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ORNL/TM-13137

Removal of Mercury from Solids Using the Potassium Iodide/Iodine Leaching Process

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REMOVAL OF MERCURY FROM SOLIDS USING THE POTASSIUM IODIDE/IODINE LEACHING PROCESS

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CONTENTS

LIST OF FIGURES

LIST OF TABLES

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ABSTRACT

Potassium iodide (KI) and iodine (I_2) leaching solutions have been evaluated for use in a process for removing mercury from contaminated mixed waste solids. Most of the experimental work was completed using surrogate waste. During the last quarter of fiscal year 1995, this process was evaluated using an actual mixed waste (storm sewer sediment from the Oak Ridge Y-12 Site). The mercury content of the storm sewer sediment was measured and determined to be approximately 35,000 mg/kg. A solution consisting of 0.2 *M* I_2 and 0.4 *M* KI proved to be the most effective leachant used in the experiments when applied for 2 to 4 h at ambient temperature. Over 98% of the mercury was removed from the storm sewer sediment using this solution.

Iodine recovery and recycle of the leaching agent were also accomplished successfully. The streams that leave the treatment process included the treated solids, spent iron (steel wool), iron hydroxide sludge, and calcium sulfate sludge. The final mercury concentrations in the sediment samples after treatment were between 500 and 1000 mg/kg; Toxicity Characteristic Leaching Procedure analysis indicated a concentration of 3 to 10 mg/L in the leachate.

Mathematical modeling was used to predict the amount of secondary waste in the process. The global and the detailed mass balances corresponded very well. It is anticipated that secondary waste is generated at a rate equal to 270 kg per 1000 kg of treated material. The stabilization of these materials remains to be studied.

Both surrogate waste and actual waste were used to study the fate of radionuclides (uranium) in the leaching process. The soluble uranium present in the solids was transferred to the leaching agent, and 90% of this uranium was removed in the iodine reduction–mercury recovery step. An additional 6% was removed in the metals precipitation step. Thus, uranium will contaminate the mercury recovered and, to a lesser extent, the other secondary wastes.

1. INTRODUCTION

Mercury has been identified as a chemically hazardous compound for many years. Mercury (Hg) and mercury compounds, when ingested, inhaled, or absorbed by the skin, are highly toxic and can affect major organs as well as the central nervous system.[1] In the environment, mercury is present in air, water, soil/sediments, plants, and animals; however, sediments are the primary sink for this metal. In order to minimize adverse health effects from exposure to mercury, the U.S. Environmental Protection Agency (EPA) has established treatment levels that must be met before disposal of mercury-containing waste. During the past several decades, some U.S. Department of Energy (DOE) sites used large quantities of mercury in enrichment processes and other defense-related activities, which resulted in the generation of significant volumes of mercury-contaminated wastes. When these wastes contain both mercury and radioactive chemicals, they are categorized as mixed waste.

The primary forms of mercury of interest to this project are elemental mercury (Hg^0), mercuric oxide (HgO), and mercuric sulfide (HgS). Since, in many instances, the speciation and exact concentration of mercury in DOE mixed waste are unknown, a mercury leaching process that is applicable to several forms of mercury at a range of concentrations is desirable.

Most forms of mercury are only slightly soluble in water, but will dissolve readily in concentrated acids such as nitric, sulfuric, hydrobromic, and hydrochloric. Mercury compounds are also soluble in other leachates such as sodium sulfide (Na_2S). For a leaching solution to be effective, it must be able to solubilize solid forms of mercury and its compounds as well as form soluble mercury complex(s) that will remain in the aqueous phase when the leaching solution is separated from the treated solids. Halides, including bromine, chlorine, and iodine, have been shown to form such soluble complexes.[2] According to chemical data, halogen ions such as I^-, Br^-, and Cl^- have large formation constants (K_f) with mercury and have low oxidation potentials, thus allowing the formation of mercury-halide complexes. The KI/I_2 leaching process, which was recently developed and patented by the General Electric Company (GE), has been tested on a large number of mercury species and found to be very effective. Demonstrations have shown that this process is both efficient and selective for leaching mercury from solid matrices. When KI/I_2 leaching solutions are applied to a mercury-contaminated solid, the solid mercury species are transformed to the soluble mercury complex HgI_4^{2-} according to the following reactions:

$$Hg^0 + I_2 \rightarrow HgI_2 \qquad (1)$$

$$HgI_2 + 2\,I^- \rightarrow HgI_4^{2-} \tag{2}$$

$$HgO + H_2O + 4\,I^{2-} \rightarrow HgI_4^{2-} + 2\,OH^- \tag{3}$$

$$HgS + I_2 + 2\,I^- \rightarrow HgI_4^{2-} + S \tag{4}$$

1.1 OBJECTIVE

The objective of this project is to evaluate leaching processes that could be used to remove mercury from solid mixed waste and thereby minimize many of the problems associated with the thermal treatment of waste containing mercury.

1.2 SCOPE

During fiscal year (FY) 1994, laboratory experiments were completed which demonstrated that mercury compounds could be removed from surrogate solid mixed waste using KI/I_2 leaching solutions. The objective of the FY 1995 studies was to demonstrate the removal of mercury from the spent leaching solution and the recovery of iodine for use in subsequent treatment cycles. One series of experiments completed in FY 1995 included the treatment of an actual mixed waste (storm sewer sediments) with the optimum leaching process established in the laboratory studies. FY 1997 activities included the estimation of secondary waste volumes and the distribution (or fate) of radionuclides in the leaching process. A summary of the completed laboratory experiments may be found in Table 1.

2. METHODS AND PROCEDURES

Two types of laboratory experiments were conducted in FY 1995: full-cycle experiments, where the soils were leached with KI/I_2 solution and the spent leaching solution was processed to remove mercury and recover iodine; and multiple-cycle experiments, where up to three successive batches of mercury-contaminated solids were treated with recycled leaching solution. Most laboratory experiments were conducted using surrogate storm sewer sediment artificially contaminated with Hg, HgO, and $HgCl_2$. Discussions concerning the selection of the target waste stream and the formulation of the surrogate storm sewer sediment have been reported elsewhere.[3]

Table 1. Laboratory experiments conducted at ORNL on the KI/I_2 technology for leaching of mercury from solids

Study phase	Scale	Solid matrix	Contaminants	Status
1	Bench (10 g/batch)	Surrogate soil; crushed glass	Hg compounds[a]	Completed FY 1994
2	Bench (10 g/batch)	Surrogate soil	Hg^0; radionuclide surrogates[b]	Completed FY 1994
3	Bench (10 g/batch)	Storm sewer sediment surrogate	Hg compounds;[c] RCRA metals;[d] radionuclide surrogates[b]	Completed FY 1994 (ref. 3)
4	Bench (10 g/batch)	Storm sewer sediment surrogate	Hg compounds[c]	Completed FY 1995
5	Bench (10 g/batch)	Storm sewer sediment	Hg compounds;[e] radionuclides;[f] PCBs	Completed FY 1995
6	Bench (25 g/batch)	Tank sludge waste	Hg compounds;[e] radionuclides[g]	Completed FY 1997 (ref. 4)

[a] Hg^0, HgS, HgO, and $HgCl_2$ (total pretreatment Hg = 20,000 ppm).
[b] CeO_2 and CsCl.
[c] Hg^0, HgO, and $HgCl_2$.
[d] Cr, Pb, Cd, and Ni.
[e] Unknown speciation.
[f] ^{99}Tc, ^{237}Np, ^{234m}Pa, ^{230}Th, ^{234}Th, and ^{238}U.
[g] U.

2.1 SURROGATE SEDIMENT PREPARATION AND CONTAMINATION

Surrogate storm sewer sediments were prepared to represent the sediments stored on the Oak Ridge Reservation (ORR). Silica sand (SiO_2) and calcium carbonate ($CaCO_3$) were added to EPA synthetic soil matrix[5] to match the carbonate and calcium levels reported in storm sewer sediments. The surrogate sediments, which were prepared in 250-g batches consisting of 37.5 g $CaCO_3$, 87.5 g SiO_2, 0.95 g CeO_2, 0.98 g CsCl, 0.12 g PbO, 0.09 g NiO, 0.075 g Cr_2O_3, and 0.002 g CdO, were thoroughly mixed prior to use in the leaching studies.

Ten-gram portions of surrogate storm sewer sediment were contaminated with multiple mercury compounds (Hg^0, $HgCl_2$, and HgO) prior to chemical leaching. In all of the sediment experiments, the initial mercury concentration was 20,000 mg/kg. It was decided that the contamination and treatment of small batch samples of soil would be utilized in the bench-scale experiments to avoid the experimental error introduced when larger samples are contaminated, often heterogeneously, and subsequently subdivided for individual experiments.

2.2 SEDIMENT LEACHING

Erlenmeyer flasks (volume, 125 mL) containing the contaminated sediments were capped after the addition of mercury and agitated for 24 h at 40°C on a rotational shaker to promote equilibration. Reagent-grade KI, I_2, and deionized water were used to prepare KI/I_2 leaching solutions at least 12 h prior to soil treatment. These solutions were prepared and stored in dark glass containers to minimize iodine losses prior to treatment. Thirty-five milliliters of leaching solution was added to each flask containing 10 g soil to be treated. Deionized water that had been pH-adjusted was added to control flasks instead of KI/I_2 leaching solution. A blank consisting of surrogate sediment without added mercury was also treated with the KI/I_2 leaching solution. The flasks containing sediment and leaching solution were capped and placed in a Lab-line environmental shaking chamber. All leaching treatments were conducted at room temperature.

After reaction, the contents of the flasks were vacuum filtered through 0.45-µm membrane filters. The residuals in the flask and the filter cake were washed with an additional 35 mL of deionized water. The volumes of the supernatant and the wash water were subsequently measured.

2.3 LEACH SOLUTION PROCESSING AND RECYCLE

During the study, the spent leaching solution was processed to remove the solubilized mercury and to recover iodine. After 10-g portions of solids had been leached with 35 mL KI/I_2 solution, the treated solids were rinsed first with deionized water (35 mL) and then with an acidified (pH = 2.5) wash solution. The spent leaching solution combined with the deionized wash water was processed to remove the dissolved mercury by contacting the solution with approximately 4 g of steel wool at a temperature of 50°C for a period of 1 h. After the leaching solution had been decanted from the steel wool, 0.5 g of CaO was added to the solution and mixed for 30 min at ambient temperature to precipitate out any dissolved metals. The solids formed during this step were separated from the liquid by filtration. The volume of the recovered liquid was measured, and the liquid was divided into two equal portions. To one portion of the liquid, 2.2 mL of concentrated H_2SO_4 and 2.2 mL of 30% H_2O_2 were added. The addition of these reagents resulted in the formation of I_2 solids that were collected by filtration. The second portion was combined with the formed I_2, and fresh KI/I_2 solution was added to give a total volume of 35 mL.

2.4 MERCURY ANALYSIS

The mercury concentrations in the post-treatment samples were measured by means of the Cold Vapor Atomic Absorption (CVAA) method (EPA method 7470A). For the surrogate waste studies, a Perkin-Elmer model 1100B Atomic Absorption Spectrophotometer equipped with an autosampler (Perkin-Elmer model 90) and a Flow Injection Mercury Hydride Analysis System (FIAS 400) was used. A Leeman Labs PS200 Mercury Analyzer was used for the actual waste studies. In both cases, a carrier solution of 3% HCl and a reductant solution of 1.1% $SnCl_2$ in 3% HCl were used during analysis. Samples were diluted to the instrument range of 1 to 20 ng/L with deionized water and analyzed immediately after dilution. The presence of iodine in concentrations greater than ~5 mg/L significantly interfered with the analysis of mercury because of the formation of the HgI_4^{2-} complex and excessive consumption of reagents by residual I_2.

At least three standards were prepared daily when mercury analysis was to be performed. These standards were prepared in a $K_2Cr_2O_7$–HNO_3 solution and made from stock solutions from the National Institute of Standards and Technology.

2.5 SEDIMENT TCLP CHARACTERIZATION

Some post-treatment sediment samples were not digested. Instead, a leaching test similar to the Toxic Characteristic Leaching Procedure (TCLP) was used to determine if the treated solids would meet Resource Conservation and Recovery Act (RCRA) hazardous waste disposal criteria. Five-gram samples of treated sediment were placed in 130-mL zero-headspace extraction vessels. One hundred milliliters of EPA-specified leaching solution was added to the sediment in each of the extraction vessels. The leaching solution was prepared by diluting 2.85 mL of glacial acetic acid to 500 mL with deionized water. The movable pistons in the extraction vessels were adjusted so that no headspace remained in the vessels following the addition of leaching agent. After the extraction vessels had been sealed, they were rotated "end over end" for 17.5 h at 30 rpm. The leaching solution was separated from the sediments by means of

0.2-μm membrane filters. To preserve the solution, HNO_3 was added to decrease the pH of the TCLP extract to less than 2. The samples were refrigerated prior to analysis.

3. RESULTS AND DISCUSSION

3.1 SURROGATE WASTE STUDIES

Laboratory studies were completed using 10-g surrogate waste samples and 35 mL of a leaching solution. The leached sediment was washed with 35 mL of water. Figure 1 shows the results of three leaching experiments conducted under different conditions. In each case the starting concentration of mercury was 20,000 mg/kg. Additional experiments were performed to further study the effects of temperature and duration of the leaching process. Based on the results of these studies, it was concluded that a leaching solution consisting of 0.4 *M* KI and 0.2 *M* I_2 would be effective if used at room temperature for 2 h (Fig. 2).

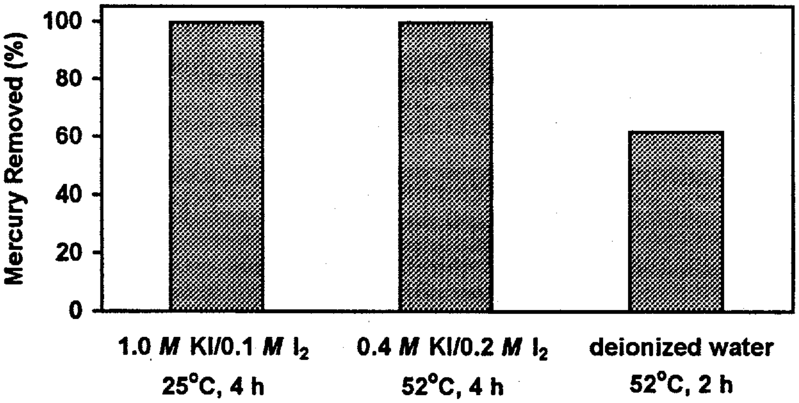

Fig. 1. Results of experiments performed on surrogate waste to study the leaching efficiency under various leaching conditions.

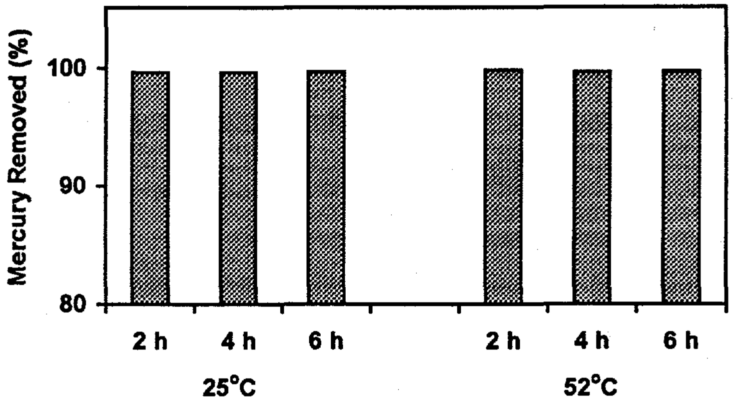

Fig. 2. Results of experiments performed on surrogate waste to study the effects of temperature and process duration on leaching efficiency. The leaching solution consisted of 0.4 *M* KI and 0.2 *M* I_2.

Multiple-cycle experiments were also performed (see Fig. 3). During these experiments, surrogate waste was treated (2 h and 25°C) and the spent leaching solution was processed to remove the solubilized mercury and to recover iodine by contacting the solution with approximately 4 g of iron fillings at a temperature of 50°C for 1 h. The solubilized iron was then removed by adding 0.5 g of lime (CaO) to the solution and maintaining the pH above 10. The solids formed during this step were separated from the liquid by filtration. The filtrate was subsequently divided into two equal portions, and 2.2 mL of concentrated sulfuric acid (H_2SO_4) and 2.2 mL of hydrogen peroxide (H_2O_2, 30%) were added to one of these portions. The addition of these reagents resulted in the formation of iodine solids that were collected by filtration. These solids were then combined with the fraction of leaching liquid previously removed, and the total volume was brought to 35 mL with fresh KI/I_2 solution for the next leaching cycle. Three such cycles were performed. The removal efficiency of recycled leaching solution is shown in Fig. 4.

3.2 LABORATORY STUDIES WITH STORM SEWER WASTE SEDIMENT

Laboratory studies were completed using actual Y-12 Site storm sewer sediment obtained from the K-25[†] waste management group. A total of 200 g of storm sewer sediment was transferred to the project for use in the experiments. The mercury content of the storm sewer sediment was measured and determined to be 34,940 ± 8,800 mg/kg. The speciation of the mercury in the storm sewer sediment was unknown,

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[†] The Oak Ridge K-25 Site has been renamed the East Tennessee Technology Park. The Oak Ridge Y-12 Site storm sewer sediment had been stored at the Oak Ridge K-25 Site.

although it was reported in the past that visible beads of elemental mercury were present in the waste when it was originally collected. A previously performed characterization included 0.022 mCi of radiological contamination per kg of sediment and an on-site survey performed by a division radiation protection technician indicated that this radiological contamination was predominantly alpha. All experiments were performed in a type C fume hood in a radiologically controlled area. Three treatment studies were completed using the storm sewer sediment, as follows.

- The first set of experiments verified that the optimum leaching conditions determined in the previous surrogate waste studies were appropriate for the storm sewer sediments.
- The second set of experiments evaluated the full process that includes both mercury removal and leach solution regeneration.
- The third and final series of experiments evaluated multiple treatment cycles with regeneration and reuse of leaching solution.

In addition to monitoring mercury concentrations in the treated solids, TCLP analysis was performed on all solids that would be considered secondary waste in the treatment process.

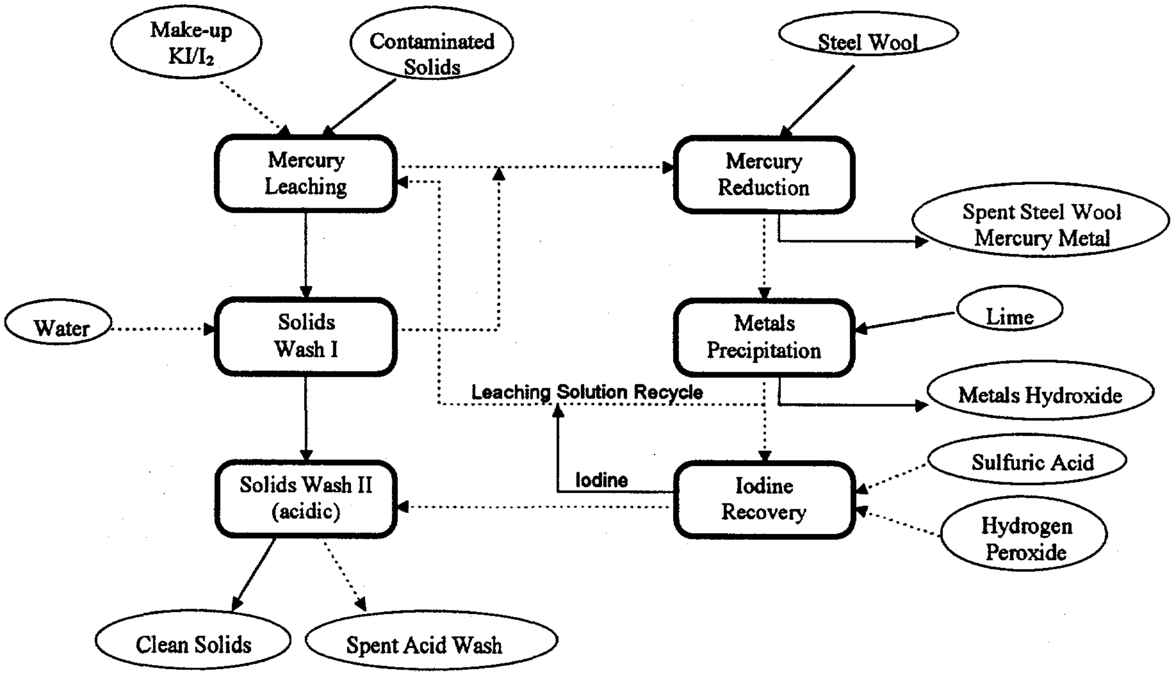

Fig. 3. Schematic of the mercury leaching process with KI/I_2 as used in the laboratory studies.

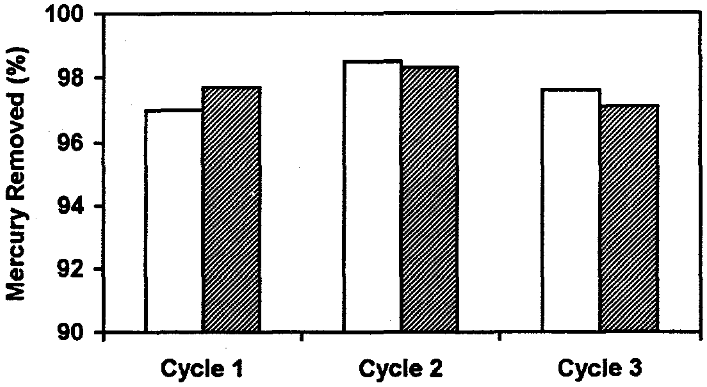

Fig. 4. Removal efficiency in multiple-cycle experiments where the leaching solution is recovered, processed, and reused. Results of duplicate experiments are shown.

3.2.1 Confirmation of Composition of Leaching Solution

Two leaching solution concentrations and treatment times were evaluated during these experiments. The solution concentrations were selected on the basis of results of previously completed surrogate waste studies. The liquid/solid ratio was held constant at 3.5/1, and all of the leaching experiments were conducted at ambient temperature. The treated solids, spent leaching solution, and spent acid wash solutions were analyzed for mercury content via the CVAA method. The results of this study are shown in Table 2.

Mercury removal efficiencies in excess of 97% were obtained by leaching with KI/I_2 solutions, indicating the robustness of the procedure. The highest removal (98%) was obtained in the sediments leached with the 0.4 *M* KI/0.2 *M* I_2 solutions for a period of 2 to 4 h. Since complete analytical results of these experiments were not available when the full-cycle experiments were initiated, treatment with 0.4 *M* KI/0.2 *M* I_2 leaching solution for a period of 4 h was selected for the subsequent full-cycle and multiple-cycle studies.

Table 2. Evaluation of various leaching conditions for treatment of Y-12 storm sewer sediments

Leaching solution	Treatment time (h)	Initial mercury concentration[a] (mg/kg)	Final mercury concentration (mg/kg)	Mercury removal (%)
DIW[b] control	2	34,900	20,600	41
DIW control	4	34,900	16,477	53
1.0 *M* KI/0.1 *M* I_2	2	34,900	1,038	97
1.0 *M* KI/0.1*M* I_2	4	34,900	909	97
0.4 *M* KI/0.2 *M* I_2	2	34,900	686	98
0.4 *M* KI/0.2 *M* I_2	4	34,900	848	98

[a] Initial concentration based on average of triplicate samples.
[b] DIW = deionized water.

In both the leaching solution optimization and the full-cycle experiments (see below), significant reductions in mercury concentration occurred in the deionized water control studies. Such results were unexpected since less than 5% mercury reduction was observed in controls in previous studies with surrogates. However, this apparent reduction in mercury may be the result of retention of the small-particle size fraction of the storm sewer sediment in the filter after leaching has been completed. The data indicated that, on average, 0.5 g of storm sewer sediment was lost during this step. If these small-sized particles also contained high concentrations of mercury, then removal of this fraction in the filter would result in an overall decrease in the mercury content of the bulk solids.

3.2.2 Full-Cycle Experiments

During this study, storm sewer sediment was treated and the spent leaching solution was processed to remove the solubilized mercury and to recover iodine. After 10-g portions of storm sewer sediment had been leached with 0.4 *M* KI/0.2 *M* I_2 solution for 4 h, the treated solids were first rinsed with water and then washed with an H_2SO_4-acidified (pH 2.5) solution. The treated and washed solids were subsequently analyzed for mercury content.

The spent leaching solution was processed to remove the dissolved mercury by contacting the solution with approximately 4 g of steel wool at a temperature of 50°C for 1 h. After the leaching solution had been decanted from the steel wool, 0.5 g of lime was added to the solution to precipitate any dissolved metals. The resulting slurry was mixed for 30 min at ambient temperature, and the solids formed during this step were separated from the liquid by filtration. The filtrate was then divided into two equal portions, and 2.2 mL of concentrated sulfuric acid and 2.2 mL of hydrogen peroxide (30%) were added to one of the portions. The addition of these reagents resulted in the formation of iodine solids that were then collected by filtration. The results of the full-cycle experiments are summarized in Table 3.

Table 3. Results of full-cycle leaching of Y-12 storm sewer sediment[a]

Leaching solution	Final mercury concentration (mg/kg)	Mercury removed (%)
DIW control	21,900	37
DIW control	21,800	37
0.4 *M* KI/0.2 *M* I_2	995	97
0.4 *M* KI/0.2 *M* I_2	536	99

[a]Duplicate experiments shown.

The mercury concentrations in the treated and washed storm sewer sediment samples from this study were similar to those measured in samples treated during the leaching solution optimization experiments. As was observed in the earlier surrogate waste laboratory studies, small volumes of leaching solution were not completely recovered in several of the stages required for the full-cycle treatment. The volumes of liquid recovered after the different treatment stages are summarized in Table 4. The average volume of solution lost during the process (i.e., retained on the filters, in the steel wool, or in the solids leaving the system) was 21 mL, or 30% of the original spent leaching solution volume (including the first wash water).

Table 4. Liquid inventory following KI/I_2 leaching

Leaching solution	Volume of leaching solution and wash water added (mL)	Volume collected after initial filtration and washing (mL)	Volume collected after steel wool (mL)	Volume collected after CaO addition (mL)
DIW control	70	60	56	48
DIW control	70	65	62	54
0.4 *M* KI/0.2 *M* I_2	70	69	55	49
0.4 *M* KI/0.2 *M* I_2	70	68	54	46

3.2.3 Multiple-Cycle Experiments

The multiple-cycle experiments were conducted to evaluate the treatment of successive batches of storm sewer sediment using recycled/regenerated leaching solutions. (Three full cycles were completed during this study.) The experimental method employed was identical to that for the full-cycle experiments, except the leaching solution in cycles 2 and 3 was prepared by combining the remaining half of the processed leaching solution with the recovered iodine. Freshly prepared KI/I_2 leaching solution (0.4 *M*/0.2 *M*) was added to the recycled leaching solution to bring the volume to 35 mL prior to the next batch of storm sewer sediment (10 g) to be treated. Also, the liquid remaining after recovery of the iodine served as a second wash solution for the treated solids instead of the acidified wash solution that was used in the full-cycle experiments. Fresh steel wool was used in the mercury and iodine reduction step in the first and second full cycles. In the last cycle, "spent" steel wool from cycle 2 was reused. The multiple-cycle experiments were conducted in duplicate. A schematic of the process may be seen in Fig. 3. The results of the multiple-cycle experiments, each summarized in Table 5, show that a high removal efficiency (>97%) was obtained in each consecutive cycle—indicating the effectiveness of the leaching solution and the steel wool recycle.

Table 5. Results of multiple-cycle leaching of Y-12 storm sewer sediment

Experiment	Leaching solution	Volume leaching solution recovered[a] (mL)	Final mercury concentration (mg/kg)	Mercury removed (%)
1a	Fresh KI/I_2	41	492	99
2a	Recycled from 1a	38	745	98
3a	Recycled from 2a	61	1168	97
1b	Fresh KI/I_2	42	605	98
2b	Recycled from 1b	40	800	98
3b	Recycled from 2b	67	847	98

[a] Volume of solution recovered after processing the spent leaching solution with both the steel wool and the CaO.

3.2.4 Residuals Analysis

Although the leaching solution and steel wool used in this process were recycled, other streams were generated that exited the treatment process and will require further processing and/or disposal. The streams leaving the treatment process (see Table 6 and Fig. 3) include the treated solids, spent steel wool, and $Fe(OH)_2$ sludge. The spent acid wash solution is actually used as the wash water and will not be a waste. The characteristics of these streams were determined to provide data that may be required for evaluating the full-scale application of this technology.

Table 6. Estimation of secondary waste volumes from the leaching process when treating 10 g of solids

Stream	Matrix	Amount generated each cycle	pH	Moisture content (%)
Treated solids	Solid	10.8 g	6	12
$Fe(OH)_2$ sludge	Solid	3.3 g	11	78
Steel wool	Solid	N/A[a]	–	–
Acid wash	Liquid	24 mL	1	–

[a] Steel wool (4 g, initially) can be reused for multiple cycles.

All solids leaving the treatment process [treated storm sewer sediment, $Fe(OH)_2$ sludge, and spent steel wool] were analyzed using TCLP in addition to direct determination of the mercury content of the solids. The TCLP extracts were digested using aqua regia and analyzed for mercury content using the CVAA method. The liquids exiting the treatment system were also analyzed using the CVAA method. The results of the residuals analysis are summarized in Table 7. As is noted, the treated solids contained high levels of mercury (i.e., high enough not to pass TCLP testing). It is likely that a second leaching step or more effective washing could improve this performance. It is also interesting to note that the iron oxide sludge after the third cycle contained high levels of mercury, which can be explained if one assumes that the reduction with recycled iron (steel wool) did not work properly. It is, however, likely that the mercury concentration of this stream will be sufficiently high to mandate that it must be handled as a hazardous waste.

3.3 MATHEMATICAL MODELING OF THE LEACHING PROCESS AND PREDICTION OF WASTE RESIDUALS

The generation of secondary waste can be estimated with good accuracy by reviewing the process described in Fig. 3 as a black box. The following global mass balance can be performed on treating 1 kg of contaminated soil, assuming complete recycle of the wash water.

Table 7. Mercury concentrations in residuals from KI/I_2 leaching of storm sewer sediment

Experiment	Waste identification	Phase	Mercury concentration (solid—mg/kg) (liquid—mg/L)	TCLP extract concentration (mg/L)
Storm sewer sediment	Untreated	Solid	34,900	2.9
Multiple-cycle 1b	Treated solids	Solid	605	8.2
Multiple-cycle 2b	Treated solids	Solid	800	6.2
Multiple-cycle 3b	Treated solids	Solid	847	9.1
Multiple-cycle 2a	$Fe(OH)_2$ sludge	Solid	6	0.31
Multiple-cycle 3a	$Fe(OH)_2$ sludge	Solid	566	28.3
Multiple-cycle 2b	$Fe(OH)_2$ sludge	Solid	8	0.41
Multiple-cycle 3b	$Fe(OH)_2$ sludge	Solid	966	48.3
Multiple-cycle 1a	Steel wool	Solid	7,912	Not measured
Multiple-cycle 2a, 3a	Steel wool	Solid	1,591	Not measured
Multiple-cycle 1b	Steel wool	Solid	7,405	Not measured
Multiple-cycle 2b, 3b	Steel wool	Solid	40,651	Not measured
Multiple-cycle 2a	Spent acid wash	Liquid	45	45
Multiple-cycle 3a	Spent acid wash	Liquid	106	106
Multiple-cycle 2b	Spent acid wash	Liquid	41	41
Multiple-cycle 3b	Spent acid wash	Liquid	45	45

Incoming streams

1. One kilogram of soil with a known moisture content (e.g., 15%) and mercury concentration (e.g., 1000 mg/kg) is being treated. <u>Equations/Variables:</u>

   M_{us} = amount of untreated soil = 1 kg
   W_{us} = moisture content = 0.15 kg/kg
   Hg_{us} = mercury concentration = 1 g/kg

2. Enough iron metal is needed to reduce all the I_2 to I^- and Hg^{2+} to Hg^0 in the leaching solution. The process calls for 3.5 L (or kg) of 0.2 M I_2 per kg of soil. Thus, at least 0.7 mol iron, or 0.039 kg, is required. <u>Equations/Variables:</u>

   LS = liquid/solid ratio in leaching step = 3.5 kg/kg
   L = amount (kg) leaching liquid = LS × M_{us}
   I_2 = concentration of iodine in leaching liquid = 0.2 M
   KI = concentration of potassium iodide in leaching liquid = 0.4 M
   M_{Fe} = amount (kg) iron needed for reduction = $MW_{Fe} \times (M_{us} \times Hg_{us}/MW_{Hg} + I_2 \times L)/1000$

3. Calcium oxide is added to precipitate the iron that is dissolved in the iodine reduction step. We will need 0.7 mol CaO, or 0.039 kg, to precipitate the iron as either $Fe(OH)_2$ or FeOOH. In practicality, we need slightly more because the pH needs to be increased from neutral to about 10, but the extra amount is small. Equation/Variables:

   M_{CaO} = amount (kg) calcium oxide needed for precipitation = $MW_{CaO} \times M_{Fe}/MW_{Fe}$

4. Hydrogen peroxide and sulfuric acid need to be added to reconvert half of the iodide in the system to iodine. We need 1 mol H_2O_2 and 1 mol H_2SO_4 to make 1 mol I_2. Thus, we need 0.07 kg of 98% H_2SO_4 and 0.079 kg of 30% H_2O_2 to generate the 0.7 mol I_2 we need. Equations/Variables:

   $L_{H_2O_2}$ = amount (kg) 30% hydrogen peroxide needed = $MW_{H_2O_2} \times I_2 \times L/(1000 \times 0.3)$
   $L_{H_2SO_4}$ = amount (kg) 98% sulfuric acid needed = $MW_{H_2SO_4} \times I_2 \times L/(1000 \times 0.98)$

Outgoing streams

1. Treated soil with a moisture content (e.g., 40%) is being generated. The water in the soil contains low levels of iodine and iodide as well as mercury, depending on the number of internal washes. The weight of the treated soil in the case of 40% moisture is 1.42 kg. Equations/Variables:

   W_{ts} = moisture content in the treated soil = 0.4 kg/kg
   M_{ts} = amount (kg) treated solid = $M_{us} \times (1 - W_{us})/(1 - W_{ts})$

2. In the conceptual process, the separated elemental mercury is not removed from the system after each batch. Instead it is removed intermittently; however, for the purpose of demonstration, let us assume that it is removed after each batch (0.001 kg mercury). Equations/Variables:

   M_{Hg} = amount (kg) mercury removed = $M_{us} \times Hg_{us}/1000$

3. Iron hydroxide/oxide is generated (0.7 mol) as a result of the precipitation. If this sludge has a moisture content of 40%, the amount is 0.1 kg. Equations/Variables:

   W_{FeO} = moisture content in iron oxide/hydroxide = 0.4 kg/kg
   M_{FeO} = amount (kg) of iron oxide/hydroxide generated = $(MW_{Fe(OH)_2} + MW_{FeOOH}) \times M_{Fe}/(2 \times MW_{Fe} \times (1 - W_{FeO}))$

4. As CaO and H_2SO_4 are added to the system, $CaSO_4$ (gypsum) is formed in a stochiometric amount (0.7 mol). If the water content is 40%, we will obtain 0.16 kg. Equations/Variables:

   W_{CaSO_4} = moisture content in gypsum = 0.4 kg/kg
   M_{CaSO_4} = amount (kg) gypsum formed = $MW_{CaSO_4} \times M_{CaO}/(MW_{CaO} \times (1 - W_{CaSO_4}))$

In addition to the above-mentioned incoming and outgoing streams, water is added to the process through the incoming soil, sulfuric acid, and hydrogen peroxide; water is lost in the treated soil, hydroxide sludge, and gypsum sludge; water is generated in the conversion of iodide to iodine; and water is consumed in the iron hydroxide precipitation step. To make the mass balance complete, the water balance must be satisfied, and in the example above, 0.45 kg of water must be added to the system. Equations/Variables:

L_{H_2O} = amount (kg) extra water added to the system = $M_{ts} \times W_{ts} + M_{FeO} \times W_{FeO} + M_{CaSO_4} \times W_{CaSO_4} + 0.3 \times L_{H_2O_2} \times MW_{H_2O}/(2 \times MW_{H_2O_2}) - M_s \times W_s - 0.7 \times L_{H_2O_2} - 0.02 \times L_{H_2SO_4} - MW_{H_2O} \times M_{CaO}/MW_{CaO} \times 0.75$

The effectiveness of the soil washing steps after the leaching determines the remaining concentration of mercury in the soil. If, in the above example, we forego washing, the amount of mercury in the soil after leaching would be equal to 110 mg/kg [or $Hg_{us} \times M_{us} \times W_{ts}/(L + M_{us} \times W_{us})$]. If the leached soil is washed twice using M_{us} × LS kg wash liquid, the mercury concentration would decrease to 2.4 mg/kg in which case the treated soil would pass TCLP testing even after drying. The number of washes is also important since some iodine and iodide are lost with the treated solids if washing is not effective. The global mass balance is summarized in Table 8.

Table 8. Constituents of streams in the leaching process as calculated by a simple global mass balance

Incoming streams	Outgoing streams
Soil, 1 kg	Soil, 1.42 kg
Fe, 0.039 kg	$Fe(OH)_2/FeOOH$, 0.10 kg
CaO, 0.039 kg	$CaSO_4$, 0.16 kg
H_2O_2 (30%), 0.079 kg	Mercury, 1 g
H_2SO_4 (98%), 0.070 kg	
Water, 0.45 kg	

The gypsum has been listed as a separate secondary waste stream. However, in practicality, this stream is always combined with either the soil or the iron oxide/hydroxide stream, depending on what is used as the initial wash liquid. In addition to the global mass balance, a detailed mass balance was performed to provide more details about the internal process streams (see Appendix A).

3.4 FATE OF RADIONUCLIDES IN THE LEACHING PROCESS

Determination of the fate of radionuclides, specifically uranium, in the leaching process was evaluated using both surrogate and actual waste.[4] Approximately 90% of the soluble uranium present in the leachate was removed during the iodine/mercury reduction step. This was proven both in surrogate studies using ^{233}U tracers and in actual waste studies using mercury-contaminated tank sludge. An additional 57% of the remaining soluble uranium was removed in the metals precipitation step. Thus, it was concluded that most of the uranium will be commingled with the elemental mercury recovered from the process.

In studies conducted with Building 9201-4 tank sludge waste that contained both uranium (44 mg/kg) and mercury (5900 mg/kg), only a fraction (1 to 11%) of the uranium was soluble in water or in KI/I_2 leaching solution. It is a safe assumption that wastes (such as tank sludges) previously in contact with water for a long time will contain little soluble uranium.

3.5 ASSESSMENT OF DOCUMENTATION NECESSARY TO CONDUCT A MERCURY LEACHING DEMONSTRATION ON THE OAK RIDGE RESERVATION

General Electric's mercury removal process has been investigated for the treatment of U.S. Department of Energy (DOE) solid mixed waste that is contaminated with mercury. As previously described, this treatment process uses a potassium iodide–iodine leaching solution to selectively remove mercury. It is possible that the technology development may lead to a leaching demonstration on the ORR. Included is an example of a planning document (Appendix B) used at the K-25 Site to collect information for site support for demonstrations. This document may be used as a guide to successfully to conduct various demonstrations with complete regulatory compliance. Of course, minor modifications might be needed to reflect more current regulatory requirements.

Another key document was prepared by Jolley et al.[6] Even though this summary/assessment was prepared for use with a specific project, it may be used as general guidance in determining which reports, procedures, permit applications, and proposals, etc., are necessary to initiate any type of demonstration activity conducted on the ORR. The content of this document is summarized below.

3.5.1 Required Proposals and Plans

The primary purpose of the Demonstration Proposal document is to specify the objectives of the demonstration, to define its scope, and to state the funding requirements. It is important that the objectives of the demonstration contain a clear statement of the goals and identify the customer. Other factors to be considered during the development of the proposal are (1) to determine whether private vendors will be contracted for conducting the demonstration, (2) to determine where the demonstration will be conducted, (3) to prepare formal funding request documentation (Technical Task Plan, Activity Data Sheet or Field

Work Plan, etc.) and, finally, (4) to obtain signature approval for the demonstration proposal from line management Energy Systems (ES) representatives, ES Site Demonstration Manager, Central Waste Management Director, Environmental Director, ES Central Management, DOE Site Manager, and Waste Management representatives.

During all stages of the demonstration activity, communication with ORR sites and DOE representatives is important. The principal investigator and appropriate staff should also interface with ES sites; the ES Site Demonstration Manager; the Waste Research and Development Coordinator; the ES Site Environmental Coordinator; ES senior management; ES division, programs, or groups (especially the Central Environmental Restoration/Waste Management organization); DOE/OR; and the DOE Site Manager.

3.5.2 Project Description

The Project Description is an extension of the basic document prepared for the original funding request. It contains information such as objectives of the project; scope of the project; background and rationale; project organization; preliminary studies; site descriptions; system design; site requirements; waste generation and disposal of anticipated waste streams; references to health and safety plans; references to quality assurance plans; permitting issues, including the National Environmental Policy Act (NEPA), Toxic Substances Control Act (TSCA) demonstration permit, Resource Conservation and Recovery Act (RCRA) demonstration permit or a Research, Development, and Demonstration (RD&D) permit; and legal issues.

3.5.3 The Project Plan

This plan provides the basis for coordination of all parts of the demonstration. It contains such information as background and purpose; funding baseline; data to be generated (including analytical, physical, treatability, and secondary waste data); project approach; permitting issues and appropriate information to obtain permits; references to an emergency plan; mobilization; an outline of the steps comprising the demonstration (including schedules, chains of command, site restoration, etc.); projected radiological controls, if necessary; references to safety and health plan(s); readiness review process and documented approvals; procedure to be used for closeout of the demonstration; references to a final report detailing results and problems; planned subcontracting and estimated costs; and ground rules for change. The Project Plan should include the following subsections: the Task Schedule and Financial Plan, Regulatory Compliance Plan, Quality Assurance Plan, and Readiness Review Plan. Alternatively, these plans may be issued as separate documents for approvals.

3.5.4 Task Schedule and Financial Plan

This plan identifies all the tasks that are involved in order to accomplish the goal(s) of the demonstration and details their initiation and duration. The timing relationship among tasks must be mapped and milestones set so that progress on the project can be measured. This timing relationship will develop the critical path that should be highlighted and discussed with members of the demonstration team. Estimated costs should be identified for each task, thus ensuring supporting facts to defend the budget.

3.5.5 Regulatory Compliance Plan

This plan reviews all of the compliance issues and covers the development of all necessary permits and permit modifications. Some of the issues that must be examined include compliance with the Waste Management Plan generated for the demonstration; State, U.S. Environmental Protection Agency (EPA), RCRA, and RD&D permits or treatability exclusions (Tennessee state limits currently allow 1,000 kg for each treatability study but has allowed variance in the past and will allow 10,000 kg per technology to be studied); state air emissions permits; site National Pollution Discharge Elimination System permit modifications; and a recorded DOE-signed NEPA decision document (such as a Categorical Exclusion Determination (CXD), a Finding of No Significant Impact, or a Record of Decision). Previous experience has shown that demonstrations of the type under consideration (soil washing to remove mercury) typically receive a CXD. Unless the waste to be treated in the demonstration contains polychlorinated biphenyls (PCBs), a TSCA permit is not required. A TSCA permit for treating more than 250 kg of PCB-contaminated (more than 50 mg PCB per kg) material is granted by the EPA Headquarters.

The regulatory compliance staff located at the ORR site chosen for the demonstration will be involved in decisions regarding which permits are necessary and which existing permits need modifications. It is important that communication with the compliance staff is initiated early during the developmental stages of the demonstration.

3.5.6 Quality Assurance Plan

This plan will include quality procedures, work plans, reports, and documentation. Quality control should be asserted through routine surveillance and on periodic audits.

3.5.7 Readiness Review Plan

This plan, or section, may include responsibilities, activities, required approvals, and the methods by which these approvals are obtained and documented. (Often, for small demonstrations, a readiness review plan may be no more than one or two pages attached to the project plan.)

3.5.8 Waste Management Plan

This plan should include schemes for the handling and treatment of the waste to be treated during the demonstration, the treated waste residues, and the materials and equipment wastes generated from the demonstration.

3.5.9 Site Safety and Health Plan

The Site Safety and Health Plan should include topics such as industrial hygiene regarding the safe demonstration of operations relative to Occupational Safety and Health Administration (OSHA) site control to limit the potential of employee exposure to radiological hazards. In general, this document will supply information regarding personal protective equipment required for work, the necessary industrial safety and hygiene controls required and their application to various activities, and radiological controls to be enforced at the demonstration site.

3.5.10 Emergency Plan

This plan must include responders (shift superintendents, fire responders, emergency squad, etc.) and must state that the responders are required to have orientation training on the demonstration prior to startup.

4. CONCLUSIONS AND RECOMMENDATIONS

The experiments with surrogate waste and actual storm sewer sediment waste revealed that KI/I_2 leaching solutions can be used to reduce mercury concentration in such waste by as much as 99%. It is capable of leaching all species of mercury. Since the initial mercury concentration in these wastes is so large, the treated solids have an appreciable mercury content even with 99% mercury reduction. There are several possible sources of mercury in the treated solids, including

- entrained leach solution containing high concentrations of soluble mercury, and
- mercury that may be trapped in inaccessible spaces within the solid matrix that may not have been contacted by the leaching solution.

In addition to having appreciable mercury concentrations, the treated storm sewer sediment did not pass TCLP standards. The mercury levels in the TCLP extracts exceeded the regulatory level of 0.2 mg/L by at least 60 times. If the entrained leaching solution could be removed, the treated solids might pass TCLP standards since the soluble mercury concentration in the entrained leach solution is very high (approximately 5000 mg/L).

The degree of mercury removal achieved may be sufficient if the KI/I_2 leaching process is to be used as a pretreatment process to thermal treatment or stabilization. If however, the process is to be used as a stand-alone treatment, further development and modifications would be required before this process would be feasible. Areas to consider for development and/or modification are as follows:

- improve liquid and solid separation steps both to decrease mercury levels in treated solids and to recover more of the leaching solution for regeneration, thereby decreasing the amount of makeup KI/I_2 solution required for each treatment cycle; and
- evaluate multiple leaching (two or three successive leaching steps) or increased washing of the solids to determine if lower mercury concentrations can be reached.

Mathematical modeling was used to predict the amount of secondary waste in the process. The global and the detailed mass balances corresponded very well. The stabilization of this waste, which is generated at a rate equal to 270 kg per 1000 kg of treated material, remains to be studied.

Both surrogate waste and actual waste were used to study the fate of uranium in the leaching process. Soluble uranium in the solids was transferred to the leaching agent. Ninety percent of this uranium was removed in the iodine reduction step, while an additional 6% was removed in the metals precipitation step. Thus, uranium will contaminate the mercury recovered and, to a lesser extent, the other secondary wastes.

5. REFERENCES

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3. D. D. Gates, K. K. Chao, and P. A. Cameron, *The Removal of Mercury from Solid Mixed Waste Using Chemical Leaching Processes*, ORNL/TM-12887, Martin Marietta Energy Systems, Inc., Oak Ridge National Laboratory, TN, July 1995.
4. W. D. Bostick, W. H. Davis, and R. J. Jarabek, *Fate of Soluble Uranium in the I_2/KI Leaching Process for Mercury Removal*, K/TSO-55, Lockheed Martin Energy Systems, Inc., East Tennessee Technology Park, TN, September 1997.
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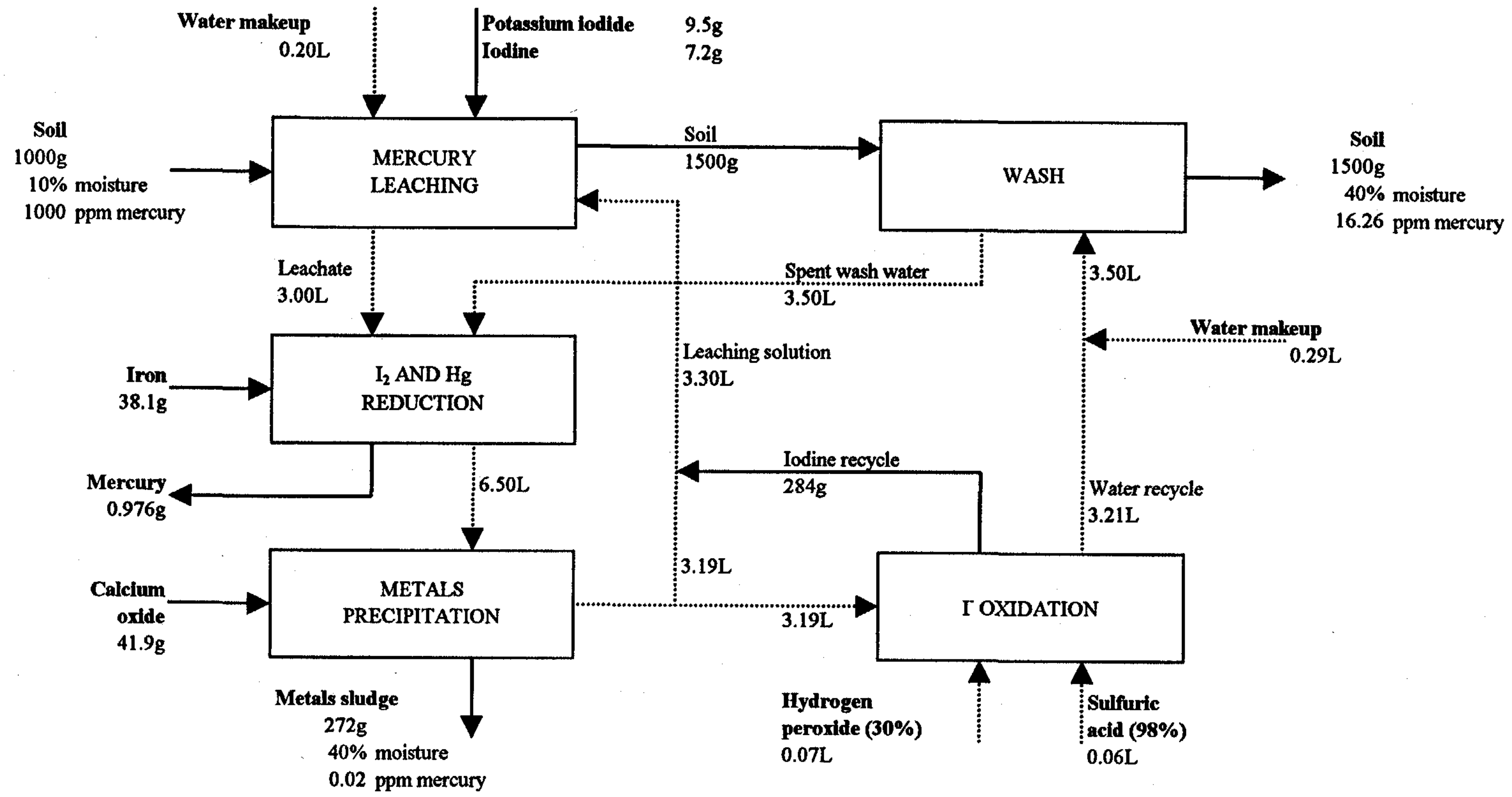
6. R. L. Jolley, M. I. Morris, and S. P. N. Singh, *Guidance Manual for Conducting Technology Demonstration Activities*, ORNL/TM-11848, Martin Marietta Energy Systems, Inc., Oak Ridge National Laboratory, TN, December 1991.

Appendix A

DETAILED SPREADSHEET CALCULATIONS FOR THE KI/I_2 LEACHING PROCESS



Summay Flow Sheet of the Leaching Process

Unit Operation A: Soil leaching

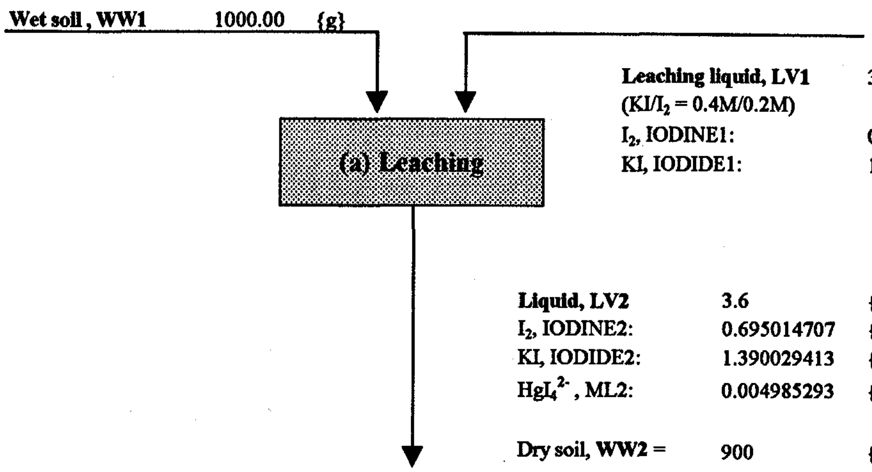
Conventions:
Red = Letters - parameters definition; numbers - assumed values
Blue = formula/equations; calculated values
Balance Units = bulk liquid {L}; bulk solid {g}; individual chemicals {mol}
Assume that all filter cakes contain the same wt% of liquid.

Calculation basis:
Treat WW1 (wet weight) {g} Hg-containing wet soils,
which contains C_Hg {ppm} of Hg and XX1 {wt%} of water.

WW1 =	1000	C_Hg =	1000	XX1 =	10%

LV1 = Liquid volume {liter} used to leach soil
LV1/WW1 = 3.5*E-3
LV1 = (3.5*E-3)*WW1

Assume XX2 leaching conversion/efficiency
XX2 = 1.00
$I_2 + Hg + 2I^- \longrightarrow HgI_4^{2-}$



Wet soil, WW1 1000.00 {g}

Leaching liquid, LV1	3.5	{L}
(KI/I_2 = 0.4M/0.2M)		
I_2, IODINE1:	0.7	{mol}
KI, IODIDE1:	1.4	{mol}

Liquid, LV2	3.6	{L}
I_2, IODINE2:	0.695014707	{mol}
KI, IODIDE2:	1.390029413	{mol}
HgI_4^{2-}, ML2:	0.004985293	{mol}
Dry soil, WW2 =	900	{g}
HgI_4^{2-}, MS2:	0	{mol}

Bulk balance:
LV2 = LV1 + (WW1*XX1)/1000 {L} (Assume DENSITY1 = water dennsity)
WW2 = WW1*(1-XX1) {g} i.e. 1000 g/liter

Balance in soil WW2:
Unleached Hg: MS2 = WW1*C_Hg*(1/1000)*(1/1000)*(1/200.59)*(1-XX2) {mol}

Balance in liquid LV2:
Hg: ML2 = WW1*C_Hg*(1/1000)*(1/1000)*(1/200.25)*XX2 {mol}
Iodine, I_2: IODINE2 = LV1*0.2 -ML2 {mol}
Iodide, I^-: IODIDE2 = LV1*0.4 - 2*ML2 {mol}

Unit Operation B: Filtration of leached soils

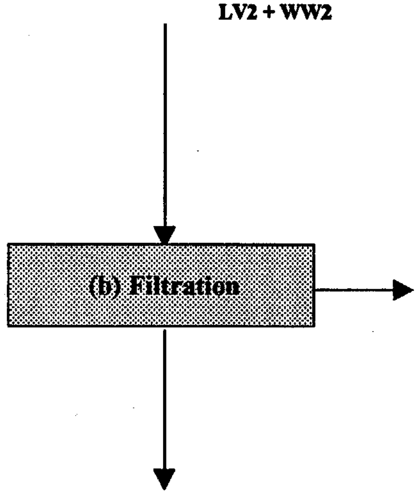
Assume that the filtered soil contains XX3 {wt%} liquid and
density of the leaching liquid LV2 is DENSITY2 {g/liter}
XX3 = 40% DENSITY2 = 1000

Bulk balance:
WW3 = WW2 + XX3*WW2/(1-XX3) {g}
LV3 = LV2 - WW3*XX3/DENSITY2 {liter}

Balance in wet solid WW3:
Hg : MS3 = MS2 +WW3*XX3*(1/DENSITY2)*(ML2/LV2)
Iodine: IODINE3S = WW3*XX3*(1/DENSITY2)*(IODINE2/LV2)
Iodide: IODIDE3S = WW3*XX3*(1/DENSITY2)*(IODIDE2/LV2)

Balance in liquid LV3:
Hg: ML3 = ML2 - WW3*XX3*(1/DENSITY2)*(ML2/LV2)
Iodine: IODINE3L = IODINE2 - IODINE3S
Iodide: IODIDE3L = IODIDE2 - IODIDE3S

Balance in LV5:
LV5 = LV3 + LV4
Hg: ML5 = ML3 + ML4
Iodine: IODINE5 = IODINE3 + IODINE4
Iodide: IODIDE5 = IODIDE3 + IODIDE4
Sulfate: SF4 = CA = FEL6



Wet soil, WW3	1500	{g}
Hg in dry soil, MSS3:	0	{mol}
Hg in retained liquid, MSL3:	0.000831	{mol}
Total Hg, MS3:	0.000831	{mol}
Iodine, IODINE3S:	0.115836	{mol}
Iodide, IODIDE3S:	0.231672	{mol}

Liquid, LV3	3	{L}
Hg, ML3:	0.004154	{mol}
Iodine, IODINE3L:	0.579179	{mol}
Iodide, IODIDE3L:	1.158358	{mol}

Unit Operation C: Wash the leached soil with H_2SO_4+K_2SO_4

WWf	1500
LV17	4.1
IODINEf	0.016952
IODINE4	0.098884
SF4	0.747927
SF15	0.876143

Assumption: Sulfate concentration in LV15 should be controlled to give a
sulfate concentration in LV4 liquid same as the calcium concentration in LV7 liquid,
i.e., SF4 = CAL(SEE Unit F)

Required moles of sulfate SF15 to match the total Ca^{2+} moles
SF15 = SF4/(1-((WWf*XXf/DENSITY17)/LV17)) (Assume liquid content in final wet soil XXf{wt%} = 40%)
DENSITY17 {g/liter} = 1000

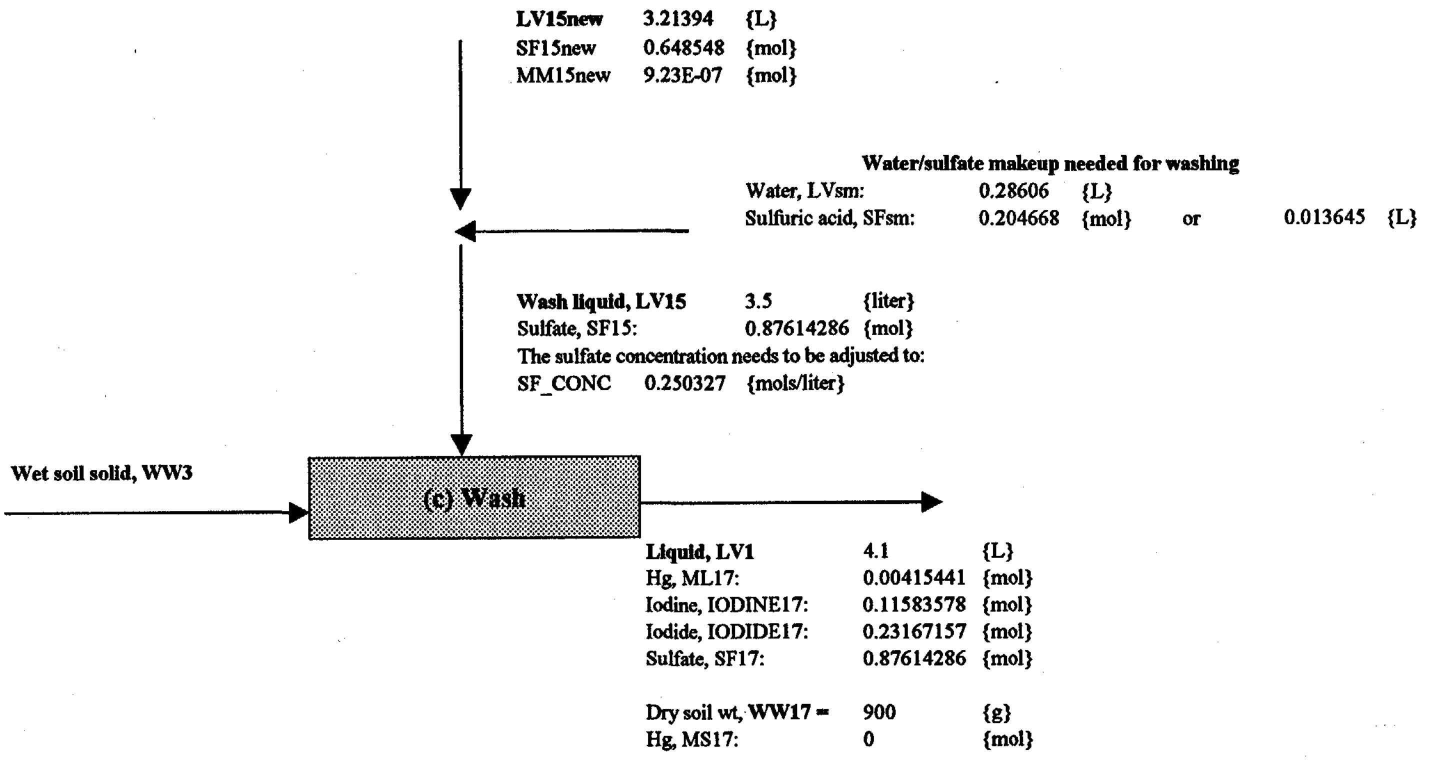
For the first cycle, assume that LV15 {liter}/WW3 {g} = 3.5*E-3 (For later cycles, LV15new)
WWf = WW3
LV17 = WW3*XX3/DENSITY2 + LV15 = WWf*XXf/DENSITY17 + LV4 (Approximation: LV4=LV15, WWf = WW3)
IODINEf = IODINE3S*((WWf*XXf/DENSITY17)/LV17)
IODINE4 = IODINE3S - IODINEf = IODINE3S(1-((WWf*XXf/DENSITY17)/LV17))
SF4 = CAL
SF15 = SF4/(1-((WWf*XXf/DENSITY17)/LV17))
In order to match the moles of Ca^{2+}, the sulfate concentration in Liquid LV15 should be controlled around
SF_CONC = SF15/LV15

Bulk balance:
LV15 = (3.5*E(-3))*WW1 {L}
LV17 = WW3*XX3/DENSITY2 + LV15 {L}
WW17 = WW3*(1-XX3) {dry wt. g}

Balance in wash liquid LV15:
Sulfate: SF15 = SF4/(1-((WWf*XXf/DENSITY17)/LV17))

Balance in LV17:
Hg: ML17 = ML3 +ML15 (Assume that ML15 = 0 for the first cycle)
Iodine: IODINE17 = IODINE3S trace for later cycles
Iodide: IODIDE17 = IODIDE3S
Sulfate: SF17 = SF15

Balance in dry soil WW17:
Hg: MS17 = MS2



LV15new	3.21394	{L}
SF15new	0.648548	{mol}
MM15new	9.23E-07	{mol}

Water/sulfate makeup needed for washing

Water, LVsm:	0.28606	{L}			
Sulfuric acid, SFsm:	0.204668	{mol}	or	0.013645	{L}

Wash liquid, LV15	3.5	{liter}
Sulfate, SF15:	0.87614286	{mol}

The sulfate concentration needs to be adjusted to:

SF_CONC 0.250327 {mols/liter}

Liquid, LV1	4.1	{L}
Hg, ML17:	0.00415441	{mol}
Iodine, IODINE17:	0.11583578	{mol}
Iodide, IODIDE17:	0.23167157	{mol}
Sulfate, SF17:	0.87614286	{mol}
Dry soil wt, WW17 =	900	{g}
Hg, MS17:	0	{mol}

Unit C - Wash

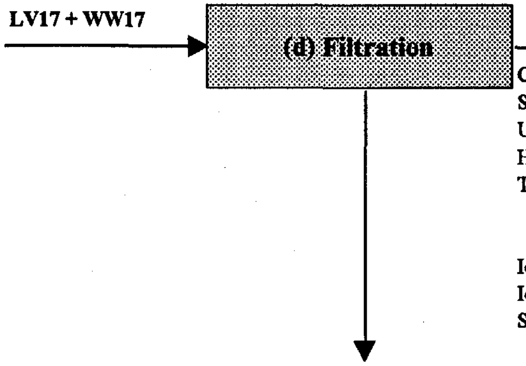
Unit D: Filtration of washed soils

Assumption:
The final soil cake contains XXf {wt%} of liquid LV17. (see Unit C sheet for value assignment)
(for the first cycle, there is no Hg in wash liquid LV15; thus, ML15 =0, see Unit C sheet)

Soil wet weight WWf = WW3
Soil dry weight DWf = WW3*(1-XXf)
Unleached Hg in dry soil: MSSf = MS2
Hg in retained liquid: MSLf = WWf*XXf*(1/DENSITY17)*((MSL3+ML15)/LV17)
Total Hg in the wet soil: MSf = MSSf + MSLf
Iodine: IODINEf = IODINE3S*WWf*XXf*(1/DENSITY17)/LV17
Iodide: IODIDEf = IODIDE3S*WWf*XXf*(1/DENSITY17)/LV17
Sulfate: SFf = SF17*WWf*XXf*(1/DENSITY17)/LV17

LV4 = LV17 - WWf*XXf/DENSITY17
Hg: ML4 = MSL3 - MSLf
Iodine: IODINE4 = IODINE17 - IODINEf
Iodide: IODIDE4 = IODIDE17 - IODIDEf
Sulfate: SF4 = CAL

SF17 -SFf =SF4

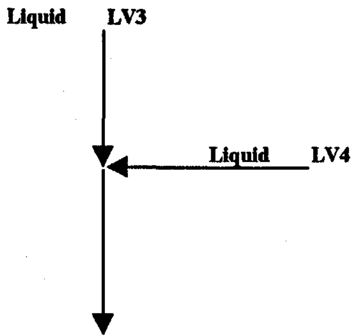


Clean soil wet weight, WWf	1500	{g}
Soil dry weight, DWf	900	{g}
Unleached Hg in dry soil, MSSf:	0	{mol}
Hg in retained liquid, MSLf:	0.000122	{mol}
Total Hg in the wet soil, MSf:	0.000122	{mol}
	16.26016	{ppm}
Iodine, IODINEf:	0.016952	{mol}
Iodide, IODIDEf:	0.033903	{mol}
Sulfate, SFf:	0.128216	{mol}

Liquid, LV4	3.5	{L}
Hg, ML4:	0.000709	{mol}
Iodine, IODINE4:	0.098884	{mol}
Iodide, IODIDE4:	0.197768	{mol}
Sulfate, SF4:	0.747927	{mol}
SF17 -SFf =	0.747927	{mol}

Stream Merge

Balance in LV5:
LV5 = LV3 + LV4
Hg: ML5 = ML3 + ML4
Iodine: IODINE5 = IODINE3L + IODINE4
Iodide: IODIDE5 = IODIDE3L + IODIDE4
Sulfate: SF5 = SF4



Liquid, LV5	6.5	{L}
Hg, ML5:	0.004864	{mol}
Iodine, IODINE5:	0.678063	{mol}
Iodide, IODIDE5:	1.356126	{mol}
Sulfate, SF5:	0.747927	{mol}

Unit E: I_2 reduction and Hg reduction (pH requirement?)

Reduction reactions:

$Fe + I_2 \longrightarrow Fe^{2+} + 2I^-$

$Fe + HgI_4^{2-} \longrightarrow Fe^{2+} + 4I^- + Hg$

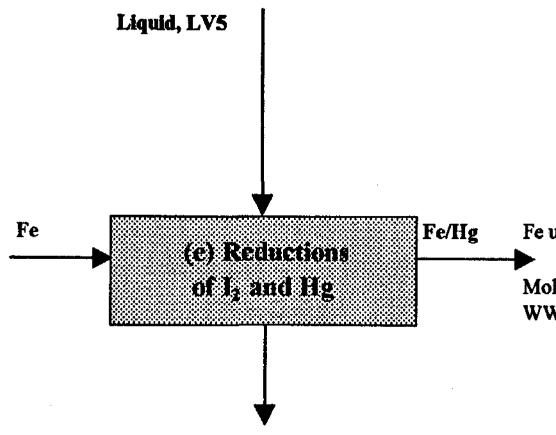
Assume 100% reduction conversion yield, i.e.,
CONV1 = 100% CONV2 = 100%

Assume that we supply FE_in 1000 {g}
Each cycle consumes Fe:
FE = (IODINE5*CONV1 + ML5*CONV2)*55.85 {g}
Fe left unused: FE_out = Fe_in - FE {g}

Fe added, FE_in: 1000 {g}
Fe consumed, FE: 38.14146 {g}

Amount of soluble Hg reduced into molecular Hg:
WWHg = ML5*CONV2*200.59 {g}

Balance in liquid LV6:
LV6 =LV5 {L}
Total Fe^{2+} generated:
FEL6 = IODINE5*CONV1 + ML5*CONV2 {mol}
Total iodide mol:
IODIDE6 = IODIDE 5 + 2*IODINE5*CONV1 + 4*ML5*CONV2 {mol}
Trace amount of molecular Hg left: MM6 = LV6* HG_eq/200.59 {mol}
(Assume HG_eq = 0.00006 {g/liter})
Sulfate: SF6 = SF5



Fe unused, FE_out: 961.8585 {g}

Molecular Hg produced:
WWHg : 0.97561 {g}

Liquid, LV6	6.5	{L}
Fe^{2+} generated, FEL6:	0.682927	{mol}
Iodide, IODIDE6:	2.731707	{mol}
Hg, MM6:	1.94E-06	{mol}
Sulfate, SF6:	0.747927	{mol}

Unit F: Precipitation of Fe^{2+} to form $Fe(OH)_2$

$CaO + H_2O + Fe^{2+} \longrightarrow Ca^{2+} + Fe(OH)_2(s)$
$Ca^{2+} + SO_4^{=} \longrightarrow CaSO_4(s)$

CaO needed to precipitate Fe^{2+} :
CAO = (FEL6 + LV6*10^{-2})*56.08 {g}

Ca^{2+} produced:
CAL = FEL6 + LV6*10^{-2} {mol}

Total iodide:
IODIDE7 = IODIDE6 {mol}

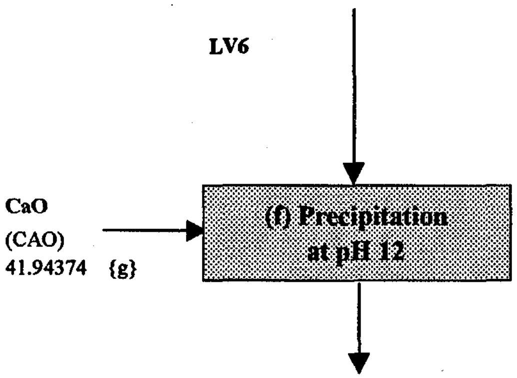
Assume that the Fe^{2+} precipitation is complete, thus the amount of $Fe(OH)_2$ precipitates:
FES = FEL6*90 {g}

Amount of $CaSO_4$ precipitates:
SFS = SF6*136.0 {g}

IODIDE7 = IODIDE6
MM7 = MM6

Compare CAL with SF6?? (THEY SHOULD BE THE SAME VALUE)

LV7 = LV6 - LVw (LVw = FEL6*18/1000 liter)



Liquid, LV7	6.487707	{L}
Ca^{2+}, CAL:	0.747927	{mol}
$SO_4^{=}$, SF7:	0.747927	{mol}
CaSO4, SFS:	101.718	{g}
$Fe(OH)_2$, FES:	61.46341	{g}
Iodide, IODIDE7:	2.731707	{mol}
Hg, MM7:	1.94E-06	{mol}

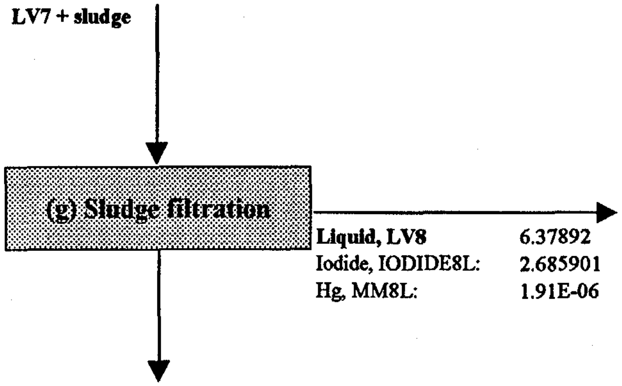
$Ca^{2+} + SO_4^{=} \longrightarrow CaSO_4(s)$

Unit G: Filtration of $Fe(OH)_2$ and $CaSO_4$ sludge

Assume that the filtered cake contains XX8 {wt%} of liquid LV7.
XX8 = 40%
Assume that liquid density of LV7:
DENSITY7 = 1000 g/liter

Sludge dry weight:
SDW8 = SFS + FES {g}
Sludge wet weight:
WW8 = SDW8 + SDW8*XX8/(1-XX8) {g}
Total iodide:
IODIDE8S = (IODIDE7/LV7)*(WW8*XX8/DENSITY7) {mol}
Trace Hg {mol}:
MM8S = (MM7/LV7)*(WW8*XX8/DENSITY7)

Balance for liquid LV8:
LV8 =LV7-WW8*XX8/DENSITY7
Iodide: IODIDE8L = IODIDE7 - IODIDE8S
Hg: MM8L = MM7-MM8S

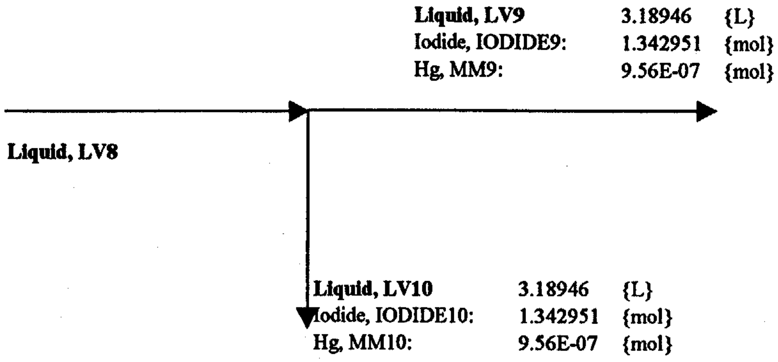


Liquid, LV8	6.37892	{L}
Iodide, IODIDE8L:	2.685901	{mol}
Hg, MM8L:	1.91E-06	{mol}

Sludge cake of $Fe(OH)_2$ and $CaSO_4$

Wet wt., WW8:	271.9691	{g}
Iodide, IODIDE8S:	0.045806	{mol}
Hg, MM8S:	3.26E-08	{mol}
	0.024045	{ppm}

Stream Splitting (50/50)



Stream Splitting

Unit H: pH adjustment to pH 3.5 by addition of H_2SO_4 (98%)

H_2SO_4 needed:

SF11 = LV9*($10^{-2}/2 + 10^{-3.5}/2$) {mol}

Assume density of 98% sulfuric acid

DENSITY11 = 1500 {g/liter}

Volume of 99% H2SO4:

LV11 = SF11*98*(1/DENSITY11) {L}

LV12 = LV9 + LV11 {L}

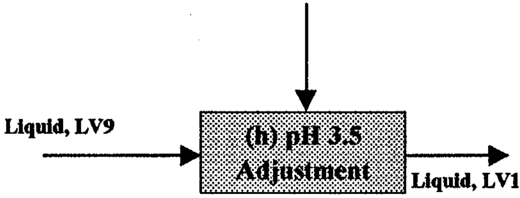
Sulfate: SF12 = SF11

Iodide: IODIDE12 = IODIDE9

Hg: MM12 = MM9

Pure H_2SO_4 needed, SF11: 0.016452 {mol}

H_2SO_4 (98%), LV11 0.001075 {L}



Liquid, LV12	3.190535	{L}
Sulfate, SF12:	0.016452	{mol}
Iodide, IODIDE12:	1.342951	{mol}
Hg, MM12:	9.56E-07	{mol}

Unit I: Iodide oxidation at pH 3.5 by addition of hydrogen peroxide

$2 I^- + H_2O_2 + H_2SO_4 \longrightarrow I_2 + 2H_2O + SO_4^{=}$

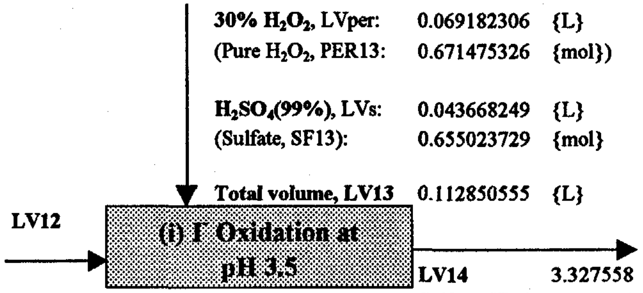
Pure peroxide needed:
PER13 = (1/2)*IODIDE12 {mol}
30% {wt%} peroxide needed:
Assume that density of 30% peroxide
DENSITY13a = 1100 {g/liter}
LVper = (1/2)*IODIDE12*34*(1/30%)*(1/DENSITY13a) {L}

Pure sulfuric acid needed to add:
SF13 = (1/2)*IODIDE12 - SF12 {mol}
Volume of 98% sulfuric acid needed to add:
LVs = SF13*98/DENSITY11/.98 {L}

LV13 = LVper + LVs {L}

LV14 = LV12 + LV13 +LVwa {L} (LVwa = IODIDE12*18/1000)
Sulfate: SF14 = SF12 + SF13 {mol}
Hg: MM14 = MM12 {mol}
Iodine solids produced :
IODINE14 = (1/2)*IODIDE12 {mol}
= IODINE14*253.81 {g} dry

30% H_2O_2, LVper:	0.069182306	{L}
(Pure H_2O_2, PER13:	0.671475326	{mol})
H_2SO_4(99%), LVs:	0.043668249	{L}
(Sulfate, SF13):	0.655023729	{mol}
Total volume, LV13	0.112850555	{L}



LV14	3.327558	{L}
Sulfate, SF14	0.671475	{mol}
Hg, MM14:	9.56E-07	{mol}
Iodine solid		
IODINE14:	0.671475	{mol}
WW14:	170.4272	{g}dry

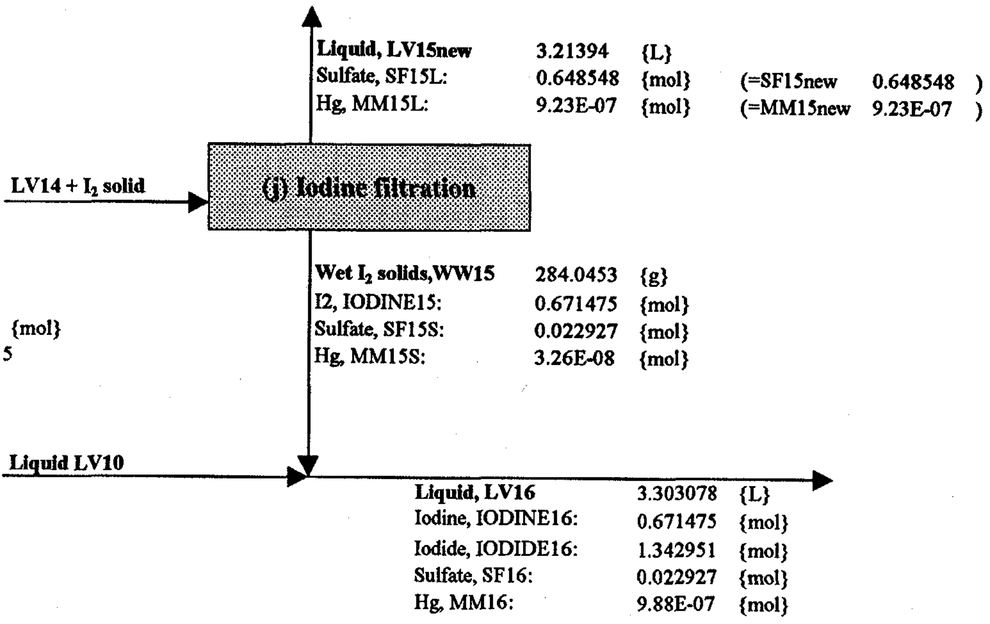
Unit J: Filtration of iodine solids

Assume that the iodine cake contains XX15 {wt%}
liquid LV15new. XX15 = 40%
Assume that the density of LV15 is
DENSITY15 = 1000 {g/liter}

(Iodine solubility in water is 0.029g/100g water)
Wet iodine solid weight:
WW15 = WW14*(1+XX15/(1-XX15)) {g}
Iodine: IODINE15 = IODINE14 {mol}
Sulfate:
SF15S = (SF14/LV14)*WW15*XX15/DENSITY15 {mol}
Hg: MM15S = (MM14/LV14)*WW15*XX15/DENSITY15

LV15new = LV14 - WW15*XX15/DENSITY {L}
Sulfate: SF15L = SF15new = SF14 - SF15S {mol}
Hg: MM15L = MM14 - MM15S {mol}

Assume that the I_2 solids can be completely dissolved in the liquid LV10.
LV16 = LV10 + WW15*XX15/DENSITY15
Iodine: IODINE16 = IODINE14
Iodide: IODIDE16 = IODIDE10
Sulfate: SF16 = SF15S
Hg: MM16 = MM15S + MM10

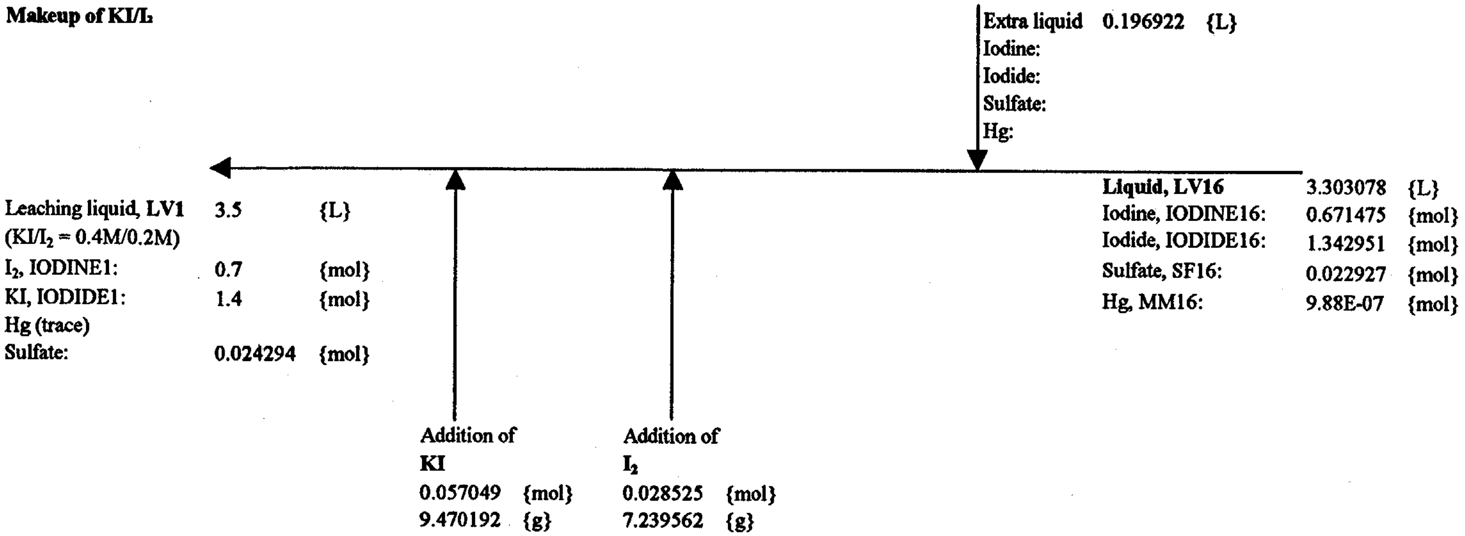


Liquid, LV15new 3.21394 {L}
Sulfate, SF15L: 0.648548 {mol} (=SF15new 0.648548)
Hg, MM15L: 9.23E-07 {mol} (=MM15new 9.23E-07)

Wet I_2 solids,WW15 284.0453 {g}
I2, IODINE15: 0.671475 {mol}
Sulfate, SF15S: 0.022927 {mol}
Hg, MM15S: 3.26E-08 {mol}

Liquid, LV16 3.303078 {L}
Iodine, IODINE16: 0.671475 {mol}
Iodide, IODIDE16: 1.342951 {mol}
Sulfate, SF16: 0.022927 {mol}
Hg, MM16: 9.88E-07 {mol}

Makeup of KI/I₂



Leaching liquid, LV1 3.5 {L}
(KI/I_2 = 0.4M/0.2M)
I_2, IODINE1: 0.7 {mol}
KI, IODIDE1: 1.4 {mol}
Hg (trace)
Sulfate: 0.024294 {mol}

Addition of
KI
0.057049 {mol}
9.470192 {g}

Addition of
I_2
0.028525 {mol}
7.239562 {g}

Extra liquid 0.196922 {L}
Iodine:
Iodide:
Sulfate:
Hg:

Liquid, LV16 3.303078 {L}
Iodine, IODINE16: 0.671475 {mol}
Iodide, IODIDE16: 1.342951 {mol}
Sulfate, SF16: 0.022927 {mol}
Hg, MM16: 9.88E-07 {mol}

Makeup KI-I2

Appendix B

EXAMPLE OF PLANNING DOCUMENT USED AT THE K-25 SITE FOR DEMONSTRATIONS

CENTER FOR ENVIRONMENTAL TECHNOLOGY TECHNOLOGY DEMONSTRATION PLANNING DOCUMENT OAK RIDGE K-25 SITE

OCTOBER 1994

prepared by
Environmental Management Division
Oak Ridge K-25 Site
Oak Ridge, Tennessee

SUMMARY

The primary mission of the Oak Ridge K-25 Site is to support the missions of the Environmental Restoration/Waste Management (ER/WM) business unit and other tenants at the site in a safe, reliable and efficient manner. Part of the mission includes hosting technology demonstrations that support ER/WM activities. The Center for Environmental Technology (CET) was created to facilitiate the selection and implementation of technology demonstrations. This planning document is intended to provide key information in planning site support for demonstrations that will be conducted at the K-25 Site. It is not intended to provide a comprehensive discussion that addresses all aspects of operating at the K-25 Site. Details on items listing in the planning list should be obtained from the appropriate technical disiplines. In addition, this document does not attempt to define how a demonstration should be managed.

The roles and responsibilities of the various participants involved in the demonstration should be clearly defined. Potential lead groups/agencies of demonstrations include:

- Martin Marietta Energy Systems (Energy Systems) personnel,
- Energy Systems subcontractors,
- Department of Energy prime contractors,
- other federal agencies, and
- prime contractors to other federal agencies.

Contracting mechanisims for conducting demonstration will also vary based on the participants involved in the demonstration. These include contracts, subcontracts, interagency agreements and cooperative research and development agreements (CRADA). The contracting mechanism and the representives conducting demonstration will have a direct impact on the actions to be taken by the K-25 Site in planning and supporting a technology demonstration.

Other factors are also important in planning demonstration support. The type and volume of material to be treated will define the organizations that need to be involved in planning and suppoting demonstration activities. The use of contaminated material/wastes will require more planning than a demonstration using only surrogates (clean material). Hazardous wastes (Resource Concervation and Recovery Act, and Toxic Substance Control Act wastes) may require various types of approvals and notifications, depending on the volume of material to be treated. The level of radioactive contamination can affect personal protection and training requirements. Limits exist for the amount of contaminated hazadous waste that can be treated by a technology demonstration; however, there are no regulatory limits on the amount of surrogate and/or radioactive material that can be treated. Other regulatory drivers may be applied if the material to be treated is a solid waste.

This planning guide should be used to determine requirements that may be applicable to a technology demonstration and what additional documentation is required prior to initiating demonstration activities. This guide can provide useful information when initiating demonstration plannig with various technical disiplines.

Center for Environmental Technology
Technology Demonstration Planning List
Oak Ridge K-25 Site

Item or Activity	Applicable (Yes/No)	Comments
1. Lead Group/Agency/Company		
2. Types of contaminants		
a. RCRA		
b. TSCA		
c. Radioactive		
d. Mixed (hazardous & radioactive)		
e. Solid waste		
3. Amount of material to be treated		
4. Regulatory permits		
a. RCRA Research, Development & Demonstration permit		
b. RCRA Part B permit		
c. EPA approval for TSCA waste		
d. Approval as a pretreatment facility (for water only)		
e. NPDES prmitted discharge point		

Item or Activity	Applicable (Yes/No)	Comments
f. CERCLA approval (under the Federal Facilities Agreement for ORR)		
g. Air permitting evaluation (exemption from air permitting/air permit required)		
5. Environmental Requirements		
a. NEPA documentation		
b. RCRA accumulation and 90-day storage areas		
c. Low level waste storage area		
d. Use/storage of hazardous materials and/or fuel (gasoline, diesel)		
e. Secondary containment for hazardous materials and hazardous wastes		
f. Monitoring requirements for air emissions		
6. Waste Transportation, Storage and Disposal		
a. Off site shipment of wastes (to and from K-25)		
b. Types and numbers of storage containers (bulk vs containers, liquids/sludges/solids)		
c. Disposal of treated and untreated wastes		
d. Types and amounts of secondary and personal protective equipment wastes and disposal method		

Item or Activity	Applicable (Yes/No)	Comments
e. Shipment of analytical samples off site		
7. Training		
a. General Employee Training		
b. 40 hr or 24 hr HAZWOPER		
c. 8 hr HAZWOPER supervisory		
d. Radiological Worker II		
e. Off road driver training		
8. Health & Safety		
a. Health & Safety plan		
b. Safety Work Permit (not required if using a Health & Safety plan)		
c. Radiological Work Permit		
d. Safety assessment		
e. Inspect demonstration equipment for health & safety concerns prior to arriving on site (preferably at vendors facility)		
f. Lock out/tag out activities/procedures/permit and electrical hazards		
g. Confined space entry/permit		
h. Hoisting and rigging activites		

Item or Activity	Applicable (Yes/No)	Comments
i. Elevated work requirements		
j. Noise hazards		
k. Flammables and combustibles to be used		
l. Respirator use/procedures		
m. Disposal/reusable/laundrable personal protective equipment/anti-contamination clothing		
n. Personal monitoring/dosimetry/bioassay		
o. Use of compressed gas cylinders		
9. Fire Protection		
a. Fuel/propane use and storage		
b. Building egress (for demonstrations conducted inside buildings)		
c. Hot work/welding/burning permit		
10. Miscellaneous Permits, Requests, Approvals, and Notifications		
a. Operational Readiness Review		
b. Excavation/penetration permit (for penetrations >4" in concrete, >12" in soil/asphalt, and for building walls)		

Item or Activity	Applicable (Yes/No)	Comments
c. Electrical service request (for electrical power, but does not include disconnects)		
d. Request for sanitary sewer connection		
e. Request for potable water		
f. Request for discharge of non-contaminated water (to discharge accumulated water to storm drain)		
g. Visitor passes		
h. Security plans for uncleared visitors in L-cleared and Q-cleared areas		
i. Request for Foreign National Unclassified visit or assignment (for non-US citizens)		
j. Notification of PSS/Emergency Preparedness of start up of operations, MMES contact, and use/storage of hazardous materials		
k. K-25 Area Manager (Facility & Property Management Dept.) facility siting approval		
l. Export Control approval for mailing/shipping documents & equipment into and out of the U.S.		
m. Road closures required and duration		
11. Community Relations/Publicity		

Item or Activity	Applicable (Yes/No)	Comments
a. Preparation of demonstration flyers/distribution		
b. Notification of Community Relations/press release		