processing rate. However, soil washing is likely to need a secondary treatment for the condensed mercury waste volume (and the condensed waste volume may possibly be a mixed waste) and potentially has a high volume waste stream that would also require some type of

treatment (i.e. contaminated wash water) and is thus not preferred over stabilization. Retorting, though a viable and applicable treatment technology, is not recommended as the best or first choice treatment alternative because of its high cost and the possibility of having to amalgamate the recovered mercury. Acid leaching is not preferred based on the potentially large secondary waste streams, high cost and availability. Additionally the acid leachate produced may potentially be a liquid mixed waste. Amalgamation was ruled out as primary soil treatment and thus should not be compared or weighed against the other technologies.

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