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MERCURY REMOVAL FROM DOE SOLID MIXED WASTE USING THE GEMEP TECHNOLOGY

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Under the sponsorship of the Federal Energy Technology Center (FETC), Metcalf & Eddy (M&E), in association with General Electric Corporate Research and Development Center (GE-CRD), Colorado Minerals Research Institute (CMRI), and Oak Ridge National Laboratory (ORNL), conducted laboratory-scale and bench-scale tests of the General Electric Mercury Extraction Process technology on two mercury-contaminated mixed solid wastes from U. S. Department of Energy sites: sediment from the East Fork of Poplar Creek, Oak Ridge (samples supplied by Oak Ridge National Laboratory), and drummed soils from Idaho National Environmental and Engineering Laboratory (INEEL). Fluorescent lamps provided by GE-CRD were also studied.

The GEMEP technology, invented by the General Electric Company, uses an extraction solution composed of aqueous potassium iodide plus iodine to remove mercury from soils and other wastes. The extraction solution is regenerated by chemical oxidation and reused, after the solubilized mercury is removed from solution by reducing it to the metallic state.

The bench-scale testing conducted for this project included: (1) GEMEP extraction tests to optimize extraction conditions and determine the extent of co-extraction of radionuclides; (2) pre-screening (pre-segregation) tests to determine if initial separation steps could be used effectively to reduce the volume of material needing GEMEP extraction; and (3) demonstration of the complete extraction, mercury recovery, and iodine recovery and regeneration process.

Initial characterization of the East Fork Poplar Creek sediments showed that the majority of the mercury and uranium in the sample was concentrated in the finer fractions. The average mercury concentration in the sediments before GEMEP extraction was 774 mg/kg. Depending on extraction conditions, concentrations in the sediments after GEMEP extraction ranged from 2.7 to 140 mg/kg. Nearly all the uranium remained with the sediments, with only 0.01 to 0.13% of the initial uranium solubilizing into the extraction solution.

For fluorescent lamps, pre-segregation to remove aluminum end caps and wire and to segregate the glass and phosphor by size proved to be very effective in reducing the volume of mercury-contaminated material that required mercury removal to pass the TCLP test. Only finer fractions need to be extracted in the GEMEP process. GEMEP extractions under various conditions

routinely removed >95% of the mercury from the lamp waste. Subsequent process steps to recover the mercury from the extraction solution were >99% efficient.

The drummed INEEL soil/sludge (after pre-screening to remove larger-size material consisting of rocks, asphalt and tar) contained on the order of 800 mg/kg mercury. The complete GEMEP cycle consisting of extraction, mercury recovery, and iodine regeneration steps was performed on the screened INEEL soils for a total of 12 cycles. As long as the iodine/iodide concentrations were kept sufficiently high (0.1 M iodine and 0.2 M iodide), greater than 95% of the mercury was extracted from the soils. Mercury recovery steps were also >99% efficient. Chemical usage costs for GEMEP extraction of INEEL soil/sludge were estimated to be $356 per treated ton, not considering costs for disposal of secondary wastes or treated solids as radioactive waste. The largest component of the cost is for iodine at $331 per treated ton. Measures for reducing iodine losses would need to be developed and employed to make the process economical for treating INEEL waste at full scale.

INTRODUCTION

The GEMEP technology was invented by the General Electric Company and is being commercialized by Metcalf & Eddy. It is a chemical extraction process that uses iodine (I_2) as an oxidant and iodide (I^-) as a solubilizing ion. General Electric Company holds a patent [1] on this process and has published a number of internal reports detailing the development of the process [2-5]. Optimization of the process involves the minimization of iodine use and loss as well as producing treated solids that are non-hazardous (i.e., materials that pass the EPA's Land Disposal Requirement (LDR) and eventually the Universal Treatment Standard (UTS) test for mercury) [6]. The technology is able to extract a variety of mercury-containing species from soils, sediments, glass wastes, and other materials, as demonstrated by numerous laboratory-scale tests conducted by General Electric.

The process is a closed-loop process that contains and recycles the extraction components. Mercury-contaminated media are subjected to an aqueous extraction with potassium iodide and iodine (KI/I_2). The pH and the temperature may be controlled to improve extraction efficiency. Mercury in its various forms is oxidized by the iodine to the 2^+ oxidation state, which is then believed to form soluble complexes of the form HgI_4^{2-} by complexation with the iodide present in the extraction medium. After sufficient reaction time to solubilize the mercury, treated media are dewatered, rinsed to remove residual extraction reagent and dissolved mercury, and backfilled or disposed. The extracted mercury remains in the aqueous phase and serves as the feed stream for the mercury precipitation and removal step, along with the water generated from the rinsing of the treated media.

The aqueous stream from the extraction step is reacted with finely divided elemental iron to reduce the mercury to its elemental form. The iron also reduces iodine to iodide:

$$Fe^\circ + HgI_4^{2-} \rightarrow Fe^{2+} + 4I^- + Hg^\circ \qquad \text{(Eq. 1)}$$

$Fe^\circ + I_2 \rightarrow FeI_2$ (Eq. 2)

The metallic mercury produced in this step is recovered and isolated for off-site recycle. The remaining aqueous phase, containing dissolved ferrous iron and iodide, is treated by pH adjustment to precipitate the iron as ferric hydroxide:

$4FeI_2 + 4Ca(OH)_2 + 2H_2O + O_2 \rightarrow 4Fe(OH)_3 + 4CaI_2$ (Eq. 3)

After dewatering, the precipitate can be combined with the treated solids from the extraction step for disposal, or it can be managed separately. A portion of the aqueous phase remaining after precipitation and dewatering becomes the feed stream for the iodine regeneration and recycle step. Iodine is regenerated through a combination of pH adjustment and chemical oxidation using hydrogen peroxide to oxidize iodide to iodine:

$CaI_2 + H_2SO_4 + H_2O_2 \rightarrow I_2 + CaSO_4 \cdot 2H_2O$ (Eq. 4)

Objectives

The primary objective of this work was to develop treatment conditions that would produce treated solids for which the mercury concentration in a TCLP extract would be less than the toxicity characteristic (TC) limit of 0.2 mg/L (200 ppb). This objective was established before EPA promulgated new Land Disposal Restriction (LDR) treatment standards for TC metal wastes. The new LDR universal treatment standard (UTS) for mercury in TC metal wastes is 0.025 mg/L (25 ppb) mercury in the TCLP extract [6]. The UTS must be attained before TC metal wastes can be land disposed. The UTS will go into effect for mixed TC metal/radioactive wastes on May 26, 2000. If the treatability tests described herein were repeated today, a test objective of 0.025 mg/L would most likely be established instead of 0.2 mg/L. However, for several wastes and test conditions it was found that the UTS was indeed attained by GEMEP treatment.

EPA's new rule also established separate LDR treatment standards for contaminated soils which are less stringent than the UTS values for hazardous constituents in TC metal wastes. The soil LDR treatment standards are 90% reduction of each hazardous constituent, or ten times the UTS if 90% reduction would be less than ten times the UTS. Ten times the UTS for mercury is equivalent to 0.25 mg/L TCLP. For DOE wastes that could be classified as soils, such as the East Fork Poplar Creek sediment tested for this project, a treatment objective based on EPA's new rule (0.25 mg/L TCLP) is not substantially different from the objective that was used (0.2 mg/L TCLP).

MATERIALS AND METHODS

The wastes tested included two wastes from DOE sites (East Fork Poplar Creek sediments and INEEL soil/sludge), and fluorescent lamps provided by GE-CRD. Bench-scale tests were conducted on the DOE wastes. Both laboratory- and bench-scale tests were conducted on the fluorescent lamps.

East Fork Poplar Creek Sediment

One sediment sample from the East Fork of Poplar Creek was collected by ORNL and shipped to CMRI in September 1997. Upon receipt at CMRI, a visual inspection was performed which showed that the sample contained high moisture, a high percentage of fine particles, and a small amount of humus such as wood chips and grass. Physical characterization of the as-received sample was performed. The moisture content was 33% and the bulk density was 0.82 (51 lb/ft^3). The specific gravity of the dry sediment was 2.58. The average mercury concencentration was 774 mg/kg and the average uranium concentration was 27 mg/kg.

Fluorescent Lamps

The lamps used for this study were used (end-of-life) 4 foot Model F40T12 CW and CW/MW lamps. These lamps were used at GE-CRD and removed from service when no longer functioning. The mercury content was found to vary dramatically (2 mg - 80 mg per lamp). The glass represents approximately 90% of the total typical lamp weight of 286 grams, and phosphor comprises approximately 6% of the weight. The remaining 4% of the weight is composed of pins, aluminum endcaps, endmounts, and basing cement.

INEEL Soil/Sludge

Three, 35-gallon drums containing waste soil/sludge from INEEL were received at CMRI on April 15, 1998. These drums were opened and a grab sample was taken from the surface of the soil in each drum. Observation of the surface indicated that the contents of the three drums were similar. Mercury analyses of the grab samples were as follows: Drum 558, 34 mg/kg; Drum 708,735 mg/kg; and Drum 710, 645 mg/kg. Drum 708 was selected for further testing. The plus 4-mesh fraction consisted of three distinctly different materials: rock, asphalt, and a light-colored tar/polymer. The balance of the sample was silty soil.

Laboratory-Scale Test Methods

Laboratory-scale tests on fluorescent lamps were conducted in GE-CRD’s laboratories in Niskayuna, New York. The lamps were prepared for extraction by removing the external pins and aluminum endcaps. The vacuum was relieved by using tweezers to break the thin wall of glass inside the exhaust tube. Needle nose pliers were then used to push in the wire mount on one end. This serves to reduce the integrity of the glass wall which was then tapped on the inside of a 1 gallon glass jar. The glass was broken until the whole lamp fit inside the jar. The jar was capped and shaken for 2 minutes. The resulting debris was passed through a ¼ inch diameter funnel (except the end caps) into a 2 L Erlenmeyer flask. The extraction solution (of appropriate concentration and solid/liquid ratio) was then added. The flask was capped with parafilm with a small hole stuck in the parafilm for venting. The flask was shaken in a Orbit Environ-Shaker by Lab Line at 160 rpm and at the prescribed temperature. Once the desired reaction time was obtained the slurry was filtered through a Büchner filter using #1 Whatman filter paper. The solids were washed twice with the same volume of water as was used for the extracting solution. In general the used extraction solution and washes were kept separate and analyzed for I_2, I^- and

Hg (depending on the experiment). The glass pieces, along with the filter paper, were extracted either with CaO (1 g in 250 mL) for I^- determination or conc. HNO_3 (200 mL)/conc. HF (100 mL) for Hg determination [7]. Iodine and iodide were determined by a method described in a separate publication [8]. Mercury was determined by cold vapor atomic absorption (low detection limit) or flame (or ICP) atomic absorption (1 ppm detection limit).

To determine whether treated solids pass TCLP, a TCLP test can be run on each batch of treated solids and the results evaluated. However, based on historical data of how fluorescent lamps behave in the TCLP test, it is known that 4 foot long, F40T12 model lamps will pass the test if the total mercury content is below 3 mg [9]. To allow for a margin of safety, a clean-up goal of 2 mg (or 7.4 ppm for a 270 g lamp) was established for the laboratory-scale tests. Treated solids with less than 2 mg total mercury were considered to have "passed" TCLP. Lamps with less than 1 mg total mercury were judged unable to fail the TCLP test as there is not enough mercury to fail even if all the mercury dissolves (270g lamp, 5.4 kg extracting solution, 1 mg mercury/5.4 kg = 185 ppb) [10].

Bench-Scale Test Methods

Bench-scale tests were conducted on all three wastes at CMRI's facility in Golden, Colorado. Bench-scale testing included four components: initial waste characterization, pre-segregation tests, bench-scale extraction tests, and locked cycle tests.

Initial Waste Characterization. The three wastes selected for testing were characterized for both physical and chemical properties prior to conducting tests. This information was used to determine whether mercury contamination resided primarily in certain fractions of the waste, in order to determine the need for pre-segregation and to effectively develop the pre-segregation and extraction tests.

A de-agglomeration test was conducted on a 5-kg aliquot of sample. Samples were tumbled for 30 minutes in a 10-gallon carboy or small cement mixer at <30% solids with small addition of surfactant (±1 gm/ton Triton X-100). The discharge from the carboy was passed through screens at sieve sizes ranging from 4 mesh to 200 mesh. Contaminant distribution was determined in the fractions and the recovered water from de-agglomeration and screening.

Pre-Segregation Tests. The potential for separation of mercury-free material and metallic mercury from the balance of the sample was determined based on observations made and analytical results from the initial waste characterization. If the mercury was found to be concentrated in 50% or less of the total weight of the sample, pre-segregation testing was conducted on the waste.

Additional 5- to 10-kg aliquots of each sample were de-agglomerated using the 10-gallon carboy or small cement mixer. Non-mercury bearing fractions (determined by initial waste characterization) were separated by size. Gravity and magnetic separation were evaluated to separate non-mercury metallics, e.g., lamp ends from the glass. The method of gravity separation was selected based on the fraction size being evaluated. Coarse materials, coarser than 16-mesh, were separated by a mineral jig, whereas finer fractions were separated using a shaking table.

To maximize dewatering of the solids prior to the chemical extraction of mercury, a large aliquot of sample, up to 40-kg, was processed using a drum de-agglomerator or cement mixer, vibrating screens, and gravity or other separators to produce the feed for the chemical extraction. Quantitative settling tests were performed to determine field dewatering requirements.

Basic data to be used for scale-up to a pilot treatment system were also collected. These data included bulk densities of the feed material and various fractions, the specific gravity of different fractions, the settling and filtration characteristics of the fine fractions, viscosity of slurries at various solids densities (10 to 50%) and top particle sizes (16- to 200-mesh).

Bench-Scale Extraction Tests. Extraction testing was conducted on each of the selected wastes to determine optimum conditions for mercury extraction. The number of tests conducted on each waste type varied, depending on the characteristics of the waste. The procedure was to prepare the extraction solution containing the appropriate amounts of potassium iodide and iodine, add the waste material, and heat to 50°C for four hours with additional acidulation of the waste as necessary to maintain the target pH.

If uranium were found to co-extract, the original test plan included tests to evaluate methods for suppressing co-extraction, as well as other process modifications to possibly segregate any co-extracted uranium. Uranium was found to co-extract only for the East Fork Poplar Creek sediments. Testing of this waste was discontinued after discussion with DOE, because all of this waste has been subsequently disposed of, and therefore no longer poses a concern for DOE. Since the testing program for this waste was not pursued to its conclusion, the issue of solubilized uranium was not addressed.

Locked Cycle Tests. Locked cycle tests were conducted to demonstrate the complete extraction process, including extraction, residue rinsing, mercury recovery, and iodine regeneration. Locked cycle tests were conducted on crushed lamp glass and on the INEEL waste. Locked cycle tests were not conducted on the East Fork Poplar Creek sediment since testing was discontinued at the direction of DOE.

The locked cycle tests were conducted on a 1-kg scale for a minimum of 6 cycles. Conditions for the locked cycle tests were selected based on the optimum conditions determined in the bench-scale extraction tests. A flowsheet for locked cycle tests as applied to crushed lamp glass is presented in Figure 1.

RESULTS

East Fork Poplar Creek Sediment

Initial characterization tests showed that over 99% of the weight and mercury and 97% of the uranium were distributed in the minus 30-mesh fraction, while 63% to 80% of the weight, uranium and mercury are distributed in the minus 200-mesh fraction. Gravity or other separation steps will not allow an economic separation of this material. Therefore, the entire sediment sample was advanced for extraction tests. No pre-segregation or settling tests were performed.

Eight extraction tests were performed on the sediment. The tests evaluated the effect of the potassium iodide and iodine molarities on the solubilization of mercury and uranium from the sediment at varying pH values. The range of conditions tested was: 0.025 to 0.4M KI, 0.0125 to 0.2 M I_2, and pH values of 4, 5 and 7. Table I summarizes the results.

TABLE I. BENCH-SCALE EXTRACTION RESULTS OF EAST FORK POPLAR CREEK SEDIMENT

Test No.	KI, M	I_2, M	pH	U Soluble, %	Residual Hg, mg/kg
A-1	0.10	0.05	4	0.13	2.7
A-2	0.20	0.10	4	0.13	6.6
A-3	0.40	0.20	5	0.06	3.1
A-4	0.40	0.20	7	0.06	2.8
A-5	0.025	0.0125	4	0.01	140
A-6	0.05	0.025	4	0.01	73
A-7	0.10	0.05	5	0.09	39
A-8	0.10	0.05	7	0.97	42

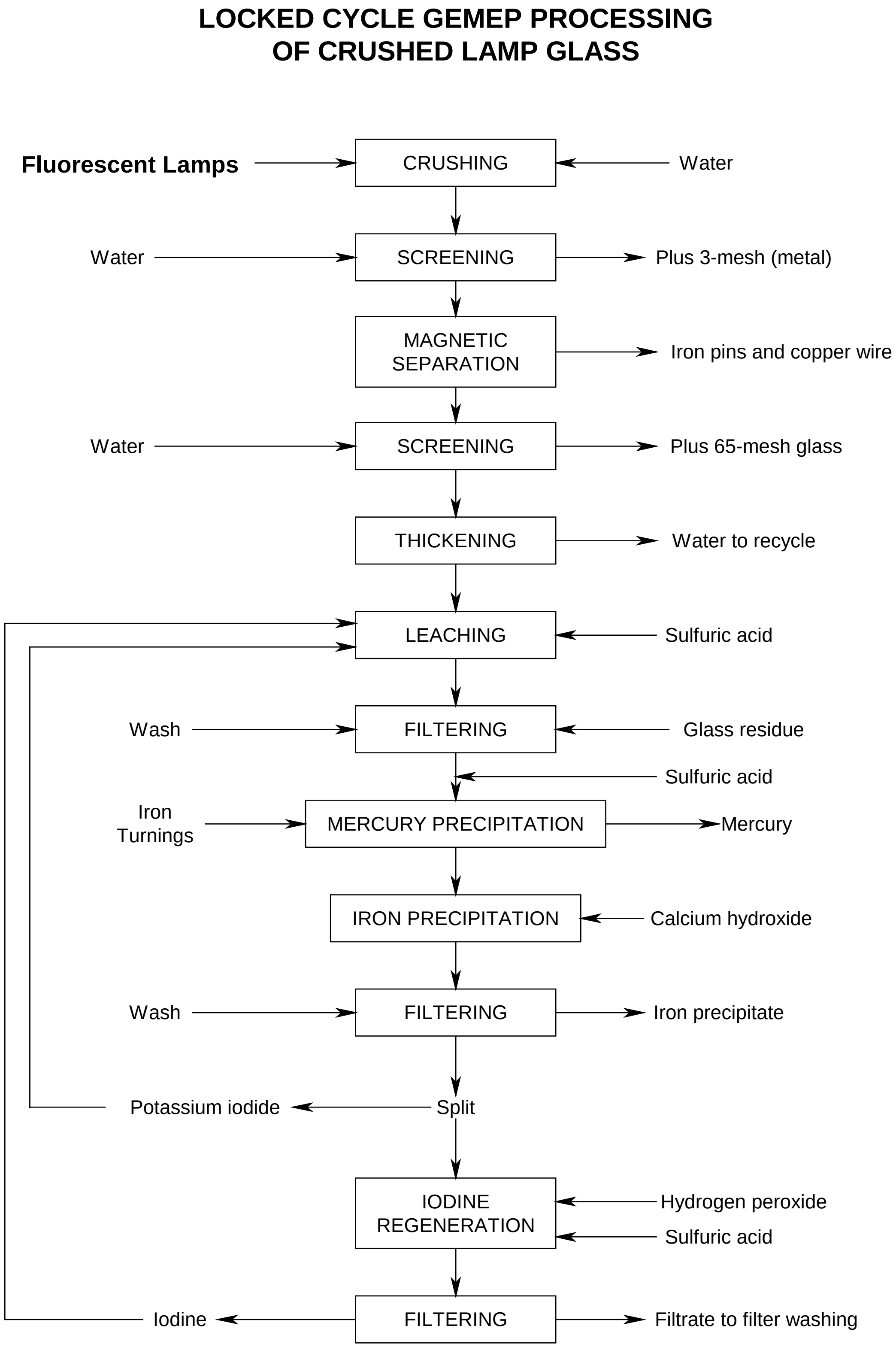

FIGURE 1. LOCKED CYCLE TEST FLOWSHEET

The solubilization of uranium was very low in seven of the tests. Only 0.01 to 0.13% of the initial uranium solubilized. The eighth test was a 7 pH leach at 0.1 M KI and 0.05M I_2. Almost one percent of the contained uranium solubilized during this test. This level of uranium solubilization appears to be anomalous since another 7 pH leach solubilized only 0.06% of the uranium and other leaches at the same iodide - iodine molarities solubilized 0.09 to 0.13% of the uranium. In any case, the bulk of the uranium (99 to 99.99%) remained with the sediment.

The extraction of mercury from the sediment into the extraction solution was very dependent on the iodine - iodide molarities. At 0.2 M KI and 0.1 M I_2 and above the treated sediment contained 2.8 to 6.6 mg Hg/kg, while the average mercury concentration before treatment was 774 mg/kg. The residual values indicate an extraction efficiency for mercury of greater than 99%.

Fluorescent Lamps

Laboratory-Scale Tests. A series of laboratory-scale tests was designed, carried out and analyzed using an analysis of variance approach to determine optimum conditions for extraction of fluorescent lamp waste that would result in residuals that pass the TCLP test while also minimizing consumption of iodine. The factors affecting residual mercury concentration that were examined were: concentration of iodine, liquid-solid ratio, time, and temperature. Initial experiments showed that the more important factors were concentration of iodine and liquid-solid ratio. Additional experiments and statistical analysis determined that conditions of 0.02 M I_2 / 0.04 M KI at a 3/1 liquid-solid ratio would produce treated solids that would fail TCLP in less than 4 per million batches.

Factors that affect iodine loss that were examined included time and temperature. Iodine loss was defined as the residual iodine found on the solids. (Although there are other sources of iodine loss, residual iodine on the treated solids is the most readily controlled source of loss). The optimum conditions for minimizing residual mercury on the treated solids and also minimizing iodine loss were determined to be: 0.02 M I_2/ 0.04 M KI, 1 hour extraction time, 3/1 liquid-solid ratio, and 45°C extraction temperature.

By dry screening the 1/4" lamp fragments through a 30 mesh sieve, it was possible to separate the phosphor (and small glass pieces) from the bulk of the glass and metal pieces. Laboratory- scale extractions were run on the minus 30-mesh fraction. Optimal conditions for the minus 30-mesh fraction were different than those for 1/4" lamp fragments, and were determined to be 0.1 M I_2/0.2 M KI, 45°C, 4/1 liquid-solid ratio, and 1 hour. After treatment at these conditions, statistical analysis predicts that the residual solids will contain, on average, 1 mg of mercury and 1.3 mg of iodine. The residual solids need to be tested to determine if the material passes TCLP since the concentration of mercury is high (~ 70 ppm). The laboratory-scale results indicated that the material will pass the TCLP test.

Confirmation of these results at larger test scales (bench and pilot) is needed because larger-scale equipment may not achieve the same efficiencies attainable at the laboratory scale. In addition, further segregation of the crushed lamp fractions would most likely be beneficial, by reducing even further the mass of material that would fail TCLP without GEMEP extraction. Practical procedures for crushing and pre-segregating lamp wastes at a larger scale were examined as described below.

Crushing and Pre-Segregation Tests. The initial evaluation of methods for crushing the fluorescent lamps included tests of both a rolls crusher and an impact mill. These tests demonstrated that dry-crushing created too much hazardous dust from the phosphor. Wet-crushing using an impact mill was therefore selected.

The product from the crushing was wet-screened at 3 mesh to first separate the large aluminum end caps. It then was passed over a magnetic separator to remove the pins and most of the wire (still attached to the pins). Finally the material was again wet-screened to separate it into size fractions. The aluminum ends were 2.5% of the weight, the magnetics were 0.2% of the weight, and the glass was 97.3% of the weight.

The combination of wet-milling and screening recovered 80% of the glass in fractions coarser than 48 mesh that contained less than 1 mg/kg Hg. The 48- x 65-mesh fraction was less than 5% of the total glass and contained 4.3 mg/kg Hg. The minus 65-mesh fraction represented 15% of the glass weight and contained 425 mg/kg Hg, which represents 99.1% of the initial mercury mass present. Since the combined glass fractions coarser than 65 mesh mathematically will pass the TC limit of 200 ppb Hg (4 mg/kg in the solids if all the mercury is soluble), subsequent tests were restricted to the minus 65-mesh fraction.

Extraction and Locked-Cycle Tests. Seventeen bench-scale extractions were performed on the minus 65-mesh portion of the crushed fluorescent lamp glass to select conditions for bench-scale locked-cycle testing. The conditions selected were: 0.04 M I_2, 0.08 M KI, 25% solids (3/1 liquid-solid ratio), recycle solutions adjusted to 6.5-7.5 pH with sulfuric acid, ±20°C, and 4 hours.

Residual mercury concentrations in the treated lamp waste for the 10 cycles ranged from 7.8 to 15.8 mg/kg, yielding mercury extraction efficiencies ranging from 96.4 to 98.3%. Five of the residues were evaluated by the TCLP. All TCLP mercury results were below the TC limit of 0.2 mg/L (200 ppb). All results but one were below the LDR Universal Treatment Standard of 0.025 mg/L (25 ppb).

The mercury-containing extraction solution was adjusted to 4.0 ± 0.5 pH using dilute sulfuric acid prior to passing the solution through two columns of iron turnings. The adjustment required an average of 0.5 grams 100% sulfuric acid/batch (0.25 lb H_2SO_4/ton whole lamps). The discharge from the iron columns was adjusted to between 10 and 11 pH by the addition of calcium hydroxide. The hydrated lime addition averaged 2.7 grams per batch (1.33 lb/ton whole lamps). This adjustment precipitated the soluble iron and any residual mercury. The efficiency of mercury removal from the combined mercury precipitation and iron precipitation steps exceeded 99.9% in six of the ten cycles.

The potassium iodide content of the iron precipitation filtrate was determined and a portion of the filtrate that contained either sufficient potassium iodide or liquid volume for the next leach cycle was set aside. The balance of the solution, if any, was advanced to iodine regeneration. A total of eight iodine regenerations were performed. After the second cycle of leaching the average make-up iodine requirement was 5.6 grams per leach (2.8 lb I_2/ton whole lamps).

Mass balance calculations were carried out using average values from the locked cycle test results and are summarized in Table II using a basis of one ton of whole fluorescent lamps. The process flow diagram is presented in Figure 2. Stream numbers on the diagram correspond to those in Table II.

TABLE II. MASS BALANCE FOR CRUSHING AND GEMEP EXTRACTION OF SPENT FLUORESCENT LAMPS: BASIS = ONE TON WHOLE LAMPS

Stream Number	Description	Solids (lb)	Liquid (lb)	Mercury (lb)
1	Whole fluorescent lamps	2,000	Zero	0.126
2	Aluminum end caps	50	Zero	Zero
3	Crushed lamp glass, pins and wire	1,950	Zero	0.126
4	Magnetic pins and wire	4	Zero	Zero
5	Crushed glass and phosphor	1,946	Zero	0.126
6	Glass, plus 65 mesh	1,650	Zero	0.0012
7	Glass and phosphor, minus 65 mesh	296	Zero	0.126
8	Screening water for reuse	Zero	Variable	< 0.001
9	Iodine make up to GEMEP process	2.8	Zero	Zero
10	Slurry from GEMEP extraction	296	888	0.126
11	Treated solids	296	Negligible	0.0036
12	93% sulfuric acid to reduce pH to 4	Zero	0.018 gallons	Zero
13	Hg-containing filtrate: feed to iron columns	Negligible	Variable	0.122
14	Discharge from iron columns	Negligible	Variable	< 0.002
15	Lime to raise pH to 10	1.33	Zero	Zero
16	Hydroxide sludge	30	Variable	0.0018
17	Supernatant from precipitation: feed to iodine recovery	Negligible	Variable	< 0.0002
18	93% sulfuric acid for iodine recovery reaction	Zero	0.53 gallons	Zero
19	50% hydrogen peroxide for iodine recovery reaction	Zero	0.41 gallons	Zero

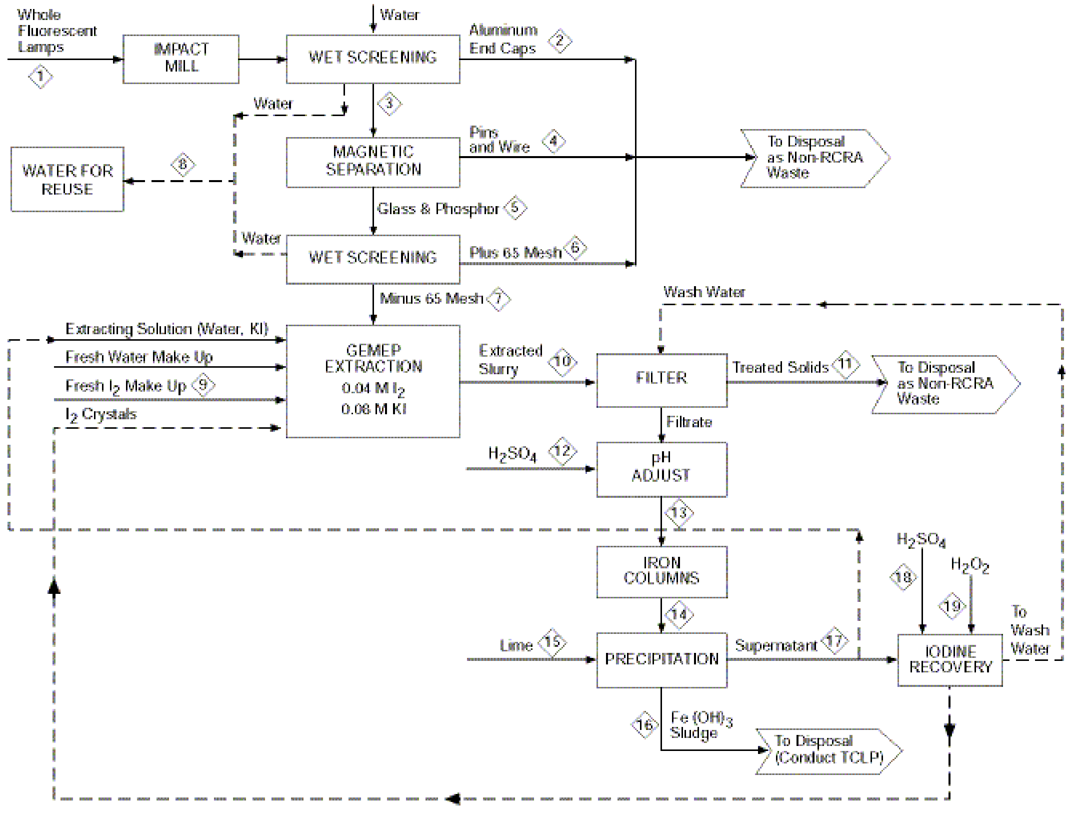

FIGURE 2. PROCESS FLOW DIAGRAM FOR FLUORESCENT LAMP TREATMENT

INEEL Soil/Sludge

Bench-scale studies were conducted on material from Drum 708, with an average mercury concentration of 700-800 mg/kg. A sub-sample was pulped with water in a cement mixer for 30 minutes and wet screened on sieves from 4- to 100-mesh. The plus 4-mesh consisted of three distinctly different materials: rock, asphalt, and a light colored tar/polymer. These three materials were separated by hand sorting and analyzed separately. Table III presents the mercury distribution. The three plus 4-mesh materials all passed the TC limit for mercury of 0.2 mg/L (200 ppb), with values ranging from 0.06 mg/L (for tar and rock) to 0.08 mg/L (for asphalt). Note that these TCLP extract values exceed the UTS for mercury of 0.025 mg/L TCLP that goes into effect for mixed wastes on May 26, 2000. Under the new rule [6] it is possible that these three fractions might require treatment to the UTS.

Pre-Segregation Tests

Feed for subsequent bench-scale and locked cycle extraction studies was prepared by first screening dry on 4 mesh. The plus 4-mesh then was de-agglomerated in a cement mixer and screened on 4 mesh. The oversize, rocks-asphalt-tar, was washed and set aside.

A settling test was performed on the minus 4-mesh material from the de-agglomeration and screening. Beaker tests were used to determine that a slightly anionic polymer showed the best flocculation; however the dosage was large. A one-liter scale test then was performed. The initial slurry was 14% solids and a dose of 0.57 lb Percol 351 was added per ton of dry solids. Percol 351 is a very high molecular weight very slightly anionic polymer. The terminal slurry density was 44.5% solids. The initial free settling rate of the slurry was six feet per hour. The calculated unit area to achieve 44.5% solids was 2.7 square feet per ton per day.

TABLE III. MERCURY DISTRIBUTION IN INEEL SOIL/SLUDGE

Size Mesh	Fraction Weight %	Weight Percent Retained	Weight Percent Passing	Mercury Analysis mg/kg	Distribution in Fraction	Percent Retained	Percent Passing
Tar	1.3%	1.3%	98.7%	19.2	0.05%	0.1%	99.9%
Asphalt	0.9%	2.2%	97.8%	18.0	0.03%	0.1%	99.9%
Rock	7.2%	9.3%	90.7%	59.4	0.9%	1.0%	99.0%
8	2.9%	12.2%	87.8%	170	1.1%	2.1%	97.9%
14	1.8%	14.0%	86.0%	275	1.1%	3.1%	96.9%
28	1.4%	15.5%	84.5%	490	1.5%	4.6%	95.4%
48	1.8%	17.2%	82.8%	895	3.5%	8.1%	91.9%
100	4.4%	21.6%	78.4%	870	8.2%	16.3%	83.7%
<100	78.4%	100.0%	0.0%	495	83.7%	100.0%	0.0%

Bench-Scale Extraction Tests

A total of seventeen batch extraction tests were performed. The first thirteen evaluated the effect of iodine concentration, temperature, and acidulation on the dissolution of the mercury. Because of the potential for some soluble mercury to be retained in the solids, four two-stage tests were performed. In the two-stage tests, the residual is repulped in iodine solution and re-filtered and washed. This allows for more efficient removal of the soluble mercury. Residual mercury concentrations in the treated solids ranged from 17 mg/kg to 64 mg/kg (92 to 98% extraction efficiency). Treated solids from nine of the seventeen tests were tested by TCLP; the extracts contained mercury concentrations of 0.01 to 0.08 mg/L, all below the TC limit of 0.2 mg/L. For four of the nine samples, the extract concentration was less than the UTS of 0.025 mg/L TCLP.

The INEEL waste is quite alkaline; any adjustment of the natural pH requires a large addition of acid. The three tests with pH adjustment required sulfuric acid additions of 400-500 lb per ton of waste just to reduce the pH about one unit. For this material, pH adjustment would not be practical at full scale. Also, the adjustment of pH provided relatively little benefit with respect to mercury concentrations in the residual, so pH adjustment would not be recommended for this waste even if acid consumption were not excessive.

Locked Cycle Tests

Locked cycle leaching studies on the de-agglomerated minus 4-mesh INEEL material were conducted at the following conditions: 0.10 M I_2, 0.20 M KI, 30% solids (2.3/1 liquid-solid ratio), natural pH, recycle solutions adjusted to 6.5-7.5 pH with sulfuric acid, ±60°C, and 2 hours in each stage. Extraction results for the locked cycle tests are summarized in Table IV.

The higher residual mercury values in the first six cycles were due to inadequate iodine concentrations during extraction. This was caused by inadequate communication to new technicians. All the TCLP mercury results were below the TC limit of 0.2 mg/L (200 ppb). However, the results exceeded the UTS of 0.025 mg/L (25 ppb). Because attaining the UTS was not an objective of this test program (since testing preceded its promulgation), no tests were performed to see if the UTS could be attained by adjustments in test conditions.

TABLE IV. LOCKED CYCLE EXTRACTION OF INEEL SOIL/SLUDGE

Cycle	Residual Mercury, mg/kg	% Extracted	TCLP Mercury, mg/L
1	250	73	0.04
2	115	87	0.04
3	155	81	0.04
4	295	62	0.04
5	210	75	0.06
6	105	89	0.06
7	28	97	0.04
8	47	95	0.04
9	50	94	0.06
10	69	93	0.18
11	28	97	Not analyzed
12	45	94	Not analyzed

The mercury-containing extraction solution was adjusted to 4.0 ± 0.5 pH using dilute sulfuric acid prior to passing the solution through the columns of iron turnings. The adjustment required an average of 6 grams 100% sulfuric acid/batch (12 lb H_2SO_4/ton material). Mercury concentrations in the influent to the iron columns ranged from 375 to 430 mg/L and concentrations in the discharge ranged from 5 to 64 mg/L (removal efficiencies of 88 to 99%).

Decreasing efficiency was observed through cycle 6 due to deposition of residue solids in the columns. The columns were cleaned during the seventh cycle, but the efficiency still was not as good as the tests with the lamp glass.

The discharge from the iron columns was adjusted to between 10 and 11 pH by the addition of calcium hydroxide. The hydrated lime addition averaged 12 grams per batch (24 lb/ton material). This adjustment precipitated the soluble iron and any residual mercury. The efficiency of mercury removal from the combined mercury precipitation and iron precipitation steps was 99.8% or greater in six of the ten cycles.

The potassium iodide content of the iron precipitation filtrate was determined and a portion of the filtrate that contained either sufficient potassium iodide or liquid volume for the next leach cycle was set aside. The balance of the solution, if any, was advanced to iodine regeneration. A total of nine iodine regenerations were performed. The efficiency of the regeneration tended to be proportional to the quantity of iodine. The range of conversion efficiency was 60 to 100% and averaged 93%.

Using the addition data subsequent to Cycle 3, the indicated iodine make-up requirement was 40 grams per leach (80 lb I_2/ton dry basis material). This requirement was larger than expected. It probably was due to leaching at 60°C. Reducing the temperature to 45 or 50°C would significantly reduce the amount of iodine volatilized during leaching. On a commercial scale, it may be practical to collect most of the volatilized iodine in a scrubber and recycle it to the process.

Mass balance calculations were carried out using average values from the locked cycle test results and are summarized in Table V. The process flow diagram is presented in Figure 3. Stream numbers on the diagram correspond to those in Table V.

TABLE V. MASS BALANCE FOR PRE-SEGREGATION AND GEMEP EXTRACTION OF INEEL SOIL/SLUDGE: BASIS = ONE TON WASTE WITH Hg = 800 mg/kg

Stream Number	**Description**	**Solids (lb)**	**Liquid (lb)**	**Mercury (lb)**
1	INEEL waste feed, Hg = 800 mg/kg	2,000	Variable	1.6
2	Oversize from pre-segregation steps	180	Variable	0.009
3	Polymer to aid settling of minus 4-mesh material	0.5 (polymer)	Polymer-specific	Zero
4	Minus 4-mesh slurry for GEMEP extraction	1,820	2,254	1.46
5	Iodine make up to GEMEP process	72	Zero	Zero
6	Slurry from GEMEP extraction	1,820	7,760	1.46
7	Treated solids	1,820	2,254	0.12
8	93% sulfuric acid to reduce pH to 4	Zero	0.8 gallons	Zero
9	Hg-containing filtrate: feed to iron columns	Negligible	Variable	1.34
10	Discharge from iron columns	Negligible	Variable	0.05
11	Lime to raise pH to 10	22	Zero	Zero
12	Hydroxide sludge	300	Variable	0.05
13	Supernatant from precipitation: feed to iodine recovery	Negligible	Variable	< 0.001
14	93% sulfuric acid for iodine recovery reaction	Zero	9.4 gallons	Zero
15	50% hydrogen peroxide for iodine recovery reaction	Zero	7.5 gallons	Zero

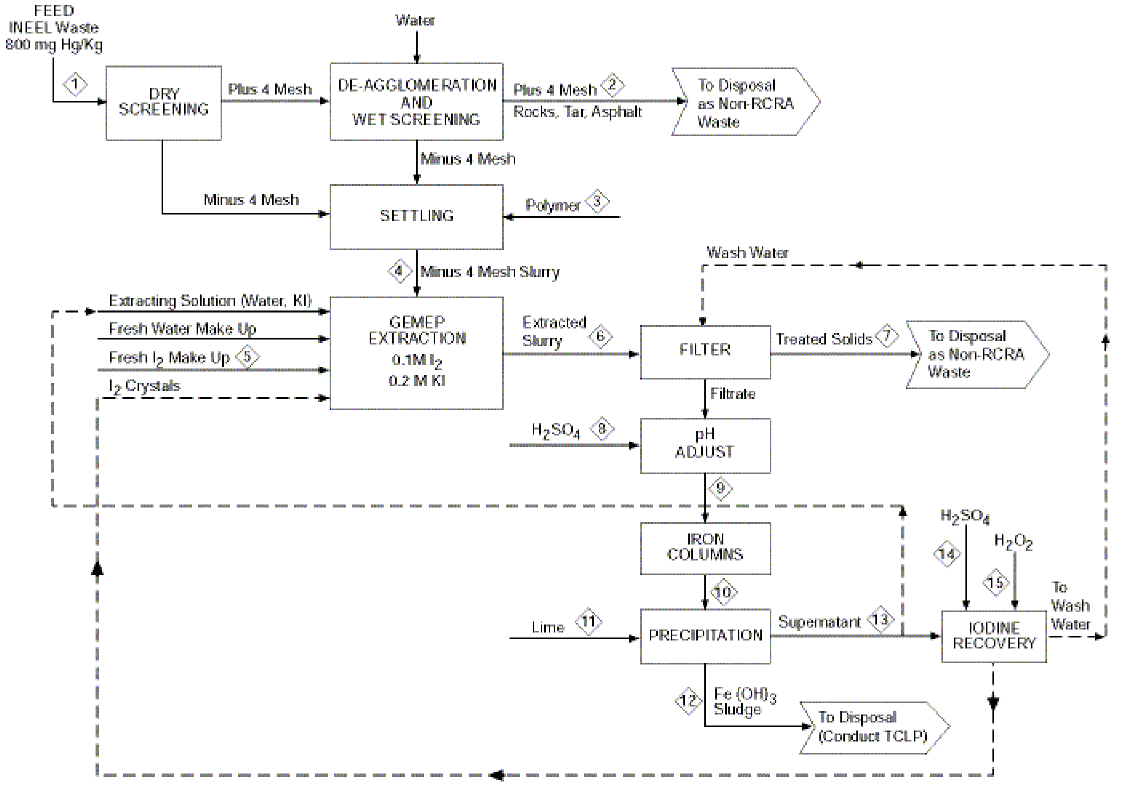

FIGURE 3. PROCESS FLOW DIAGRAM FOR INEEL WASTE TREATMENT

CHEMICAL USAGE COSTS

The mass balance data presented in Tables II and V for fluorescent lamp glass treatment and INEEL waste treatment were used to estimate operation and maintenance (O&M) costs related to chemical usage for treatment of these wastes by the GEMEP process. The costs are summarized in Table VI.

TABLE VI. CHEMICAL USAGE COSTS FOR TREATING INEEL WASTE AND FLUORESCENT LAMP WASTE

		INEEL Waste		**Fluorescent Lamp Waste**	
Chemical	**Unit Cost**	**Quantity per ton waste**	**Cost per ton waste**	**Quantity per ton whole lamps**	**Cost per ton whole lamps**
Iodine	$4.60/lb	72 lb	$331.20	2.8 lb	$12.88
93% sulfuric acid	$0.725/gal	10.2 gal	$7.40	0.548 gal	$0.40
50% hydrogen peroxide	$2.16/gal	7.5 gal	$16.20	0.41 gal	$0.89
Hydrated lime	$0.06/lb	22 lb	$1.32	1.33 lb	$0.08
		TOTALS:	$356.12		$14.25

Note that the costs in Table VI do not include all O&M costs. Costs for labor and utilities have not been estimated because they are sensitive to the scale of the treatment facility, which in turn depends on the quantity of waste requiring treatment and the time available to treat it. Costs for disposal of secondary wastes and treated solids also have not been estimated.

The chemical usage costs for treating INEEL waste are driven by the iodine make up cost of approximately $330 per ton. This cost is sensitive to the unit cost of iodine (which varies according to market conditions and cannot be controlled), and to the quantity of make-up iodine needed. To make the GEMEP process economical for treating INEEL waste, it will be necessary to reduce the iodine make up requirement. The locked cycle tests on INEEL waste were done at 60°C, and it is suspected that there were substantial iodine losses due to volatilization. Operation at a lower temperature, coupled with iodine capture and recovery equipment (i.e., using enclosed tanks and adding a scrubber to recover iodine vapor) could possibly reduce the iodine make up requirement and make the process more economical.

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is exceeded are classified as D009 wastes (40 CFR 261.24 - Toxicity Characteristic).

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