

Using the Sulfur Polymer Stabilization/Solidification Process to Treat Residual Mercury Wastes from Gold Mining Operations

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ABSTRACT

Large quantities of mercury are generated as a by-product during the processing of gold ore following mining operations. Newmont Mining Corporation (NMC), which operates some of the world's largest gold mines, sought a method to permanently "retire" its mercury by-products, thereby avoiding potential environmental liability. Sulfur Polymer Stabilization-Solidification (SPSS) is an innovative technology developed at Brookhaven National Laboratory (BNL) for treatment of mercury and mercury contaminated materials, such as soil, sludge and debris. BNL conducted a treatability study to determine the potential applicability of SPSS for treatment of Newmont mercury, and the treated product passed the U.S. Environmental Protection Agency (EPA) test for toxicity. The SPSS process has been shown to be effective on radioactive and non-radioactive mercury and mercury-contaminated materials with a pilot-scale batch system capable of producing 0.03 m³ (1 ft³) per batch. Engineering scale-up issues are discussed and material property tests addressing these issues are described.

INTRODUCTION

Historically, mercury has been mined for its intrinsic value, which included use as a pigment (cinnabar), in alchemy, in barometers and thermometers, and in the recovery and purification of gold and silver through amalgamation. Until the 20th century, the latter was the primary use of the elemental liquid metal form (Jasinski, 1994). Elemental mercury is also generated from the processing of gold ore following mining operations, as a significant by-product from the standpoint of the quantities produced. Depending on ore composition, mercury may be produced at a rate of up to one ounce per ounce of gold.

Traditionally, excess elemental mercury from gold mining operations (designated as

secondary production) has been recycled for use in industrial and commercial consumer applications. Such applications include chlor-alkali production, fluorescent light bulbs, mercury switches, and dental amalgams. However, declining markets for recycled mercury and increased environmental liabilities have contributed to make this secondary production option much less attractive. Jasinski (1994) has noted that the last direct mercury mine closed down in 1990, the same year that U.S. consumption of mercury in industrial and commercial products dropped below 1,000 metric tons (t). U.S. consumption of mercury continued to drop through the 1990s, to less than 500 t after 1995 (Sznoppek, 2000). This represents quite a dramatic drop, from a relatively constant 2,000 t per year during the 1970s. A similar decline in mercury use has occurred in Europe as well.

The drop in mercury usage may be attributed to its toxicity and potential as a pollutant. Increased regulation of emissions, and liabilities associated with products made from mercury, add to manufacturers' concerns about mercury in all applications. Disposal of mercury represents a final uncertainty, because its disposal in landfills is closely regulated in the United States. In fact, the current US Environmental Protection Agency (EPA) regulations on mercury do not allow for any treatment or disposal of elemental mercury. Despite the steady decrease in the industrial use of mercury, it is assumed that all excess elemental mercury can and will be recycled back to industry. EPA is currently reviewing this policy and issued a Notice of Proposed Rulemaking [USEPA, 1999]. For mercury contaminated soil and sludge, the material is subjected to the EPA Toxicity Characteristic Leaching Procedure (TCLP), and if the leachate contains more than 0.2 mg/L of mercury, the material must be handled and disposed of as hazardous waste (USEPA, 2002a). EPA's regulations require the treatment of materials containing greater than 260 ppm mercury by retort and recovery,

so that the elemental mercury can be recycled to industry (USEPA, 2002b). For materials containing less than 260 ppm mercury, the waste can be stabilized as long as the final product meets Universal Treatment Standard criteria ($< 25 \mu\text{g/L}$) following TCLP testing. Interestingly enough, a treatment alternative does exist for elemental mercury contaminated with radioactive materials (i.e., mixed waste elemental mercury), namely amalgamation with any one of several metals or with sulfur. Again, the final product must meet Universal Treatment Standard criteria for the TCLP leachate.

Because of the decline in the mercury recycling market in the United States, and the likelihood that a similar decrease in mercury use will eventually occur in developing countries, Newmont Mining Corporation began looking for a means to permanently “retire” by-product mercury generated during gold mining operations.

Meanwhile, Brookhaven National Laboratory had recently developed the SPSS process, initially for the treatment of radioactively contaminated elemental mercury (i.e., mixed waste mercury) and mercury contaminated soil, sludge and debris. SPSS was based on the previously successful application of sulfur polymer cement (SPC) for the microencapsulation of radioactive, hazardous, and mixed waste. (Kalb and Colombo, 1985; Kalb, et al, 1991; Colombo et al, 1997) Both SPC Microencapsulation and SPSS use a modified sulfur polymer material devised by the U.S. Bureau of Mines as a means of utilizing by-product or waste sulfur for construction applications. The final product is a durable, solid monolithic waste form that resists leaching of contaminants. In the case of SPSS treatment of elemental mercury, the final product is a solid mercuric sulfide in the

same stable chemical and physical form (cinnabar) that mercury is found in nature.

SULFUR POLYMER STABILIZATION/SOLIDIFICATION

Initial laboratory studies and proof of concept work showed that elemental mercury reacted with SPC to form mercuric sulfide (Fuhrmann, et al, 2002). Mixing mercury with excess quantities of SPC at 40°C produced a powdered black material, essentially an intimate mixture of mercuric sulfide and SPC. Raising the temperature of this reacted mixture to 130°C while continuing mixing melted the SPC and encapsulated the mercuric sulfide at a microscopic scale. It was found that the use of small quantities of sodium sulfide catalyzed the initial formation of mercuric sulfide. All products made with elemental mercury were non-toxic as tested under EPA’s TCLP. In most cases leachate mercury concentrations were low enough to meet EPA’s land disposal restrictions for mercury contaminated soils and sludge, expressed as leachate concentrations, i.e. less than $25 \mu\text{g/L}$ (EPA, 2002b). The entire process, using SPC, a catalyst, and melting for micro-encapsulation, was patented as the Sulfur Polymer Stabilization /Solidification process (Kalb et al, 2001)

Subsequent work with SPSS focused on pilot-scale studies with actual mixed hazardous and radioactive waste. The ability of SPSS to immobilize radioactive and hazardous constituents was demonstrated for elemental mercury and mercury-contaminated soils (Kalb, et at, 2001) and for a simulated (non-radioactive) sludge with 1000 mg/kg mercury (Adams et al, 2001). For the pilot-scale studies, the SPSS process was carried out in a vertical cone mixer-dryer system obtained from Ross Industries (Happaugue, New York).

Figure 1 is a schematic of the mixer, which is sized to allow the production of 0.03 m³ (about 1.0 ft³) batches. A screw mounted on a planetary rotating arm provides mixing action, while heating is by conduction through the oil-filled jacketed sidewall. A separate unit heats and circulates the oil. The melted product is drained into 5-gallon cans through the ball valve in the base of the cone for shipment for disposal.

Because elemental mercury and radioactive isotopic contaminants are heated in the process, an extensive off-gas treatment system is installed to prevent their release to the atmosphere. The system has, in order from the mixer to the off-gas:

- 1) A water-cooled trap to remove water vapor,
- 2) A liquid-nitrogen-cooled trap,
- 3) An activated carbon filter, and
- 4) A HEPA filter.

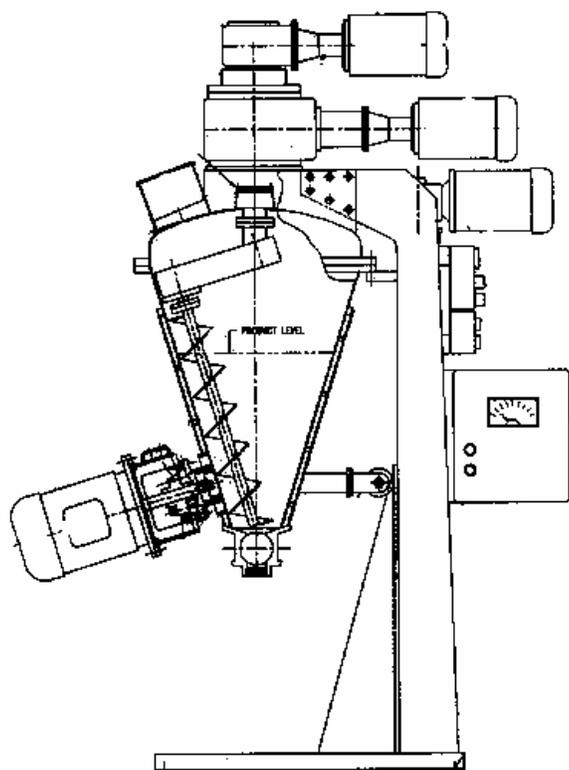


Figure 1. Schematic View of the Ross

Mixer

NEWMONT VERIFICATION TESTS

In November 2000, Newmont Mining Corporation contracted BNL to demonstrate the SPSS process for mercury treatment and potential application to its gold mining operations in Yanacocha, Peru. Newmont shipped a standard 34.5 kg (76 pound) flask for treatment, and BNL produced two batches using its laboratory scale equipment, i.e. a 5-gallon can shaker. (The Ross mixer was being used to test radioactive materials at that time.)

SPC was from stock supplied by Martin Resources, Odessa TX, ground to a fine powder (<1mm). Sodium sulfide (Na₂S·9H₂O technical grade) was obtained from Fisher Scientific. The two batches were prepared using two forms of sulfide additive: hydrated and anhydrous. Both were crushed to pass a 1mm sieve, but the anhydrous form was prepared from the hydrated form by oven-drying first.

In Batch 1, about 500 mL of mercury (6,687.4 grams) were processed using the previously developed formulation: 33 wt% Hg, 65 wt% SPC, and 2 wt% hydrated sodium sulfide. The ingredients were shaken at a temperature of 40°C, with quartz aggregate added to enhance the stirring action. Batch 1 was mixed for 8 hours, twice as long as the four hours needed in previous runs with similar sized batches in the paint shaker. The process was usually judged complete when the mixed powders and mercury show a color change characteristic of one of the forms of mercuric sulfide (HgS), i.e., red (cinnabar) or black (metacinnabar). For Batch 1, the color change to red occurred when additional heating (to > 50°C) was applied. The color change was accompanied by the usual exotherm, which provided additional heat to help melt the mixture. After the mixture was fully melted, three jars were filled for subsequent TCLP sample preparation.

Because Batch 1 had an extended mixing time, the volume of Batch 2 was reduced one half, and anhydrous sodium sulfide was used. About 250 mL (3,672.2 g) of mercury were processed. Because of a calculation error, the final composition was 37 wt% Hg, 61 wt% SPC and 2 wt% sodium sulfide. A black color was observed after only one hour, but mixing was continued for 4 hours before melting and pouring out the product.

Pellets for TCLP testing (approximately cylindrical with largest dimension of 9.5 mm) were prepared by re-melting the batches and casting the melt in a Teflon mold. In addition, 50 by 100 mm (2 by 4 inch) cylindrical demonstration samples were fabricated. These were shipped to Newmont in February 2001.

Newmont tested the BNL produced pellets at an independent analytical laboratory. Results are shown in Table 1. For both batches, TCLP leachates were less than 0.2 mg/L, and for Batch 1, the leachate concentration passed (was below) the land disposal restriction limit for mercury contaminated soil of 0.025 mg/L. Just as importantly, the SPSS process successfully treated by-product elemental mercury from gold mining operations. This showed that SPSS was robust, in that pure (ACS reagent grade) mercury, as had been used in initial development of the process, was not required.

Table 1
Verification Batch Mercury TCLP Results

	Hg in Leachate (mg/L)
Batch 1	0.009
Batch 2	0.039
TCLP Limit	0.200
LDR Limit	0.025

ENGINEERING SCALE DEVELOPMENT WORK

Following the demonstration of meeting TCLP goals, Newmont negotiated an exclusive-use license for application of the SPSS technology to treat mining residuals in August 2001. The objective is to build a facility at Newmont's Yanacocha Mine in Peru, to treat by-product mercury, thereby preventing potential mercury releases to the environment.

During the design phase of this project, BNL has supported NMC with measurements of engineering properties of the molten SPC mercuric sulfide mixture. To date this has included differential scanning calorimetry (DSC) and viscosity measurements. Tests were performed using archived Batch 1 pellets and freshly reacted SPC/elemental mercury. The freshly reacted SPSS material was prepared in the same proportions as Batch 1. This powdered material is representative of the amalgamated but un-encapsulated waste prior to melting of the SPC matrix.

DSC Measurements

DSC is used to measure the heat input required to melt the reacted powder, from which the specific heat and phase transition enthalpy changes can be calculated. The temperature difference (ΔT) between the sample and an inert reference material is measured as a function of increasing temperature (T). In plots of ΔT vs. T, negative peaks reflect endothermic (energy consuming) reactions such as melting, whereas positive peaks indicate exothermic (energy producing) reactions. In ΔT vs. T plots, peak areas are proportional to the heat energy for a known volume of material.

DSC was performed using a Shimadzu DSC-50 and Thermal Analysis (TA50) software. Powder samples, between 0.004 and 0.007 gram, were weighed into 6 mm diameter aluminum sample crucibles with crimped aluminum covers. An identical crucible with no sample was used as a reference. Temperatures were controlled from ambient to 200 °C at a rate of 5 °C/min in a nitrogen atmosphere. Scans were run in triplicate for archived SPSS pellets (crushed to powder using a glass mortar and pestle), freshly reacted SPC/33 wt% elemental Hg (identical to the formulation given above), and pure SPC powder. Single samples of reagent grade sulfur powder and mercuric sulfide (HgS) powder were also run.

Figure 2 overlays DSC thermograms for each material type for the temperature range of 90 to 130 °C. Two endothermic peaks are evident for each material. The first corresponds to the solid phase transformation from orthorhombic to monoclinic forms for sulfur and the second representing the transformation from solid to liquid state (melting). Figure 2 also details the excellent reproducibility observed for the triplicate DSC runs. For pure sulfur (the heavy black line) the peaks are sharp and resolved to baseline whereas for SPC (the blue lines) the two peaks are shifted approximately 5 degrees lower with the peaks only half as high. The melting peaks for SPSS/Hg materials (green lines) are 3 to 4 degrees even lower in temperature than for pure SPC and are again reduced in intensity by approximately half. For samples of freshly reacted, unencapsulated powder (the red lines), the orthorhombic to monoclinic peak is not clearly discernable, indicating a relatively major conversion, or consumption of elemental sulfur in the matrix. This scan is similar to the single melting peak ideally observed for pure SPC. Analysis of the endotherms for the freshly reacted powder melting yielded mean normalized heat inputs of -32.45 ± 2.36 J/g (-7.75 ± 0.56 cal/g) and a center peak temperature of 111.8 °C

Not shown in Figure 2 is a third peak, which was clearly evident only for pure sulfur, and occurred at about 165 °C. This peak corresponds to breakdown of the sulfur S₈ ring structure usually present in the solid, and indicates formation of the polymeric state in sulfur liquid.

Viscosity Measurement

Viscosity, or the internal friction of a fluid, is a function of the torque required to rotate a spindle immersed in the liquid. Viscosity measurements are important for evaluating the mixability of the molten SPSS product and its ability to readily discharge from the mixer. Viscosity of the SPSS melt was quantified using a Brookfield DV-II+ calculating digital viscometer. Pyrex beakers with a flared top were fabricated so that a minimum amount of material could be tested, while still accommodating the viscometer spindle guard. Approximately 230-gram batches of SPSS product (33 wt% mercury) were preheated in a laboratory oven, then placed within a temperature-controlled oil bath, during the viscosity measurement. Once molten, the batches were thoroughly stirred to ensure thermal and physical homogenization.

Two runs were performed to attempt to melt reacted SPSS and maintain the mixture in molten form while testing viscosity.. It became obvious that temperature control of the melt was poor, due to the relative large mass-to-heat ratio and poor thermal conductivity of the melt. Thermal gradients from hotter to cooler zones formed from the heated wall to the center of the batch and from the center of the batch to the surface, resulting in parts of the mix freezing prematurely. A hot-air gun was used intermittently to keep the material at the surface molten. In spite of these problems, initial tests indicated viscosities of approximately 2700-3700 centipoise (cP) at a melt temperature of approximately 140 °C (LV4 spindle, 100 RPM).

With continued testing of the material, it became apparent that non-Newtonian behavior of the melt was influencing test measurement. While a Newtonian fluid produces a linear shear stress (F')-shear rate (S) behavior, for non-Newtonian fluids the relationship of F'/S is not constant. In terms of experimental measurement, a Newtonian fluid would measure the same viscosity regardless of spindle speed. For the SPSS melt, viscosity decreased significantly with increasing spindle speed (shear rate), indicative of pseudoplastic behavior. This type of flow behavior is also referred to as "shear-thinning". At a temperature of approximately 155 °C, viscosity measurements varied from 50,000 cP at 1RPM (using LV4 spindle) to 3400 cP at 100 RPM. Furthermore, for a given shear rate (spindle speed), viscosity measurement decreased slightly with time without disturbing the system; for example, viscosity decreases of 500 cP or more were noted over a period of five minutes. This decrease with time is called "thixotropy".

To characterize the SPSS product viscosity as a function of temperature while minimizing thermal gradient problems, three separate batches were prepared for three runs at 125 °C, 145 °C, and 165 °C. All measurements were made with the same LV4 spindle. The highest torque (most accurate reading) was generally taken at the highest RPM available (100 RPM). Thus, for each temperature, a baseline reading was taken at 100 RPM. Non-Newtonian behavior was characterized by measuring viscosity as spindle speed was ramped, first up then down, in the following sequence: 1, 5, 10, 50, 100, 50, 10, 5 and 1 RPM. Finally, measurements were taken at 100 RPM without disturbing the system to characterize time-dependency of the viscosity measurements. Figure 3 illustrates the time-dependent decrease in viscosity at 100 rpm.

All results are summarized in Table 2.

Table 2
Viscosity Results Summary
(Centipoise)

RPM	125 °C	145 °C	165 °C
100	1,550	2,800	Over-range
50	2,000	3,650	Over-range
10	4,830	9,200	26,000
5	7,400	15,500	35,000
1	21,300	42,000	101,000

DEPLOYMENT PLANS

Newmont is currently conducting engineering design activities for the installation of the SPSS process at the Yanacocha mine. A batch process will be designed with overall capacity to meet or exceed the current generation of mercury of approximately five metric tons of mercury per month. A production-scale double planetary cone mixer with a working capacity of 1 m³ (35 ft³) is planned. This system will have a design throughput of approximately 525 kg of mercury per shift, which can easily meet current demand and allows for additional treatment capacity if needed.

Newmont and its contractors are taking the lead on design, procurement and installation of the system. Scientific and engineering support is being provided by BNL on factors affecting process scale-up including bench-scale thermal analysis, viscosity, density determination, materials handling, metering of materials, etc. The current schedule calls for procurement of long lead-time equipment by the middle of 2003 for delivery and installation in early 2004. It is anticipated that the full-scale SPSS process for treatment of by-product mercury will be operational by the middle of 2004.

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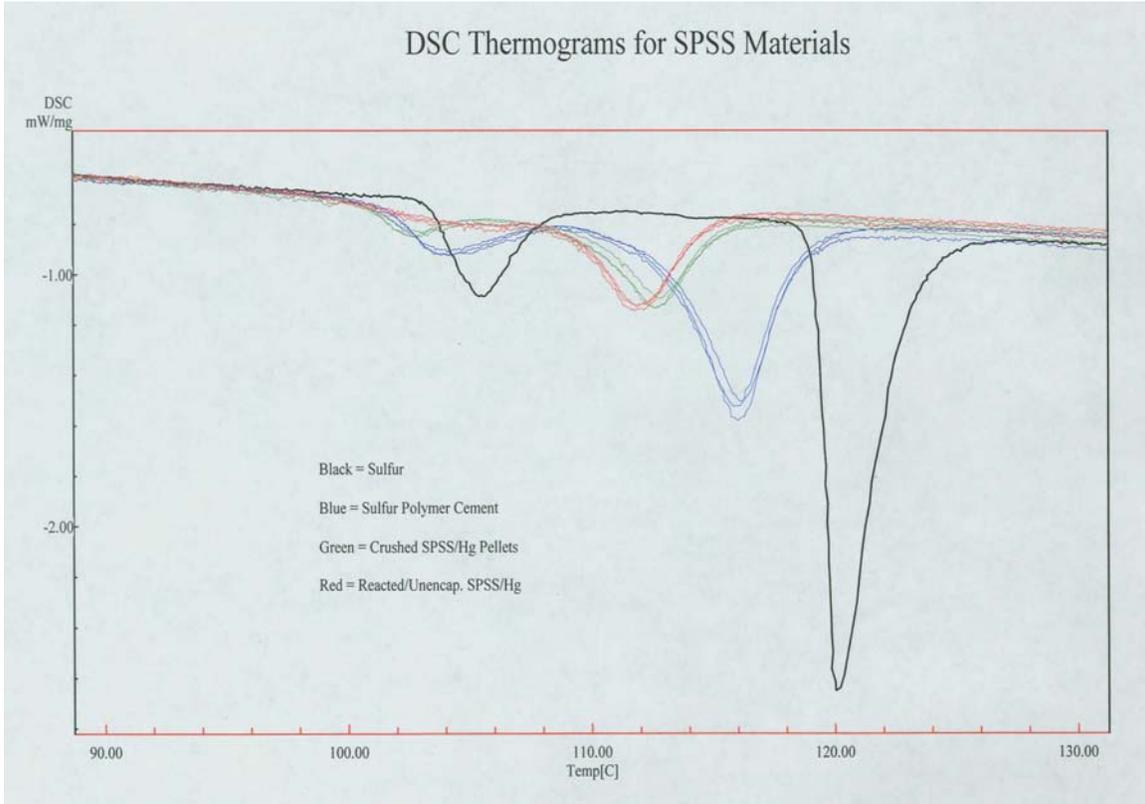


Figure 2. DSC Scans of SPSS Materials

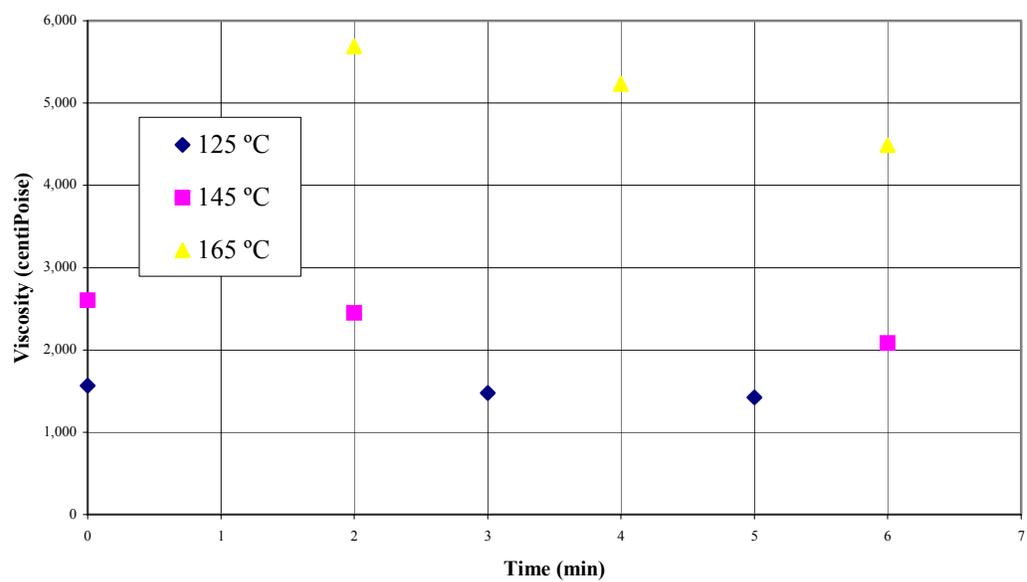


Figure 3. Viscosity of SPSS Materials