INDUSTRIAL-SCALE PROCESSES FOR STABILIZING RADIOACTIVELY CONTAMINATED MERCURY WASTES

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ABSTRACT

This paper describes two industrial-scaled processes now being used to treat two problematic mercury waste categories: elemental mercury contaminated with radionuclides and radioactive solid wastes containing greater than 260-ppm mercury. The stabilization processes were developed by ADA Technologies, Inc., an environmental control and process development company in Littleton, Colorado. Perma-Fix Environmental Services has licensed the liquid elemental mercury stabilization process to treat radioactive mercury from Los Alamos National Laboratory and other DOE sites. ADA and Perma-Fix also cooperated to apply the >260-ppm mercury treatment technology to a storm sewer sediment waste collected from the Y-12 complex in Oak Ridge, TN.

The elemental mercury treatment process is a patented process that converts elemental mercury to meta-cinnabar (HgS) through a reaction with sulfur under intense mixing. To date, this process has been used to treat 6,100 kg of waste elemental mercury. The patent-pending process for the greater than 260-ppm mercury waste has been demonstrated on an industrial-scale and is awaiting approval from the Utah Department of Environmental Quality Division of Solid and Hazardous Waste to allow treatment of the mixed waste by amalgamation/stabilization (A/S) technology. The A/S technology is an alternate treatment to the current EPA-approved thermal treatment method for the >260-ppm mercury wastes. Both the elemental mercury and >260-ppm mercury treatment processes have demonstrated the ability to generate a stable waste with less than 0.025 mg/L leachable mercury.

INTRODUCTION

Over the past five years, ADA Technologies, Inc. has developed mercury treatment technologies to address two problematic mercury waste categories: elemental mercury contaminated with radionuclides and radioactive solid wastes containing greater than 260-ppm mercury. The Department of Energy (DOE) has significant quantities of these types of wastes within the DOE complex and is currently developing management strategies to process and dispose of these mercury wastes in an environmentally responsible manner. ADA has developed applicable treatment technologies for these waste types so that they are no longer characterized as a mixed waste, and can therefore be disposed as a radioactive waste with the hazardous characteristic of the waste being de-listed for leachable mercury.

Mercury and mercury-contaminated wastes are some of the more pervasive and troublesome wastes in the DOE waste inventory. Most of the larger DOE sites have radioactively contaminated liquid elemental mercury and mercury containing sludges in their mixed waste inventories. In 1997, the Mixed Waste Focus Area Mercury Working Group (HgWG) revised the inventory of mercury-containing waste throughout the DOE complex and found 7,300 m^3 of mercury waste that must be treated. The HgWG estimates there are approximately 17 m^3 (230 metric tons) of elemental mercury, 6,000 m^3 of waste having less than 260 ppm mercury, 325 m^3 of waste with more than 260 ppm mercury and 925 m^3 of waste with unknown quantities of mercury (1).

For radioactively contaminated elemental mercury wastes, the current approved treatment is amalgamation as defined by the U.S. Environmental Protection Agency (EPA) in 40 CFR 268.42, Table 1, which states that "Amalgamation of liquid elemental mercury contaminated with radioactive materials utilizing inorganic reagents such as copper, zinc, nickel, gold, and sulfur that results in a nonliquid, semi-solid amalgam…". Further, the DOE's Mixed Waste Focus Area established a Technology Development Requirement Document (TDRD) (2) that outlined specific criteria for a successful mercury amalgamation process besides meeting the EPA's definition of amalgamation;

- The waste form must pass EPA's 0.2 mg/L treatment standard based on Toxic Characteristic Leaching Procedure (TCLP);
- The mercury vapor concentration above the waste form must be less than 50 $\mu g/m^3$;
- The process must be readily scaleable; and
- The process must be economically viable.

In 1997, ADA Technologies, Inc. and its subcontractor Colorado Minerals Research Institute (CMRI) developed a mercury treatment process to meet the above criteria. Following process development, ADA participated in the DOE sponsored MER01 program and demonstrated the elemental mercury stabilization process on actual mixed waste provided by Los Alamos National Laboratory (LANL) and Fernald. In all, ADA treated 132 kg of radioactively-contaminated elemental mercury waste in five batches with a typical batch size of 25 kilograms. Waste elemental mercury treated in the process consistently passed the 0.2 mg/L treatment standard based on the TCLP (3).

Although the chemistry of amalgamation is well known, the practical engineering of a sizable amalgamation process capable of treating a substantial batch of elemental mercury (>50 kg) has not been available until now. ADA has succeeded in taking the process from a laboratory-scale to an industrial-scale, and has shown that the batch process is a scaleable and economic mixing technology. The patented elemental mercury stabilization process converts elemental mercury to meta-cinnabar (HgS) using commercially available mixing equipment that can be sized for specific applications. Currently, Perma-Fix Environmental is licensed to use the ADA process to stabilize radioactively-contaminated elemental mercury from the DOE complex.

ADA has also developed a treatment technology for treating wastes with greater than 260-ppm mercury using a non-thermal, direct stabilization method that addresses not only elemental mercury but also speciated inorganic and organic forms of mercury. The current EPA-approved treatment method for solid wastes and soils contaminated with more than 260-ppm mercury is thermal retort followed by stabilization of the recovered mercury. Thermal retort is expensive and often fails to reduce mercury concentrations to the point where the treated waste passes TCLP. Often the waste from which the mercury is recovered must still be managed as mixed waste. Moreover, mercury recovered from radioactive waste cannot be recycled, so it must be amalgamated. Thus, thermal retort is an expensive, complex, multi-step process for the DOE that ultimately fails to significantly reduce waste volumes.

Besides being easier and more cost-effective, the direct stabilization approach is more technically sound for many waste streams, especially those that are co-contaminated with heavy metals, organics and radionuclides. The EPA is aggressively pursuing alternative technologies, but limited data are available to establish regulatory and process limits for direct stabilization of wastes that are highly contaminated with mercury. Effectiveness of alternative treatment methods must be demonstrated to the EPA with data to show that the waste passes the Universal Treatment Standard (UTS) for mercury and also that the treated waste is stable over time.

ADA Technologies, Inc. was awarded in 1999 a DOE project to develop and demonstrate an alternative mercury-stabilization method for solid wastes having more than 260 ppm mercury contamination. The new stabilization method was developed using surrogate soils and sludge waste matrices spiked with elemental mercury, mercuric chloride and heavy metals to demonstrate the ability of the process to stabilize co-contaminants. Leachable mercury for the treated wastes was consistently less than the 0.025 mg/L UTS limit for mercury. The process was later demonstrated in the MER03 program by stabilizing mercury in radioactive contaminated soils from Brookhaven National Laboratory. ADA has applied for a patent for this stabilization method.

Currently, Perma-Fix has a contract with the DOE to treat 235,000 kg of the Basin Storm Sewer Sediment (BSSS-1) material from the Y-12 complex. The BSSS-1 has nearly 2 % by weight of mercury, most of which is a speciated form of mercury. In cooperation with the Perma-Fix development laboratory in Gainesville, Florida, the ADA stabilization process was tailored to treat the BSSS-1 material so that the product consistently meets the UTS for mercury. The process has since been demonstrated on an industrial scale of nominal 100-kg batches. A variance with data from both laboratory and scale-up mixes has been submitted to the Utah Department of Environmental Quality Division of Solid and Hazardous Waste for review and approval to allow treatment of the BSSS-1 mixed waste by the amalgamation/stabilization (A/S) technology. The patented-pending process will be used by Perma-Fix under a license from ADA Technologies, Inc. to treat the BSSS-1 mercury bearing waste.

DESCRIPTION OF WASTE TREATMENT PROCESSES

Description of the Elemental Mercury Treatment Process

ADA's patented amalgamation process (4) consists of reacting liquid mercury with a proprietary sulfur mixture in a commercially available paddle mixer to produce mercuric sulfide (HgS) in a granular form. Paddle mixers are commonly used in metallurgical and chemical operations where intense mixing of pasty material is required. The full-scale mixer being used at the Perma-Fix/M&EC (referred to as M&EC) facility in Oak Ridge, TN is a single-shafted paddle mixer manufactured by Marion Mixers. The mixer is constructed of T-304 stainless steel with an internal mixing capacity of 0.28 m^3 (10 ft^3). This mixer is routinely used to stabilize 75 kg of mercury per batch, but larger batch sizes could be treated limited only by mixer motor amperage. Figure 1 shows the stabilization equipment as it is installed at the M&EC facility.

Fig. 1. Elemental mercury stabilization process at M&EC

Instrumentation is provided to monitor two important process parameters: mix temperature and motor amperage. Mix temperature is measured using a type K thermocouple mounted in a stainless steel thermo well. The thermocouple is located near the bottom center of the mixer trough. The mixer also has a double-wall jacket to control the temperature of the mixture during processing. Air is pumped through the jacket to pre-heat the mixer and to help cool the mixture at the end of the treatment cycle. A digital readout is provided to display the mix temperature continuously. The mixer motor amperage is monitored using a current sensing coil. The induced current is displayed on a digital readout. The mixer motor can be operated at three speeds to promote a high-degree of mixing at the start of the stabilization process and can be slowed at the end of the process to prevent grinding of mercuric sulfide granules to too fine a size.

It is important to limit the amount of oxygen in the mixer during the treatment process. Exposing the mixture to oxygen could lead to the formation of oxidized mercury compounds, which are not as leach-resistant as mercuric sulfide. To limit the oxygen in the mixer, the mixer is purged with a nitrogen gas stream. Purge gas exits the mixer through a 6" diameter duct mounted on one of the mixer lids and is routed through activated carbon and HEPA filters. As a safety precaution, pressure in the mixer is controlled at a slightly negative value to minimize mercury emissions from the mixer. Pressure in the mixer is monitored by a gauge located near the mixer and is adjusted by opening or closing dampers in the vent system.

The reaction of mercury with sulfur is an exothermic process. During the treatment process the mix temperature increase rapidly as mercury and sulfur combine to form mercuric sulfide. The mixture temperature is monitored continuously to time the addition of reagents to the mix. Mixing is concluded when the exothermic reaction subsides. Once the mixer is cooled, the mercuric sulfide is discharged from the mixer through a 6" knife gate valve located on the bottom center of the mixer into a 55-gallon drum. Total mix time for a 75 kg batch of mercury is nominally 3 hours. A process flow diagram for the process is shown in Figure 2.

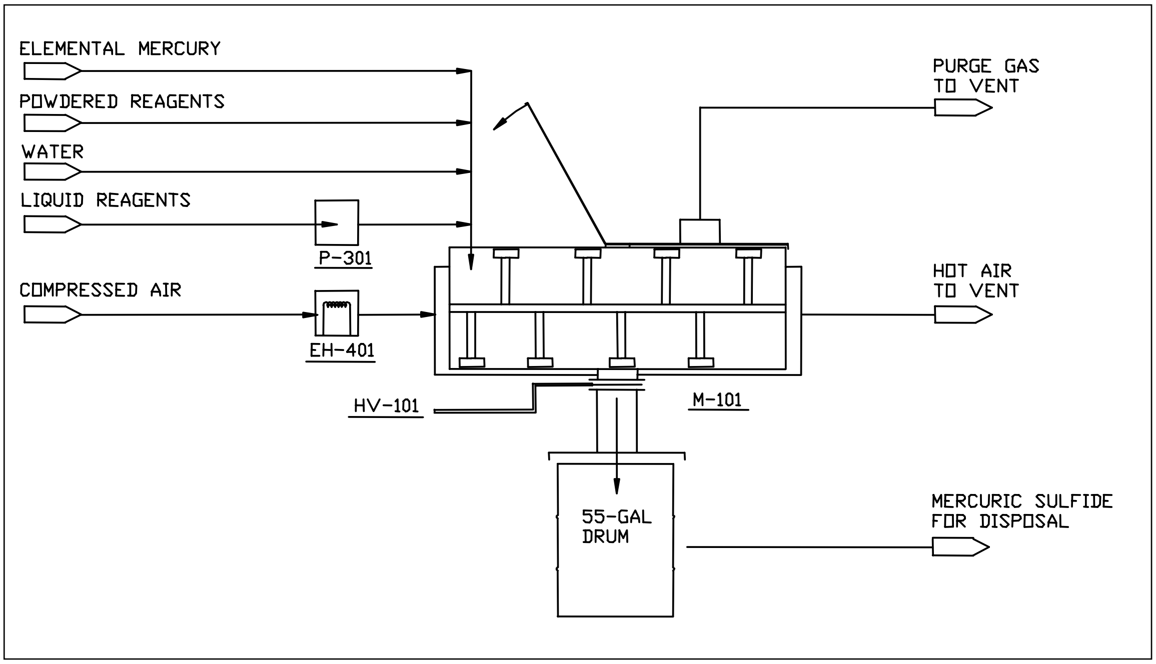

Fig. 2. Process flow diagram for the elemental mercury stabilization process

Description of the >260-ppm Mercury Treatment Process

The stabilization process for >260-ppm mercury wastes consists of adding reagents to the mercury-contaminated waste followed by thorough mixing to promote contact between the dispersed mercury, mercury compounds, and the reagent chemicals. The ratio of the reagent mass to waste mass and mixing time required have been shown to be dependent on the properties of the waste matrix and the concentration of mercury compounds present.

In general terms, there are four steps to the treatment process. The first step is a pretreatment step in which oxidized forms of mercury are reduced to elemental mercury. Secondly, the mixture is treated with a sulfur source to sulfide the elemental mercury in the waste mixture. In the third step, a neutralizing chemical is added to react with excess sulfides to reduce the possibility of forming leachable mercury polysulfides. Finally, a proprietary blend of chemicals is added to the mixture to de-water the treated waste and to generate a granular product. Processing of the waste is performed at ambient temperature conditions over a 4-hour treatment cycle. The details of the process are the subject of a patent application.

A large-scale treatment system is currently being assembled at the M&EC facility in Oak Ridge, TN. The process mixer installed at the facility is a refurbished Marion mixer single shafted paddle mixer. The mixer is constructed of carbon steel with an internal volume of 2.5 m^3 (90 ft^3). A typical batch size will be 0.8 m^3 (27 ft^3). Unlike the elemental mercury treatment process, the treatment for >260-ppm mercury wastes does not raise the temperature of the mixture significantly as it is processed. Therefore, the mixer does not need to be jacketed to control the temperature of the mixture during treatment.

STABILIZATION RESULTS FOR RADIOACTIVE WASTES

Test results for the elemental mercury treatment process

After the elemental mercury treatment process skid was fabricated, the unit was proven in two test runs in Denver, CO prior to shipping the equipment to the M&EC facility in Oak Ridge, TN. Two additional test batches were treated at the M&EC facility once the process equipment was re-assembled to provide training to operators on the stabilization procedure. Triple-distilled mercury was purchased from Bethlehem Apparatus to use as a surrogate material for these demonstration tests. Following the demonstration runs Perma-Fix began stabilizing radioactive elemental mercury from the Los Alamos National Laboratory (LANL), Fernald, Mound, and Lawrence Livermore National Laboratory (LLNL). Table I summarizes the amounts of elemental mercury treated by Perma-Fix using the ADA process by end-of-year 2002.

Table I. – Summary of Mercury Wastes Streams Treated

Mercury Source	Mercury Treated (kg)	No. of Batches
LANL	3,611.34	48
Mound	274.216	3
Fernald	1,548.59	21
LLNL	728.216	10

In all, 6,162.37 kg of mercury were treated using the same stabilization formulation. The mercury waste loading in all batches was consistent at 55%, which is above the 50% requirement stated in the TDRD. Mercuric sulfide samples from each of the batches were submitted to an outside EPA-certified laboratory for TCLP analysis. The TCLP data was statistically analyzed and was found to have a mean of 0.069 mg/L and standard deviation of 0.042 mg/L. Based on the statistical analysis, the stabilization process is capable of meeting the 0.2 mg/L limit virtually 100% of the time barring any process upsets with a probability of satisfying the 0.025 mg/L UTS limit 28% of the time. The measured leachate mercury levels showed a consistent downward trend as experience was gained with operation of the treatment system.

Test results for the BSSS-1 mercury waste treatment process

A series of reagent formulations was evaluated in the BSSS-1 treatability study conducted at the Perma-Fix development laboratory in Gainesville, FL. One-kg batches of the BSSS-1 were stabilized with the different stabilization formulations and monitored over a six week period to assess the stability of the treated mercury waste. Out of that effort the two most promising formulations were identified. These formulations were used to treat BSSS-1 material on a larger scale, scaling up the treatment process by a factor of 100:1. The larger mixes were stabilized at the M&EC facility in Oak Ridge, TN using the 0.28 m^3 (10 ft^3) elemental mercury stabilization mixer.

The 1-kg laboratory-scale mixes stabilized with the two formulations showed that the resulting mercuric sulfide reaction product had leachable mercury levels less than the ICP detection limit of 0.0002 mg/L and has remained below that level for a period of four weeks indicating that the treated material is stable over time. BSSS-1 waste stabilized in the larger mixer at M&EC has shown similar results with leachable mercury less than the ICP detection limit of 0.0002 mg/L since December 11, 2002. Samples from the large mixes are being tested for leachable mercury on a weekly basis to monitor stability of the treated waste.

CONCLUSIONS

ADA Technologies, Inc. and it commercial partner Perma-Fix Environmental Services have recently demonstrated two cost-effective mercury treatment processes on an industrial-scale. The amalgamation of radioactively contaminated elemental mercury is currently being performed in batch sizes up to 75 kg using ADA's patented process. The process satisfies the EPA's definition of amalgamation as given in 40 CFR 268.42, Table 1. Thus far, the process has been used to stabilize 6,162 kg of waste elemental mercury from the DOE complex at the M&EC waste treatment facility. The extent of conversion of mercury to mercuric sulfide is nearly complete passing the 0.2 mg/L TCLP limit for leachable mercury. Treated mercury is being disposed of either at the originator's site or at Envirocare of Utah.

The treatment process for >260-ppm mercury waste has been shown to produce a stable product from both laboratory-scale and large-scale mixes. Treated materials are being tested for leachable mercury on a weekly basis to assess the stability of the stabilized waste. Leachable mercury for treated materials has remained below the analytical method detection limit of 0.0002 mg/L since December 11, 2002. Perma-Fix/M&EC are currently installing a full-scale mixer at the M&EC facility for treating a substantial inventory of the BSSS-1 mercury waste.

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