



**FATE OF SOLUBLE URANIUM IN THE
I₂/KI LEACHING PROCESS FOR
MERCURY REMOVAL**

W. D. Bostick, W. H. Davis, and R. J. Jarabek

**Materials and Chemistry Laboratory
East Tennessee Technology Park**

September 1997

MASTER

**Prepared by
the East Tennessee Technology Park
Oak Ridge, Tennessee 37831-7133
managed by
LOCKHEED MARTIN ENERGY SYSTEMS, INC.
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-84OR21400**

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

**MANAGED BY
LOCKHEED MARTIN ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
DEPARTMENT OF ENERGY**

A handwritten signature in dark ink, appearing to be "R. J. Jarabek", located in the bottom right corner of the page.

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P. O. Box 62, Oak Ridge, TN 37831; prices available from (423) 576-8401, FTS 626-8401.

Available to the public from the National Technical Information Service U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency or agent thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency or agent thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

**Portions of this document may be illegible
in electronic image products. Images are
produced from the best available original
document.**

K/TSO-55

**FATE OF SOLUBLE URANIUM IN THE I₂/KI
LEACHING PROCESS FOR MERCURY REMOVAL**

W. D. Bostick, W. H. Davis, and R. J. Jarabek

**Materials and Chemistry Laboratory
East Tennessee Technology Park**

September 1997

CONTENTS

LIST OF FIGURES	iii
ABSTRACT	iv
1. INTRODUCTION	1
2. METHODS AND MATERIALS	5
2.1 EXTRACTANT SYSTEMS	5
2.1.1 Iodine/Iodate Reagent	5
2.1.2 Hypochlorite/Chloride Reagent	5
2.2 RADIOLOGICAL TRACERS	5
2.2.1 Uranium-233	6
2.2.2 Mercury-203	6
2.3 GAMMA COUNTING	6
2.4 OXIDANT (IODIDE) MONITORING	6
2.5 MEASUREMENT OF SOLUTION PH AND REDOX POTENTIAL (EH)	6
2.6 FILTRATION MEDIA	7
2.7 ZERO-VALENT IRON (REDUCTANT) REAGENTS	7
2.7.1 Granular Scrap Iron Reagent	7
2.7.2 Steel Wool Reagent	7
2.8 MIXED WASTE SLUDGE SAMPLE	8
2.9 INITIAL SLUDGE EXTRACTION TESTING	8
3. RESULTS	9
3.1 EXTRACTION STEP: EXTRACTION OF AUTHENTIC MIXED WASTE SLUDGE	9
3.2 REMOVAL OF SOLUBLE MERCURY AND URANIUM WITH USE OF STEEL WOOL REAGENT	11
3.2.1 Testing with Surrogate Extraction Media	11
3.3 REMOVAL OF SOLUBLE OXIDANT AND URANIUM WITH USE OF GRANULAR SCRAP IRON	12
3.3.1 Reduction of Excess Iodine with Granular Particulate Iron	12
3.3.2 Reduction of Soluble Uranium with Granular Particulate Iron	14
3.4 METALS PRECIPITATION BY TREATMENT WITH LIME SLURRY	15
3.5 REGENERATION OF IODINE REAGENT	17
4. CONCLUSIONS AND RECOMMENDATIONS	19
5. REFERENCES	21

LIST OF FIGURES

	Page
1. Flowchart for I ₂ /KI Extraction Process	2
2. Response of Chlorine Electrode to Iodine Concentration ([I ₂], mol/L). Diluent is 0.4 mol/L KI; temperature 23 °C.	13
3. Reduction of Iodine with use of MasterBuilders Iron: Relative Kinetics as a Function of Temperature, as Monitored with Use of a Chlorine Electrode	14
4. Removal of Soluble Uranium (²³³ U Tracer) with use of MasterBuilders Iron at 50 °C	15
5. Precipitation from pH Adjustment Using 20% Lime Slurry (Mixture Settled)	16

LIST OF TABLES

1. Analysis of 9201-4 Sludge and Supernate	9
2. Extraction of 9201-4 Sludge Centrifuge Cake	10
3. Mass Balance for Extraction of Mercury and Uranium from 9201-4 Sludge Filtercake	11
4. Treatment of Traced Solutions with use of Steel Wool (Nominal Dosage 40 g/L): Effect of Dehalogenation with use of Sodium Bisulfite (NaHSO ₃)	12
5. Treatment of Simulated Spent I ₂ /KI Extraction Medium: Soluble Uranium Tracer Activity	17

ABSTRACT

General Electric Corporation has developed an extraction and recovery system for mercury, based upon the use of iodine (oxidant) and iodide ion (complexing agent). This system has been proposed for application to select mercury-contaminated mixed waste (i.e., waste containing radionuclides as well as other hazardous constituents), which have been generated by historic activities in support of U.S. Department of Energy (DOE) missions.

This system is compared to a system utilizing hypochlorite and chloride ions for removal of mercury and uranium from a sample of authentic mixed waste sludge. Relative to the hypochlorite ("bleach") system, the iodine system mobilized more mercury and less uranium from the sludge.

An engineering flowsheet has been developed to treat spent iodine-containing extraction medium, allowing the system to be recycled; this flowsheet is presented as Figure 1 of the text. The fate of soluble uranium in this series of treatment unit operations was monitored by tracing isotopically-enriched uranyl ion into simulated spent extraction medium (i.e., a solution containing 0.2 mol/L I_2 , 0.4 mol/L KI, and saturated with calcium sulfate in the form of gypsum). Treatment with use of elemental iron is shown to remove >85% of the traced uranium while concurrently reducing excess iodine to the iodide ion. The next unit operation, adjustment of the solution pH to a value near 12 by the addition of lime slurry to form a metal-laden sludge phase (an operation referred to as "lime-softening"), removed an additional 57% of soluble uranium activity, for an over-all removal efficiency of ~96%. However, the precipitated solids did not settle well, and some iodide reagent is held up in the wet filtercake.

Additional steps in the flowsheet include treatment of half of the filtrate from the lime-softening operation with hydrogen peroxide and sulfuric acid, to convert iodide ion to insoluble elemental iodine. The filtrate from this oxidation step is used as a rinse, to help remove residue of spent extractant from the waste solids; this liquid is ultimately recycled through the iron reduction step. The solids from the peroxide oxidation step contain precipitated elemental iodine and calcium sulfate. The iodine component is dissolved with the reserved iodide-containing solution from the lime-softening operation, yielding a solution with proportions of iodine and iodide reagent comparable to the original extraction medium formulation. However, successful execution of the peroxide oxidation unit operation requires care to avoid a rapid decomposition of the peroxide reagent.

1. INTRODUCTION

General Electric Corporation has developed a mercury leaching process utilizing a combination of iodine (oxidant, to convert reduced mercury to the soluble mercuric ion, Hg^{2+}) and iodide (chelating agent, to form the stable complex ion HgI_4^{2-}) (Foust, 1993). This process has been proposed for use in the removal of mercury from select mixed (radiologically contaminated and chemically toxic) waste inventories originating from past and present activities of the U.S. Department of Energy (Gates et al., 1994).

An engineering flowchart based upon this process is presented in Fig. 1 (Klasson, 1997). This flowchart allows recycling/reuse of extraction medium, thus enhancing the economics of the process. Spent extraction medium and rinsate solution are treated with zero-valent (i.e., elemental) iron to recover solubilized mercury by reduction of mercuric ion (Hg^{2+}) to form liquid elemental mercury (Hg) (Bostick et al., K/TSO-6); see Eq. 1:



The standard cell potential, $E^0(\text{cell})$, can be computed from tabulated half-cell data; by sign convention, a positive cell potential represents a thermodynamically favored reaction. Zero-valent iron is also noted to remove other regulated metal ions, including the radionuclides uranium (U) and technetium (Tc) (Bostick et al., K/TSO-35). For soluble uranium (as the uranyl ion, UO_2^{2+}), reduction at near-neutral pH values is less favorable:



The predominant removal mechanism for soluble uranium may be sorption to ferric iron (Fe^{3+}) corrosion products (Bostick et al., K/TSO-35).

Excess iodine (I_2) in the solution is concurrently reduced to iodide ion (I^-):



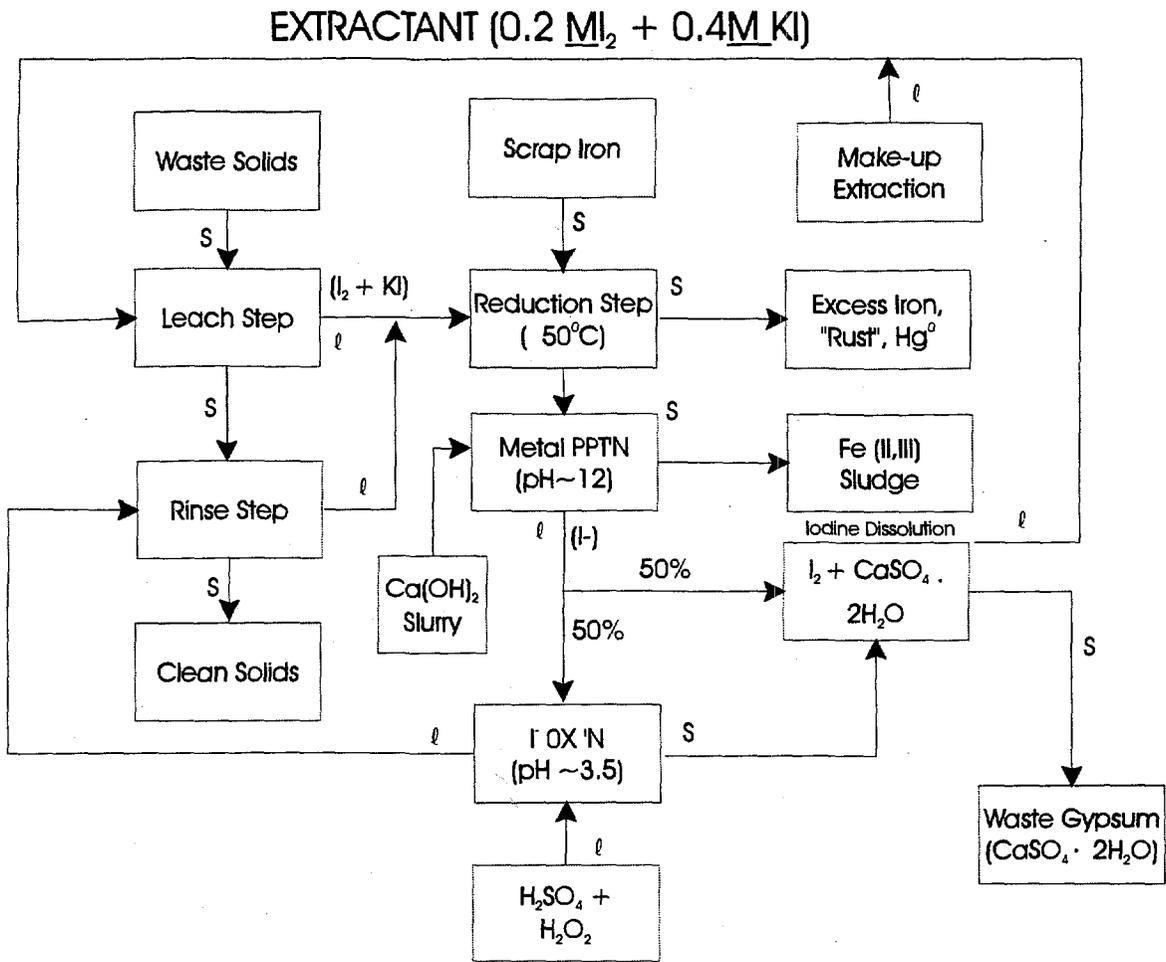


Fig. 1 Flowchart for I_2/KI Extraction Process

The aqueous supernate from the reduction unit operation is next treated with lime slurry (a mixture of $\text{Ca}(\text{OH})_2$ and CaCO_3), raising the pH to a value near 12, in order to precipitate residual heavy metals (predominantly iron, in the form of ferrous ion (Fe^{2+}) from the reduction step (Eq(s). 1 and 3), as well as any ferric ion that may have subsequently formed by oxidation upon exposure to air).

The aqueous supernate from the lime-softening unit operation is split into equal portions. Half of the solution is reoxidized with use of hydrogen peroxide, with careful addition of sulfuric acid to maintain a pH value near 3.5; see Eq. 4:



The aqueous supernate from the iodide oxidation unit operation will be saturated with sparingly-soluble gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and is used as the rinse solution to remove the bulk of spent extraction medium from the treated waste solids. The solid residual from the oxidation step contains excess gypsum plus crystallized iodine. The iodine precipitate is combined with the KI solution reserved from the lime-softening step, where it is redissolved to form a recycled leachant solution containing I_2 and KI in proportions similar to the original leachant composition.

The purpose of the present investigation is to document the fate of uranium, which may be partially solubilized in the processing of mercury-laden mixed waste. Gates et al. (1995) performed some preliminary investigations for the extraction of cerium, used as a nonradiological surrogate for uranium, which was added to synthetic soil and crushed fluorescent lamp matrices. No appreciable cerium (which was added in the form of insoluble cerium oxide, CeO_2) was mobilized by the extraction medium.

We report on the extraction of mercury, uranium, and other metals from authentic mixed waste sludge, which originated from decontamination activities at the Oak Ridge Y-12 Plant Building 9201-4 ("Alpha-4") facility; historic activities in this facility included the Colex process, which used mercury as a solvent (Fellows et al., Y/ER-159/V1). Investigations with this waste stream confirm that the I_2/KI leachant system is very effective for the solubilization of mercury, with only a small mobilization of uranium.

We also investigated the fate of soluble uranium, traced into simulated recycled leachant, in the various unit operations depicted in Fig. 1. Treatment with use of zero-valent iron reductant effectively removed >85% of the traced soluble uranium. Of the residual soluble uranium, ~57% was removed in the lime softening unit operation.

2. METHODS AND MATERIALS

2.1 EXTRACTANT SYSTEMS

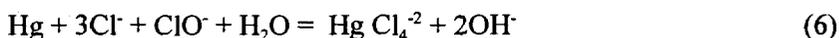
2.1.1 Iodine/Iodate Reagent

General Electric Corporation has developed a mercury leaching process utilizing a combination of iodine (oxidant, to convert reduced mercury to the soluble mercuric ion, Hg^{2+}) and iodide (complexing agent, to form the stable complex ion HgI_4^{2-}) (Foust, 1993). Further documentation of the process has been reported by Gates et al. (1995). For our testing, we used the currently recommended composition of 0.2 mol/L I_2 and 0.4 mol/L KI (Klasson, 1997). For 100 mL aqueous solution, we add 6.64 g KI and 5.08 g I_2 . To simulate recycled medium, we added 0.3 g gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) per 100 mL solution. This solution has a specific gravity (SG) of 1.08. For dissolution of elemental mercury, the nominal reaction stoichiometry is:



2.1.2 Hypochlorite/Chloride Reagent

This reagent was prepared to give similar oxidant and complexant concentrations to the iodine/iodide system (above). Sodium hypochlorite is the active ingredient in household bleach (e.g., Clorox®). For our investigations, we used a stock hypochlorite reagent from EM Scientific (Product SX0610-6), with nominal 4-6 wt% NaOCl (~0.5-0.7 mol/L). Twenty mL of stock hypochlorite reagent and 2.34 g NaCl are used to prepare 100 mL of solution, yielding a nominal ~0.1 mol/L hypochlorite (oxidant) and 0.4 mol/L NaCl. The solution pH is adjusted from an initial value of ~11.8 to a value near 6.5 with use of HCl. The SG of the resulting solution is 1.04. For dissolution of elemental mercury, the nominal reaction stoichiometry is:



2.2 RADIOLOGICAL TRACERS

2.2.1 Uranium-233

In order to facilitate rapid, in-house determination of the fate of soluble uranium, we supplemented some solutions with a tracer solution containing uranyl nitrate that was enriched in the gamma-emitting isotope ^{233}U . Traced solutions containing a total uranium content of 1 mg/L give an equivalent response of ~300 CPM/g with use of our counting equipment.

2.2.2 Mercury-203

Naturally-occurring (nonradiological) solutions of mercuric chloride are supplemented with ^{203}Hg , a gamma-emitting isotope with a radioactive half-life of 46.9 days. The tracer was obtained from Amersham International as a mercuric chloride solution (Product UC0751); see also Bostick et al., K/TSO-6. The tracer solution used in this study was aged nearly two years, and had a relatively low residual activity level, which limits the detection sensitivity.

2.3 GAMMA COUNTING

Aliquots (~2 g) of filtered traced solutions containing gamma-emitting nuclides are counted with use of a Packard Auto-gamma 5000 C radiation measurement system.

2.4 OXIDANT (IODIDE) MONITORING

Active halogen oxidant activity is monitored with use of an Orion Model 97-70 Residual Chlorine electrode. The electrode contains a platinum (redox) sensing element and an iodide-sensing reference element. The combination of the platinum and iodide-sensing elements thus measures the iodine concentration (i.e., the measured potential is proportional to the logarithm of the iodine concentration) (Orion, 1991).

2.5 MEASUREMENT OF SOLUTION PH AND REDOX POTENTIAL (EH)

Solution pH values are determined with temperature-compensated combination pH electrodes, calibrated with standard buffer solutions. It was noted that pH measurements on unbuffered solutions containing iodine were unstable, drifting to higher values when exposed to

air.

Redox potential difference (Eh) is determined with use of a platinum working electrode and Ag/AgCl reference electrode. Observed values are corrected to equivalent values vs the Standard Hydrogen Electrode (SHE) by correcting for the reference electrode potential: $Eh(SHE) = Eh(\text{observed}) + 236 \text{ mV}$. Redox electrode performance was checked against Light's solution (VWR Scientific Cat. No. VW3872-2), which has a reference $Eh(SHE) = +675 \text{ mV}$; readings are deemed acceptable if within $\pm 10 \text{ mV}$ of the reference value (Greenberg et al, 1992).

2.6 FILTRATION MEDIA

Unless otherwise specified, the activity or concentration of *soluble* constituents were determined by measurement on ~2 mL aliquots of solution filtered through 0.2- μm -pore media (Acrodisc, Gelman Sciences Product No. 4192), mounted on disposable Becton-Dickinson plastic syringes.

Bulk phase filtrations were performed using 0.45- μm -pore Nalgene disposable filterware (Nalge Product No. 126-0045).

2.7 ZERO-VALENT IRON (REDUCTANT) REAGENTS

2.7.1 Granular Scrap Iron Reagent

The fine grade (~40 mesh) granular iron product was obtained from MasterBuilder. This and similar products have been previously demonstrated in batch equilibrium and column testing for the removal of soluble heavy metals and chlorinated hydrocarbons from groundwater samples (SAIC, 1997).

2.7.2 Steel Wool Reagent

Coarse steel wool reagent is removed from a Kodak Chemical Recovery Cartridge Model II (catalog no. 173-9953); see also Bostick et al., 1996. The material is used "as-received" (i.e., with no preconditioning).

2.8 MIXED WASTE SLUDGE SAMPLE

A sample of wet sludge from Oak Ridge Y-12 Plant Building 9201-4 ("Alpha-4") was received for this treatability study. Chain-of-Custody paperwork associated with this sample indicates that the sample originated from drummed sludge and debris from tank clean out at Building 9201-4, occurring in September, 1990. The Request for Disposal (RFD) for this lot of material is 12543; the waste carries the EPA hazard code of D009, i.e., it is characteristically hazardous due to mercury (data from the RFD indicates that the mean mercury content in TCLP leachate is 0.51 ± 0.31 mg/L vs the toxicity criterion of 0.2 mg/L).

The subsample that we received for testing (hgtreat.2, RFD #112543.1) was from material stored at Building K-1065. The as-received sludge sample had noticeable free liquid present (i.e., bleed water above a settled sludge layer). The resuspended slurry had a specific gravity (SG) of ~ 1.13 , and a moisture content of ~ 77 wt% (i.e., solids content ~ 23 wt%).

Examination of the dried sludge residue by X-ray diffraction indicated crystalline goethite (FeOOH) which is known to be a very efficient sorbent for the removal of soluble mercuric ion (Bostick et al., K/TSO-35). There was also evidence for meta-cinnabar (HgS), a highly-insoluble form of mercury.

2.9 INITIAL SLUDGE EXTRACTION TESTING

In the initial series of sludge extraction tests, resuspended 9201-4 sludge slurry (25 g) was concentrated by centrifugation (~ 30 min at setting #5, with use of an IEC clinical centrifuge) to yield a centrifuge cake (~ 14 g). The clear supernate (pH ~ 7.5) was removed for separate analysis; it was preserved by the addition of 2% (by volume) ultrapure nitric acid (Ultrex II, Prod. No. 6901-05, J.T. Baker).

The resulting centrifuge cake had a SG ~ 1.26 and a solids content of ~ 35 wt%. The filtercake was contacted with 25 g of extractant medium; resuspension of the paste-like centrifuge cake was not easy, and may affect the efficiency of the solid and liquid phase contact. The resuspended slurry-medium was agitated for 1-h with use of a wrist-action shaker, then allowed to stand quiescent overnight before separating the phases by centrifugation. The supernate (spent extraction medium) was removed with use of a transfer pipette and preserved for analysis. The filtercake was then resuspended in 25 g of deionized water (rinse medium) and shaken for ~ 30 min before again separating the phases by centrifugation. The rinsate solution was removed with use of a transfer pipette and preserved for analysis.

3. RESULTS

3.1 EXTRACTION STEP: EXTRACTION OF AUTHENTIC MIXED WASTE SLUDGE

The effectiveness of the extraction step was evaluated, using authentic mixed waste sludge from the Oak Ridge Y-12 Plant (see Section 2.8). Table 1 compares the analytical results for the raw, as-received sludge slurry (~23 wt% solids) and the supernate solution obtained from centrifugation. The centrifuge supernate has relatively low concentrations of regulated metals.

Table 1. Analysis of 9201-4 Sludge and Supernate

Analyte	As-Received Raw Sludge (A972450-030)	Centrifuge Cake Supernate (A972450-034)
Aluminum	1,900 ug/g	<0.10 mg/L
Arsenic	<11 ug/g	<0.25 mg/L
Barium	61 ug/g	.011 mg/L
Beryllium	1.8 ug/g	<0.0015 mg/L
Cadmium	3.8 ug/g	<0.015 mg/L
Calcium	6,200 ug/g	280 mg/L
Chromium	16 ug/g	<0.050 mg/L
Copper	130 ug/g	<0.020 mg/L
Iron	59,000 ug/g	<0.025 mg/L
Lead	37 ug/g	<0.25 mg/L
Magnesium	450 ug/g	40 mg/L
Mercury	5,900 mg/g	<0.05 mg/L
Nickel	260 ug/g	0.073 mg/L
Phosphorous	290 ug/g	1.9 mg/L
Selenium	12 ug/g	<0.25 mg/L
Silver	<1.3 ug/g	<0.03 mg/L
Sodium	660 ug/g	590 mg/L
Uranium	44 ug/g	0.63 mg/L
Zinc	260 ug/g	0.053 mg/L

In this testing, the isolated centrifuge cake was contacted with extractant (NaOCl/NaCl or I₂/KI)

at a dosage of 25 g extraction medium to ~13.8 g centrifuge cake (equivalent to 25 g of original wet sludge slurry or ~5.75 g dried solids). The centrifuge cake was resuspended in the extraction medium, and the sealed container was shaken for 60 min, then the phases were separated by recentrifugation. The supernate was removed, representing spent extraction medium. The centrifuge cake was rinsed by resuspending in 25 mL of deionized water, and shaking the sealed container for 60 min. The supernate was removed, representing a water rinse. Analytical data are summarized in Table 2. Results for mercury and uranium, expressed as a mass balance (i.e., % of initial value recovered in each treatment step), are presented in Table 3.

Table 2. Extraction of 9201-4 Sludge Centrifuge Cake

Analyte (mg/L)	System: NaOCl/NaCl		System: I2/KI	
	Extract A972450-037	Rinse A972450-032	Extract A972450-036	Rinse A972450-031
Aluminum	<1.0	<0.40	<4.0	<0.40
Arsenic	<2.5	<1.0	<10	<1.0
Barium	0.18	0.066	<0.2	0.052
Beryllium	<0.015	<0.006	<0.06	<0.006
Cadmium	0.22	<0.06	0.91	<0.06
Calcium	1,300	440	1,200	410
Chromium	<0.50	0.27	<0.20	<0.20
Copper	<0.20	<0.08	<0.80	<0.08
Iron	<0.25	<0.10	<1.0	<0.10
Lead	<2.5	<1.0	<10	<1.0
Magnesium	64	19	66	20
Mercury	1,100	580	4,200	1,300
Nickel	0.57	<0.20	<2.0	<0.20
Phosphorous	<10	<4.0	13,000	350
Potassium	53	19	9,900	2,900
Selenium	<2.5	<1.0	<10	<1.0
Silver	<0.30	<0.12	<1.2	<0.12
Sodium	14,000	4,600	260	79
Uranium	3.50	1.10	2.10	0.83
Zinc	0.31	0.36	0.57	0.11

**Table 3. Mass Balance for Extraction of Mercury and Uranium
from 9201-4 Sludge Filtercake**

Percent Recovery from Sludge Sample	Extractant: Deionized Water	Extractant: NaOCl/NaCl	Extractant: I ₂ /KI
Mercury:			
Centrifuge Supernate:	<0.003%	<0.003%	<0.003%
Extractant:	0.13%	18.4%	64.2%
Water Rinse:	<0.003%	10.0%	22.4%
Total:	0.13%	28.4%	86.6%
Uranium:			
Centrifuge Supernate:	0.16%	0.14%	0.14%
Extractant:	0.78%	7.85%	4.31%
Water Rinse:	0.38%	2.55%	1.92%
Total:	1.32%	10.54%	6.37%

Compared to the NaOCl/NaCl system, I₂/KI extraction system appeared to be more aggressive for removing mercury from the sludge waste; in contrast, it was somewhat less aggressive for the mobilization of uranium.

3.2 REMOVAL OF SOLUBLE MERCURY AND URANIUM WITH USE OF STEEL WOOL REAGENT

3.2.1 Testing with Surrogate Extraction Media

Aliquots of simulated recycled extraction media were spiked with gamma-emitting tracer (either ²⁰³Hg or ²³³U). Batch tests were performed to determine the fate of the tracer after treatment with use of steel wool (nominal dosage: 40 g steel per liter of solution; phases are contacted with use of a wrist-action shaker for ~12-h at ambient temperature). Data are summarized in Table 4. Removal efficiencies for soluble Hg and U, in either NaOCl/NaCl or I₂/KI medium, were typically >90%. The low activity of the mercury tracer prevented an accurate assessment of removal efficiencies (due to the low initial activity and a residual activity that was typically near the detection limit). Treatment with iron reagent also appeared to remove excess oxidant (i.e., treatment decolorized the I₂/KI medium).

In a parallel test, excess oxidant was first removed by addition of a stoichiometric excess of sodium bisulfite (NaHSO₃) solution (added in an amount sufficient to decolorize the I₂/KI

medium), before contact with the steel wool reagent. Apparently, the steel wool also removed the excess bisulfite reagent, since the steel wool turned black, and the vapor in the container headspace smelled like sulfide ion, or "rotten eggs". Removal efficiency for the tracers was no better for solutions that were pretreated to remove excess active halogen oxidant before treatment with steel wool.

Table 4. Treatment of Traced Solutions with use of Steel Wool (Nominal Dosage 40 g/L)*: Effect of Dehalogenation with use of Sodium Bisulfite (NaHSO₃)

Sample	Nominal Initial Conc. (Tracer)	Initial Activity (CPM/g)	Final Activity (CPM/g)	Removal Efficiency for soluble tracer
Blank (distilled water)	NA	0.36 (± 0.63)	NA	NA
NaOCl/NaCl	Hg(tot) ~54 mg/L (Hg-203)	11.80 (± 1.57)	0.47 (± 0.47)	96%
	U(tot) ~4.3 mg/L (U-233)	998.2 (± 5.71)	22.75 (± 1.74)	98%
NaOCl/NaCl + NaHSO ₃	Hg(tot) ~54 mg/L (Hg-203)	10.21 (± 1.84)	1.17 (± 0.77)	89%
	U(tot) ~4 mg/L (U-233)	1042 (± 11.75)	60.50 (± 6.56)	94%
I ₂ /KI	Hg(tot) ~54 mg/L (Hg-203)	10.78 (± 2.00)	1.81 (± 0.75)	83%
	U(tot) ~4 mg/L (U-233)	577 (± 3.88)	27.54 (± 1.01)	95%
I ₂ /KI + NaHSO ₃	Hg(tot) ~54 mg/L (Hg-203)	8.20 (± 0.84)	0.98 (± 0.98)	88%
	U(tot) ~4 mg/L (U-233)	544 (± 6.14)	90.89 (± 5.16)	83%

*Solution (10 mL) and Kodak steel wool (~0.4 g) shaken for ~12-h before phase separation. Aqueous phase, containing soluble radionuclide tracer, is obtained by filtration through 0.2- μ m-pore media.

3.3 REMOVAL OF SOLUBLE OXIDANT AND URANIUM WITH USE OF GRANULAR SCRAP IRON

3.3.1 Reduction of Excess Iodine with Granular Particulate Iron

The relative kinetics for reduction of iodine in KI medium were monitored at both ambient temperature (~20°C) and at the recommended treatment temperature of ~50°C, with use of a residual chlorine selective electrode (the response of which is proportional to the logarithm

of the active halogen oxidant concentration; see Fig. 2). For this series of experiments, 30 mL of simulated recycled I_2/KI medium was contacted with 3 g MasterBuilders iron (nominal dosage 100 g/L) by shaking the mixture in a sealed container mounted on a platform shaker. Results, illustrated in Fig. 3, indicate that elevated temperature greatly accelerates the reduction of iodine in iodide medium.

The solution, before treatment with iron, was strongly oxidative ($Eh(SHE) = +536$ mV at pH 3.14), whereas afterward it was strongly reductive ($Eh(SHE) = -239$ mV at pH = 5.69).

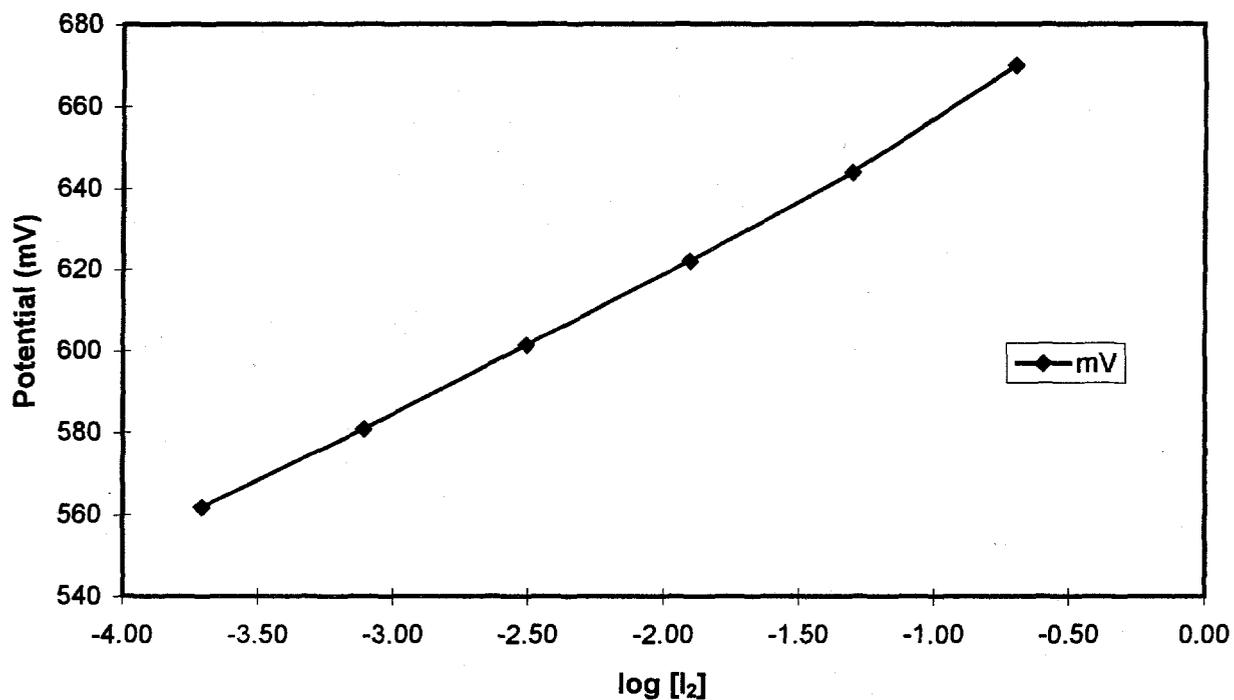


Fig. 2. Response of Chlorine Electrode to Iodine Concentration ($[I_2]$, mol/L). Diluent is 0.4 mol/L KI; temperature 23°C.

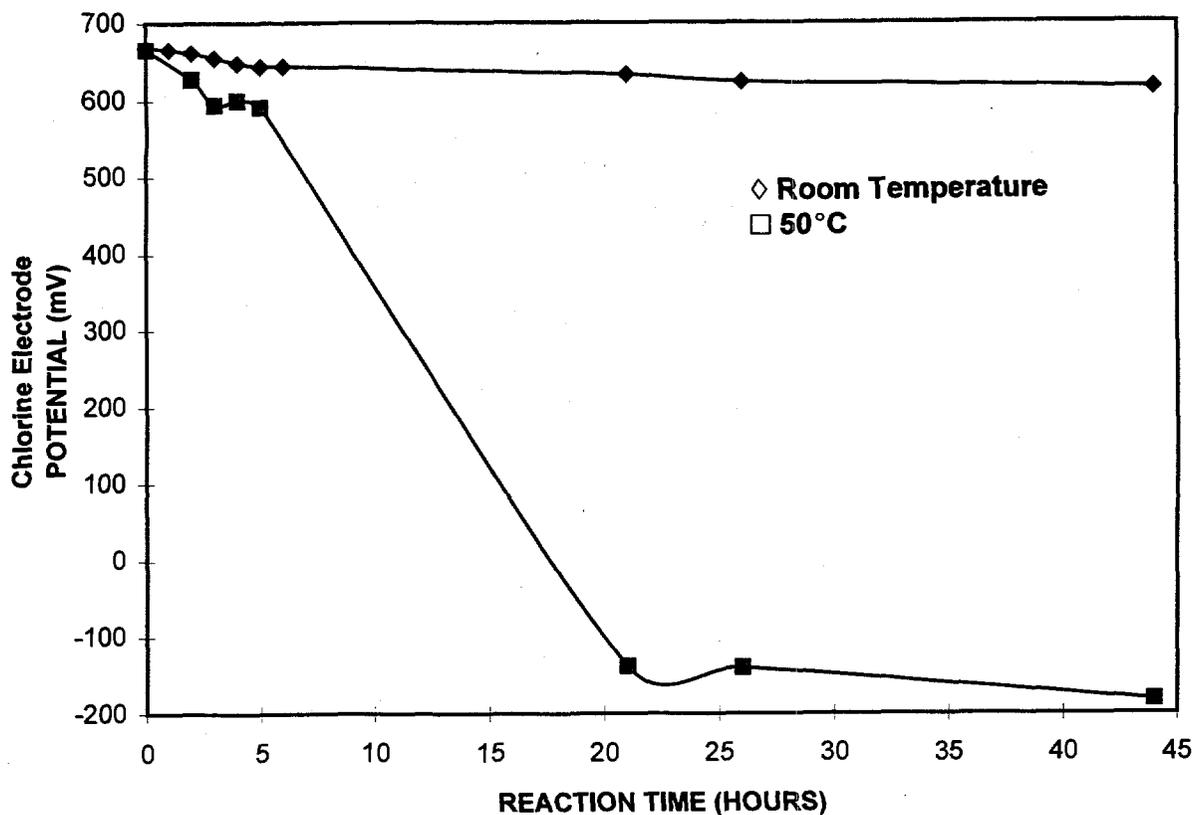


Fig. 3 Reduction of Iodine with use of MasterBuilders Iron: Relative Kinetics as a Function of Temperature, as Monitored with Use of a Chlorine Electrode

3.3.2 Reduction of Soluble Uranium with Granular Particulate Iron

Figure 4 illustrates the relative kinetics for removal of soluble uranium with use of MasterBuilders iron (nominal dosage 100 g/L) by shaking the mixture in a sealed container mounted on a platform shaker in a bath maintained at 50°C for >8-h (heating failed at some time between 8 and 24 hours elapsed time). The apparent half-life for the removal of uranium under these conditions of temperature and mass transfer was ~4.8-h. After ~24-h, the residual soluble uranium concentration in this experiment was ~0.25 mg/L, which represents a removal efficiency of >86%. The solution at 24-h was colorless, indicating that excess iodine was concurrently reduced (the solution was observed to have been progressively decolorized during the initial 7-h of reaction).

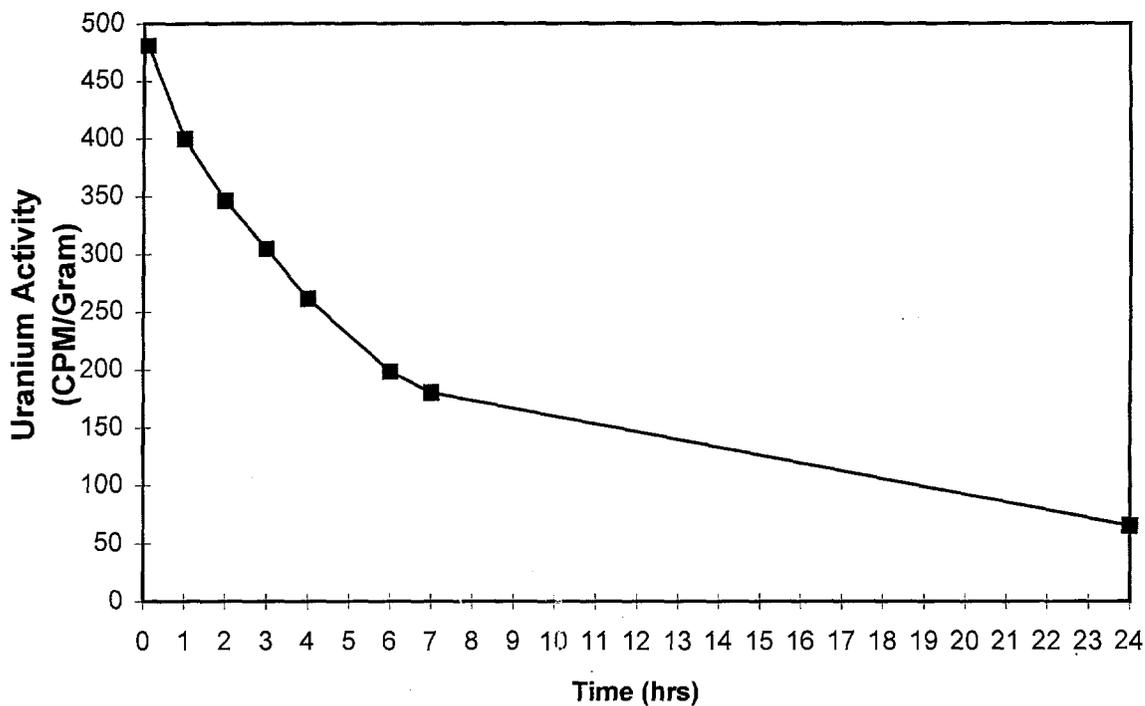


Fig. 4 Removal of Soluble Uranium (^{233}U Tracer) with use of MasterBuilders Iron at 50°C .

3.4 METALS PRECIPITATION BY TREATMENT WITH LIME SLURRY

After treatment of spent extraction medium with iron reagent, the solution will contain an appreciable concentration of soluble ferrous ion (Fe^{2+}); see Eq(s). 1–3. Decantate from the treatment of traced solution with iron particulate (see Section 3.3.2), 79.6 g, was adjusted from an initial pH value of ~ 4 to a final value of ~ 12 by the addition of 20.3 mL of 20 wt% lime slurry. The solution adjusted to pH ~ 12 was somewhat viscous and had a blue-green coloration (presumably due to the presence of “ferrous rust”), and the precipitate settled poorly (see Fig. 5).

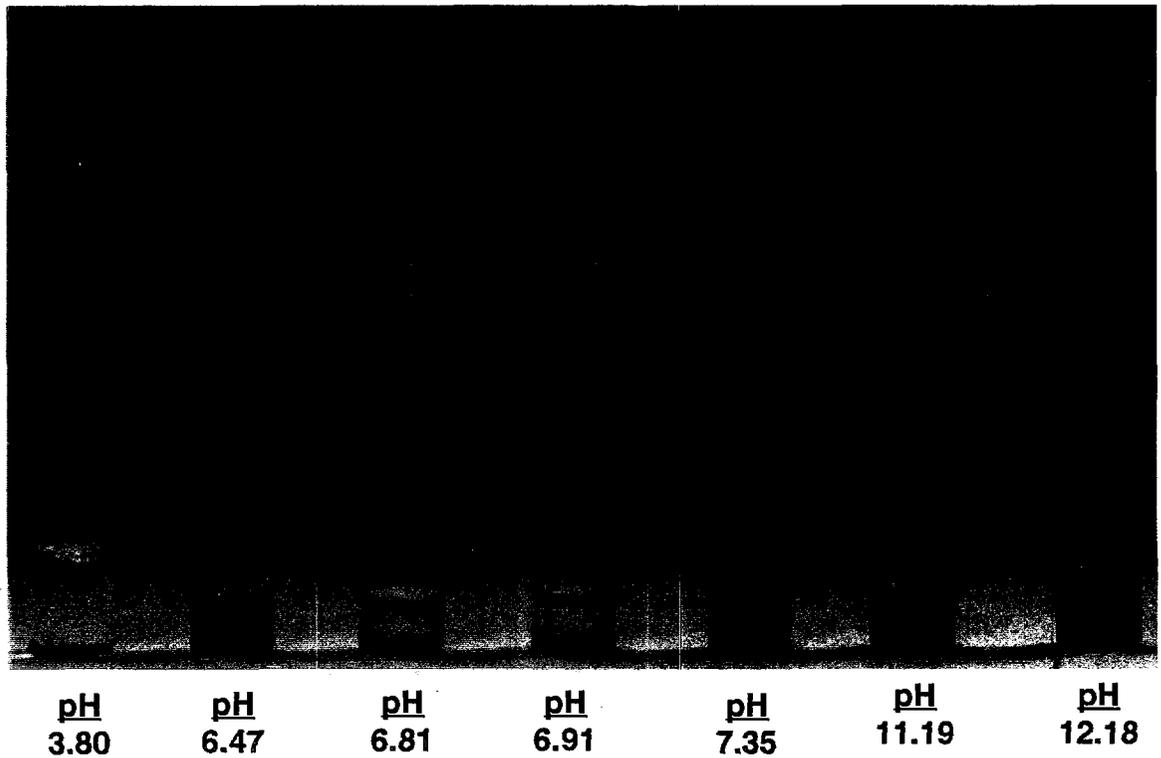


Fig. 5 Precipitation from pH Adjustment Using 20% Lime Slurry (Mixture Settled).

In order to enhance the flocculation of the slurry, we added ~5 mL of ~0.15 wt% Betz 1138 polymer solution. Liquid and solid phases were then separated by vacuum filtration through 0.45- μ m-pore Nalgene disposable filterware. This resulted in recovery of 76.8 g of clear filtrate and 35.9 g of wet sludge (equivalent to ~9.3 g dry solids).

Mass balance calculations for the first two unit operations in the flowchart are given in Table 5. By mass balance calculations, the lime softening filtrate contained ~43% of the total activity of the slurry. Thus, treatment of the decantate from the iron treatment unit operation with lime slurry removed ~57% of the already-low soluble uranium activity.

**Table 5. Treatment of Simulated Spent I₂/KI Extraction Medium:
Soluble Uranium Tracer Activity**

Unit Operation	Soluble U Tracer Activity (CPM/g)	Mass of Liquid Phase Recovered (g)	Total Soluble Uranium Activity (CPM)	% of Original Activity Remaining
None	481	105.5	50,746	100
Reduction with Iron Particulate	64.9	79.6	5,166	10.2
Lime Softening	28.7	76.8 *	2,204	4.3

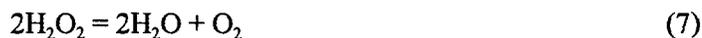
*Total includes liquid contributions from treatment with lime slurry and flocculant solutions.

3.5 REGENERATION OF IODINE REAGENT

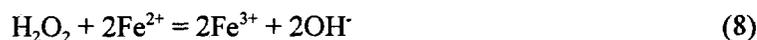
As depicted in Fig. 1, half of the recovered lime-treatment filtrate is to be treated with sulfuric acid and hydrogen peroxide to reoxidize iodide ion and precipitate iodine crystals, as described in Eq. 4.

This treatment step was found to be somewhat difficult to control, and was not successfully performed using the traced solution. It is not anticipated that any additional soluble uranium would be removed by reoxidation of the solution and precipitation of calcium sulfate (gypsum).

Although concentrated peroxide reagent (~30 wt% solution) is relatively stable, dilute solutions are unstable and can decompose to form oxygen and water (Eq. 7).



Rapid exothermic decomposition, involving hydroxy free radical, is catalyzed by traces of impurities such as iron or other heavy metals (Laitenin, 1960); see, e.g., Eq. 8:



In order to minimize unwanted effervescence/foaming and heat production, it is necessary to perform the oxidation at ice-bath temperature and to alternately add aliquots of peroxide and acid reagents to maintain the solution pH at an acidic value, e.g., pH ~3-4 (Whisenhunt, 1997).

Observing these precautions, we were successful in recovery of iodine from an untraced

solution containing KI. To 200 mL deionized water, we added 26.53 g KI (0.16 equivalents). The beaker containing the solution (~0.8 mol/L KI) was placed in an ice bath. The recommended procedure is to add ~20% stoichiometric excess of both peroxide and acid reagents; this corresponds to the addition of ~21.8 g of 30% hydrogen peroxide reagent and ~9 mL (~13.25 g) of 18 N H₂SO₄ reagent. (The latter was prepared by a 1:1 dilution of concentrated sulfuric acid in deionized water). The reagents were added iteratively in the sequence of ~1 mL acid and then ~2 mL peroxide, until the reagents were consumed. In this manner, it was possible to maintain the solution pH value near 2–3 during peroxide addition; intense color was formed, with no foaming. The flask was covered and allowed to set overnight. By morning, iodine crystals were precipitated (some fine crystals floated at the surface). The phases were separated by vacuum filtration (with ~50 mL of deionized water used to rinse the fine crystals out of the beaker), yielding ~24.2 g of moist iodine crystals (compared to the 20.3 g of iodide ion added), and ~250 mL of slightly-colored filtrate (pH ~5.6). Trace iodine in the presence of excess iodide forms the triiodide ion (I₃⁻); an aliquot of the filtrate solution was completely decolorized by the addition of a few grains of sodium thiosulfate (to convert residual triiodide ion to iodide), Eq. 9:



4. CONCLUSIONS AND RECOMMENDATIONS

The I₂/KI extraction system is demonstrated to be very efficient for the solubilization of mercury in a mixed waste sludge, with only a moderate concurrent solubilization of uranium (Table 3). Performance may vary for other waste streams, depending upon the manner in which the contaminants are associated with the waste (e.g., the chemical form (speciation) of the contaminant, sorptive properties of the matrix material, etc.).

Soluble uranium added to an aliquot of extraction medium is effectively removed by treatment with iron reagent (typically >90% removal). It appears that treatment with steel wool at ambient temperature may be nearly as effective for removal of soluble uranium as treatment with granular scrap iron at elevated temperature (~50°C), probably due to the more efficient solid-liquid contact (Krause, 1995).

The next unit operation, adjustment of the solution pH to a value near 12 by the addition of lime slurry to form a metal-laden sludge phase (an operation referred to as "lime-softening"), removed an additional 57% of soluble uranium activity, for an over-all removal efficiency of ~96%. Due to a relatively large concentration of ferrous ion (from the corrosion of iron due to the reaction with iodine reagent), the solids that were formed upon addition of lime reagent did not settle well. We facilitated settling by the addition of flocculent polymer, but a significant amount of sludge was produced (with a corresponding loss of iodide ion in the wet sludge).

Regeneration of iodine reagent by the addition of hydrogen peroxide requires care to avoid a rapid exothermic reagent decomposition that can occur if there are pH excursions; this unwanted reagent decomposition reaction may be a challenge to control in a large-scale application.

5. REFERENCES

- Bostick, W. D., D. E. Beck, K. T. Bowser, D. H. Bunch, R. L. Fellows and G. F. Sellers, *Treatability Study for Removal of Leachable Mercury in Crushed Fluorescent Lamps*, Report K/TSO-6, Lockheed Martin Energy Systems (February 1996).
- Bostick, W. D., R. J. Jarabek, W. A. Slover, J. N. Fiedor, J. Farrell, and R. Helferich, *Zero-Valent Iron and Iron Oxides for the removal of Soluble Regulated Metals in Contaminated Groundwater at a DOE Site*, Report K/TSO-35, Lockheed Martin Energy Systems (September 1996).
- Fellows, R. L. (Compiler), *Y-12 Plant Decontamination and Decommissioning Technology Logic Diagram for Building 9201-4. Volume 1*, Report Y/ER-159/V1, Martin Marietta Energy Systems, Inc. (September 1994).
- Foust, D. F., *Extraction of Mercury and Mercury Compounds from Contaminated Material and Solutions*, U.S. Patent 5,226,545 (July 13, 1993).
- Gates, D. D., K. K. Chao, and P. A. Cameron, *The Removal of Mercury from Solid Mixed Waste Using Chemical Leaching Processes*, Report ORNL/TM-12887, Martin Marietta Energy Systems, Inc. (July 1995).
- Greenberg, A. E., L. S. Clesceri, and A. D. Eaton (Eds), *Standard Methods for the Examination of water and Wastewater*, 18th Edition, American Public Health Association, Washington DC (1992).
- Klasson, K. T., Oak Ridge National Laboratory, personal communication to W. D. Bostick, July 21, 1997.
- Krause, C., "Mercury: Recent Advances," pp. 111-120 in *Oak Ridge National Laboratory REVIEW*, Number Four, 1995.
- Laitenin, H. A., *Chemical Analysis*, McGraw-Hill Book co., New York (1960).
- Orion Research Incorporated, *Instruction Manual for Model 97-70 Residual Chlorine Electrode* (1991).
- Science Applications International Corporation, *Phase I report on the Bear Creek Valley Treatability Study, Oak Ridge Y-12 Plant, Oak Ridge, Tennessee*, Report Y/ER-285, Lockheed Martin Energy Systems (April 1997).
- Whisenhunt, D., General Electric Corporation, personal communication to W. D. Bostick, September 9, 1997.

DISTRIBUTION

LMES

1. W. D. Bostick
2. W. H. Davis
3. R. L. Fellows
4. J. L. Frazier
5. R. J. Jarabek
6. Records Center (3)*

LMER

7. D. A. Bostick
8. T. A. Conley
9. S. E. Herbes
10. D. D. Gates
11. K. T. Klasson
12. Technical Library

Paducah Gaseous Diffusion Plant

13. PGDP Library

Portsmouth Gaseous Diffusion Plant

14. Technical Library

***Two copies to the Office of Scientific and Technical Information**