POLYELECTROLYTE ENHANCED REMOVAL OF MERCURY FROM MIXED WASTE DEBRIS

Barbara F. Smith, Thomas W. Robison, Yvonne C. Rogers, Christopher Lubeck

Los Alamos National Laboratory
Los Alamos, New Mexico 87544

ABSTRACT

We have developed a process for dissolving and removing elemental and ionic forms of mercury from solid surfaces. The process uses water-soluble chelating polymers (WSCP) that have been designed for mercury-ion selectivity and performance in the presence of dilute acid and mild oxidant. After a solution of the polymer is used to selectively leach the solids (e.g., mixed waste debris) and assist in the oxidation of elemental mercury, Hg(0), to ionic mercury, Hg(II), the resulting aqueous wash and rinse phases are treated by ultrafiltration with commercially available membranes to concentrate the mercury-polymer complex. The metal ion concentrate is released from the WSCP by adjusting the chemistry of the system, and the polymer and the original permeate waters are recycled for further debris-leaching, greatly reducing secondary wastes. The mercury concentrate is precipitated as the stable sulfide (HgS) for solid waste management.

INTRODUCTION

Mercury, a RCRA (Resource Conservation and Recovery Act) metal is found in numerous processes and waste streams at many US Department of Energy (DOE), Department of Defense (DOD), and commercial facilities. Hg-containing wastes are generated in decontamination and decommissioning (D&D) operations and exist as old process wastes that require treatment and stabilization. Hg exists in solutions, as part of sludges, or as contaminants on soils or solid surfaces in a variety of oxidation states from elemental Hg(0) to ionic Hg(I) or (II). It can exist individually or as a mixture with other RCRA elements, as a mixture with radioactive metals such as actinides (defined as mixed waste) or as a mixture with a variety of inert metals. Discharge limits for Hg are based upon toxicity and dictated by state and federal regulations (e.g., drinking water, process permits, etc). When Hg is in the presence of radioactive wastes, it is uniquely regulated and has caused considerable waste management problems for DOE (*1*). If Hg can be removed to a level such that the waste can pass TCLP (Toxic Characteristic Leaching Procedure) at < 0.200 ppm, the material can be buried as low level radioactive waste. Though there is no regulatory level set as of yet, it has been debated that if Hg can be removed to the level of 1 ppm total Hg for light debris, the debris could be incinerated in a low-level radioactive waste incinerator.

There is a need to selectively remove and concentrate Hg from a variety of waste or process streams, particularly mixed wastes that are either solids or liquids, to meet discharge limits of a process solution, to meet soil and debris decontamination requirements, and to pass TCLP for proper waste management. The objectives of our work have been to (1) develop and optimize a Hg(0) dissolution method that is mild, rapid, and selective, and minimizes secondary waste; (2) test the method for removing Hg(0) from solid surfaces; (3) optimize the concentration and recovery of Hg(II) from aqueous solutions including those produced by dissolution of Hg(0);

and (4) to have a resultant waste form that will either meet incineration standards or can be buried as low-level radioactive waste. The long-term goal is to obtain the fundamental scientific information needed to be able to perform a successful full-scale demonstration on mixed waste debris followed by technology transfer to the private sector.

Metal-ion removal from aqueous solutions is a major industrial activity covering processes ranging from water softening to hydrometallurgical recovery from ores to detoxification of waste-waters and contaminated natural waters. Attaching metal-ion-specific ligands or chelators to solid polymers is an important approach to solving such problems and has received considerable attention over the past 20 years (*2*). Note: the terms "chelate" and "multidentate" refer to a ligand that contains two or more binding sites for coordination with a metal ion. Solid chelating polymers are the basis of a number of successful selective industrial separations, including the removal of calcium to part-per-billion levels from brine and the removal of radioactive cesium from alkaline waste waters (*3*).

The application of water-soluble chelating polymers (WSCP) (often termed polyelectrolytes) in combination with ultrafiltration for the treatment of waste-waters contaminated with low levels of RCRA metal ions is a relatively new separation technology, which is being developed and implemented at Los Alamos National Laboratory (*4-7*). Bayer and coworkers (*8,9*) demonstrated that it is possible to selectively retain certain metal ions on water-soluble polymers, concentrate the metal-loaded polymer by ultrafiltration, and then recover the metals using either acid elution or electrodeposition processes. The basis for metal-ion separation involves the retention of metal ions bound to the chelating groups on the water-soluble polymer, while smaller unbound species and water pass freely through the ultrafiltration membrane. The Polymer Filtration™ process (*10,11*) allows for the selective concentration of dilute solutions of metal-ion contaminants. The reduced volume containing the polymer/metal-ion-complex can go directly to disposal or the metal ions can be recovered by a regeneration reaction and the polymer recycled for further metal-ion recovery. The advantage of this separation approach for dilute metal-ion solutions is in the rapid metal-binding kinetics. This rapidity results from binding metal ions in a homogenous solution as compared to a heterogeneous, two phase system such as ion exchange resins, where metal-binding/release is often diffusion controlled into and out of the resin beads. This translates into small equipment footprints and more concentrated eluent solutions. Other advantages include low temperature and pressure operation, no hazardous organic solvents, and high metal-ion selectivity from careful choice of chelating functionality.

We have chosen the water-soluble polymer or polyelectrolyte approach to tackle the mixed-waste debris-leaching problem, as solid polymeric resins are unable to leach other solid surfaces efficiently. The approach to and results of our methods-development studies are presented in this paper.

EXPERIMENTAL

Equipment: Equipment used in our studies included a mercury analyzer (Perkin Elmer, Model 100), pH meter (Fisher Accumet, model 610A) with a general purpose combination electrode (Orion Ross), diode array ultraviolet-visible spectrophotometer (Hewlett Packard, Model 8451A), inductively coupled plasma–atomic emission spectrometer (ICP-AES) (Thermo Jarrell Ash, Iris), pipetors (Rainin), wrist action shaker (Burrell, Model 75), pressure reactor (Parr), orbital shaker (Lab-line™, Orbit-Environ Shaker), hot plates (Corning, Model C-351), ultrafiltration concentrators (Amicon, 5 mL Centricon-10 units with a 10,000 molecular weight cut off (MWCO) and 20 mL Centraprep-10 units with a 10,000 MWCO), refrigerated centrifuge (Eppendorf, Model 5810R), 4 mL conical vials (Wheaton), heating block (VWR), and ultrasonic cleaning baths (Brunson 3200, Fisher FS9, Fisher FS7652H).

Chemicals: Elemental mercury (Fisher Scientific), ionic mercury standards (Spex Chemicals), $Hg(NO_3)_2$ (Fisher), trace metal grade nitric, hydrochloric and sulfuric acids (Fisher), 40% Stannous Chloride (LabChem Inc.), technical grade 34-37% hydrogen peroxide (Fisher). Stainless steel coupons were planchetts used for radiological counting (Oxford Instrumental). The polymers were prepared, obtained commercially, or obtained from our industrial partner. Because of their proprietary nature we will not discuss their composition.

Mercury Analysis Method: Aqueous samples requiring analysis for Hg were diluted to volume in HNO_3-cleaned glass volumetric flasks with 2% HNO_3/2% H_2SO_4 solution to stabilize the sample, making the final Hg concentration < 40 ppb. Analysis was performed by cold vapor atomic absorption spectroscopy using a Perkin-Elmer Flow Injection Mercury System (FIMS), which is a dedicated instrument specifically designed to measure the absorption of Hg. The detector is a photocell with maximum sensitivity at 254 nm. $SnCl_2$ solution (1.1%) was pumped into the mixing manifold along with 3% HCl, where the sample was injected. The two fluid streams were mixed, and the resulting reduced Hg vapor was carried by argon gas into the FIMS cell after passing through the liquid/gas separator. Calibration was performed with 10, 20, and 40 ppb standards, which were prepared in 2% HNO_3/2% H_2SO_4. Fresh standards were prepared daily. Quality assurance (QA) included a continuous calibration blank, reagent blank, continuous calibration standard, and laboratory control standard. These checks were run after each calibration curve and had to be within ±10% of the expected values. Carryover of approximately 1 ppb between consecutive samples had been observed to interfere with sensitivity when very low levels of mercury were present. By running water blanks between samples and batching samples in similar concentration ranges, reproducibility and accuracy were improved to acceptable levels.

Hydrogen Peroxide (H_2O_2) Facilitated Mercury Dissolution Studies: Hg(0) (10 to 30 mg) was placed in conical shaped 5 mL vials equipped with triangular Teflon™ stir bars or in 25-mL Erlenmeyer flasks. WAB-30 polymer solutions (4 mL, 0.1 to 1 % w/v) with pH adjusted between 1 and 5 with HNO_3were added to the Hg(0). H_2O_2 (<0.25 mL of 34-37%) was added to make the final concentration in the range of 0.5 to 2%. The solutions were mixed using either an air heated orbital shaker at 300 rpm or with a magnetically stirred heating block and heated between 30 and 60^oC. The experiments with and without H_2O_2 were performed in triplicate. Other Hg oxidative dissolution studies were performed where the polymer type, polymer concentration, H_2O_2 concentration, pH, vessel shape and material, temperature, mixing mode, and oxidant were varied. The oxidative dissolution reactions were qualitatively followed by the disappearance of the Hg bead.

Iron(III) Facilitated Mercury Dissolution Studies: Hg(0) (10 to 30 mg) was placed in conical shaped 5 mL vials equipped with triangular Teflon™ stir bars or in 25-mL Erlenmeyer flasks. Various amounts of polymer or ligand were added to give solutions between 0 to 1 % w/v. The acid strength was adjusted between 2 to 0.001 M with HNO_3, and various amounts of $Fe(NO_3)_3$ from 0 to 160 mg were added to the Hg-containing vials to make 0 to 0.1 M Fe(III) solutions.

The solutions were mixed using either an air heated orbital shaker at 300 rpm or with a magnetically stirred heating block and heated between 30 and 60^oC. The oxidative dissolution reactions were followed by the disappearance of the Hg(0) bead.

Mercury Binding, Capacity, and Retention Studies:
Effect of pH on Hg retention: Mercury Spex standard was added to 1% polymer solutions to give 10 or 100 ppm Hg solutions, which were adjusted to the pH ranges of 0 to 9. The solutions were mixed and the entire volume of each sample was filtered through a Centriprep-10 unit or Centricon-10 using centrifugal force, and permeates were analyzed for Hg using FIMS. The same procedure was used for the blanks except the polymer was absent.

Effect of H_2O_2 on Hg(II) retention: Mercury Spex standard was used to give 10, 100, 500, and 1000 ppm Hg in 1% WAB-30 polymer solution at pH 7 with and without 2% H_2O_2 to determine if H_2O_2 interferes with the polymer's Hg-binding ability. Measurement of Hg using FIMS was performed on permeates from Centricon-10 units. $H_2O_2$was quantified by permanganate (0.02 M) titration to a pink endpoint. Our 34-36% H_2O_2 solution was determined to be 36.8%.

Polymer capacity studies: Mercury Spex standard was added to 0.1 to 1% polymer solutions to give 1000 ppm Hg solutions which were adjusted to pH 7 or 1. The solutions were mixed and each sample was filtered through a Centricon-10 unit using centrifugal force and permeates were analyzed using FIMS. The capacity was determined by difference.

Mercury Precipitation Studies: Direct removal of Hg(II) from the polymer by precipitation of HgS with NaHS was attempted. Sulfide as NaHS solution was added to 1% w/v WAB-30 polymer solutions that contained 100 ppm or 1000 ppm of Hg(II) and ranged in pH from 1 to 7. The molar ratio of S:Hg was adjusted to 0.25:1, 0.5:1, 1:1, and 2:1. The solutions turned black, but remained clear and no precipitation was observed. Similarly generated solutions at pH 4 were filtered through 1000K, 300K, and 100K MWCO membrane filters using centrifugal force or were passed through a 0.45 μm filter disk using pressure created by a syringe. The filtrates were compared by visual examination and were analyzed for Hg using FIMS.

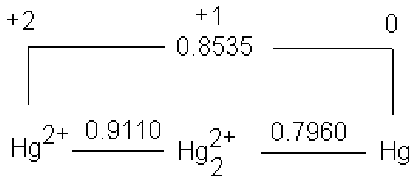
Decontamination of Stainless Steel Coupons: Stainless steel coupons were coated with Hg(0) by contacting the coupon with a pool of Hg(0) at 50^oC to 80^oC for 2 hours in a sealed glass container. Excess Hg was poured from the coupon. Extracting solution was added to the coupon in a flask and it was agitated for 2 hours at various temperatures. The agitation modes included an orbital shaker and ultrasonic cleaning bath. In some cases multiple washings were performed. The extracting solutions ranged from strong acids (conc. HNO_3) to mild polymeric solutions. A total dissolution of the remaining coupon was accomplished in aqua regia to obtain the mass balance for Hg. The resulting solutions were analyzed for the presence of Hg using FIMS.

RESULTS AND DISCUSSION

To meet the goal of a rapid, mild, selective, and low-waste oxidative dissolution of Hg(0) required developing an oxidation system that was thermodynamically and kinetically favorable. From our initial proof-of-principal experiments the dissolution of Hg(0) was quite rapid under the harsh conditions of concentrated HNO_3 (16 M), but ceased under mild HNO_3 conditions (1-2 M). Even though thermodynamic calculations indicate that Hg(0) can be readily oxidized at 1-2

M HNO_3, as shown in Eq. 1 (*12*), this was not observed experimentally. Hg(0) oxidation is partially complicated by the possibility of two oxidation states, Hg(I) and Hg(II), having close oxidation potentials. It is normally considered that most conditions that oxidize Hg(0) to Hg(I) will also oxidize Hg(0) to Hg(II), and Hg(I) readily disproportionate to Hg(0) and Hg(II) as shown in the Hg potential diagram (Scheme 1) (*13*).

$NO_3^- + 4H^+ + 3e^-$ ---------> $NO + 2H_2O$ 0.957 volt (Std. Conditions, 25°C, 1 M acid) (1)



Scheme 1

Oxygen under neutral conditions in pure water is not a strong enough oxidizer for Hg(0) as shown in Eq. 2 (*14*).

$O_2 + 4H^+ (10^{-7}\ M) + 4\ e^-$ ---------> $2H_2O$ 0.815 volt (25^0C, 1 atm.) (2)

But under acid conditions, O_2 becomes a stronger oxidizer as shown in Eq. 3. (*14*)

$O_2 + 4H^+ (1\ M) + 4e^-$ ---------> $2H_2O$ 1.229 volt (25^0C, 1 atm.) (3)

Hydrogen peroxide in acid can be even a stronger oxidizer than O_2 or HNO_3 as shown in Eq. 4. (*15*)

$H_2O_2 + 2H^+ + 2e^-$ ---------> $2H_2O$ 1.763 volt (25^0C) (4)

Oxidative dissolution can also be complicated by the formation of oxide barriers on the Hg(0) surface. Conditions have to be optimized such that once Hg solubilizes it does not precipitate as the oxide or adsorb on surfaces of materials. Having a chelator in solution to capture Hg(II) should help eliminate absorption problems. The presence of a Hg-binding ligand should also shift the equilibrium to favor oxidation of Hg(0) under milder conditions (*16-18*). Though the potential for oxidation may be reasonable (thermodynamically favorable), the kinetics appear to be unfavorable. The kinetics should be improved by increasing temperatures and vigorous mixing. It has been our premise that certain chelating ligands might also enhance the kinetics of dissolution by facilitating the electron transfer process

Mercury Dissolution Studies: Since our goal was mild, rapid, and selective Hg removal from debris, our tests included evaluating different water-soluble metal-binding polymers at various concentrations, mixing conditions, acid strengths, temperatures, and, non salt-forming oxidizers to develop mild conditions to oxidize and dissolve Hg(0). We had earlier performed some proof-of-principle experiments that seemed to indicate that we could oxidatively dissolve Hg(0) in the presence of water-soluble chelating polymers under mild HNO_3 conditions. To systematically test the concept we performed several survey studies of Hg(0) dissolution to determine the parameters that had the most influence on the rate of oxidative dissolution. The parameters evaluated included polymer type, temperature, mixing mode, and oxidant. Table 1 gives a summary of the survey results where we observed the rate of disappearance of Hg(0) beads.

Using the same stirring mode (i.e., magnetic bar), an increase in the Hg(0) dissolution rate with increase in temperature was observed. At the same temperature the stirring bar was a more effective mixing mode than the orbital shaker, and no Hg(0) dissolution occurred in the absence of stirring. Thus mixing is critical for the Hg(0) oxidative dissolution process. We observed that when a stirring bar was used, it dispersed the Hg(0) bead into smaller beads, resulting in more surface area. When the stir bar was not in intimate contact with the bead we observed that dissolution results were irreproducible.

The value of pH 4 was chosen for the studies in Table I, as we wanted to use as mild a pH as possible and still cause dissolution to occur. The use of less HNO_3 would produce less secondary waste in any process that could be developed, and the conditions would not be harsh on debris surfaces that needed to be decontaminated from Hg. Though it is known that Hg(II) hydrolyzes at pH 3 and precipitates as the oxide, it was thought that the hydrolysis would be perturbed by the presence of a chelating polymer. Indeed, we were generally able to solublize Hg(0) at pH 4 with minimal yellow-orange precipitate being formed.

The oxidant is an important factor in that even at elevated temperatures and with good mixing, no Hg(0) dissolution occurred in the absence of an added oxidant. The oxidant H_2O_2 was chosen, because it would leave no hazardous secondary waste as would be generated by the use of halogen-containing oxidizers (*19-21*) or concentrated HNO_3. Even though O_2 has the potential to be an oxidant under acidic conditions, we did not observe dissolution of the Hg(0) bead even at long treatment times in the presence of air, sparging air or O_2, or even under a 40 psi O_2 overpressure using a Parr pressure/shaker apparatus. For these initial studies in the presence of 1% WSCP, anything less than 2% H_2O_2 gave no dissolution, and more peroxide did not seem to increase the disappearance rate of the Hg(0) bead.

Table I. Hg(0) Oxidative Dissolution Survey: Time Required for the Disappearance of Hg(0) Beads under Various Conditions.

Temp, ^oC	**Stirring Mode**	**Polymer**	**Oxidant**	**Dissolution Time, hrs**
30	+(bar)	+	H_2O_2	3
30	-	+	H_2O_2	>5
30	+(orbital)	+	H_2O_2	4
40	+(bar)	+	H_2O_2	2.5
40	-	+	H_2O_2	>5
50	+(bar)	+	H_2O_2	2
50	-	+	H_2O_2	>5
60	+(bar)	+	H_2O_2	1
60	-	+	H_2O_2	>5
60	+(bar)	-	H_2O_2	>5
60	+(bar)	+	-	>5

Conditions: pH 4, HNO_3, Hg(0) = 10 mg, 1% w/v WAB-30 polymer, 2% hydrogen peroxide, + = present, - = absent; > 5 hr. means Hg(0) never dissolved.

For comparison we tested the dissolution of Hg(0) with an equal weight of an chelating ion exchange resin, Chelex-100 (Bio-Rad), under conditions that gave dissolution when using the water-soluble polymer. The bead of Hg(0) never went into solution even with long reaction times. Several amine ligands, diethylenetriamine (DETA) and triethylenetetraamine (TETA), both good Hg(II) binding ligands (*17*), were also tested for their ability to dissolve Hg(0) under conditions that gave good dissolution with the WSCP. Again, no Hg(0) dissolution was observed even when the ligands were present at 1% w/v as shown in Table II.

Table II. Hg(0) Dissolution Studies using Chelating Ligands and Resin.

Organic Chelator	Acid (M)	Oxidant	Time (hr.)	Result	Comments
1% Chelex-100	10^{-3}	H_2O_2	>24	-	clear, colorless
1% DETA	10^{-3}	O_2	>24	-	clear, colorless
1% DETA	10^{-3}	H_2O_2	>24	-	clear, colorless
1% TETA	10^{-3}	O_2	>24	-	clear, colorless
1% TETA	10^{-3}	H_2O_2	>24	-	clear, colorless

Conditions: 10 mg Hg(0), HNO_3, temperature range 50-60^{0}C, in glass conical vials with magnetic stir bar, - =Bead present, + = Bead gone, >24 hr. means Hg(0) did not dissolve.

While we were testing for Hg(0) dissolution, we also surveyed the dissolution of HgO and a number of Hg salts as a function of pH and the presence of WSCP as shown in Table III. We observed that $HgCl_2$ dissolved instantly in both the absence and presence of WSCP. Hg_2Cl_2 was insoluble in the presence and absence of WSCP at acidic pH values. We did observe in other tests that under neutral to basic and under acidic and oxidizing conditions that Hg(I) disproportionated as was indicated by the observance of gray-black Hg(0). HgO dissolution was aided by both decreasing the pH or by adding the WSCP at higher pH values. HgS was insoluble under all conditions tested. Thus, if these materials were present on a solid mixed waste, it is assumed that all but HgS would be solubilized under the mild process conditions that we are trying to develop. The HgS would remain in the waste and this waste would qualify for burial as low-level radioactive waste, as it would pass TCLP.

A study was performed to determine the effect of pH and vessel type at constant H_2O_2 and WSCP concentration and temperature on the dissolution of Hg(0). Table IV summarizes the results and indicates that as the pH increases the rate of Hg(0) dissolution decreases. For the duration of the experiment, both pH 3 and 4 gave similar dissolution rates. We looked at several types of vessel material because we had previously observed

Table III. HgO and Hg Salts Dissolution Study.

Hg salt	**pH**	**polymer**	**Dissolution Time, (min)**
$HgCl_2$	6	-	instantly
$HgCl_2$	4	+	instantly
Hg_2Cl_2	6	-	did not dissolve
Hg_2Cl_2	4	+	did not dissolve
HgO	2	-	10
HgO	6	-	did not dissolve
HgO	4	+	20
HgO	7	+	55
HgS	2	+	did not dissolve

Conditions: Temp. 55-60^{0}C, Stirring with bar in conical vial, HNO_3, Hg salts = 10 mg, 1% w/v WAB-30 polymer, + = present, - = absent;

irreproducibility in the dissolution rate of Hg(0). Although we think the irreproducibility arises from inadequate mixing, we decided to test the vessels to determine if there might be some wall affects. The difference in vessel types did not appear to affect dissolution.

Table IV. The Effect of pH and Vessel Type on Hg(0) Dissolution.

pH	Final % H_2O_2	ppm Hg in solution
3.92	1.94	2400
4.72	2.13	1451
5.29	1.82	507
3.12[1]	1.92	2158
3.03[2]	1.94	2311

Conditions: 30 mg Hg(0) in 12 mL of 1% w/v WAB-30 polymer initially with 2.2% H_2O_2 after 24 hr. at 50^{0}C on an orbital shaker. [1] glass tube, [2]Teflon tube.

In another study we evaluated the effect of WSCP and H_2O_2 concentration on Hg(0) dissolution as shown in Table V. One might think intuitively that increasing the WSCP concentration might improve the Hg(0) dissolution. This improvement was not observed. To the contrary, as we lowered the WSCP concentration we observed better performance. The actual rate of the Hg(0) bead disappearance was the same, but with the lower WSCP concentration the resulting solution was clear and contained no white solid. In the presence of the higher WSCP concentration, copious amounts of white milky material formed, which took many more hours to dissolve than the original Hg(0) bead. At the constant WSCP concentration of 0.1%, we varied the H_2O_2 concentration. As the H_2O_2 concentration was reduced by half, the dissolution rate decreased by a factor of 16. Lowering the temperature from 50°C to 30°C lowered the dissolution rate by a factor of 10. Thus both temperature and H_2O_2 concentration have major effects on Hg(0) dissolution.

Alternative Approaches to Hg(0) Dissolution - Fe(III) Catalyzed Systems:

Although the results with H_2O_2 as an oxidant were promising, we were concerned about the stability of the WSCP to 2% H_2O_2. Thus, we continued our search for another possible mild method for Hg(0) oxidative dissolution that might be less likely to oxidize an organic polymer. It is known that iron(III) can act as an oxidant by an electron transfer from certain metals to Fe(III) to form Fe(II). The reaction where Fe(III) is added in a catalytic amount does not depend on the dissolution of oxygen in water for the forward reaction. It does appear to require that both the solubilized mercury and the iron be complexed such that their redox potentials become more favorable.

Table V. Influence of WSCP and H_2O_2 Concentration on Hg(0) Dissolution.

[Polymer]	[H_2O_2]		
% w/v	2%	1%	0.5%
	hrs.	hrs.	hrs.
1.0%	0.5[1]	--	--
0.1%	0.5[2]	8	15
0.1%[3]	5	--	--

Conditions: pH 1 in HNO_3, 10 mg Hg(0), 4 mL sample at 50°C with rapid stirring with magnetic bar; polymer WAB-100; time is when bead disappeared; [1] copious amounts of white solid formed immediately and took many hours to dissolve after the bead was gone; observed HgO in bubbles on stirrer. [2] Clear, colorless. [3] Run at 30°C.

When Fe(III) is uncomplexed, the reduction of Fe(III) to Fe(II) by Hg(0) under neutral conditions is not favored whether Hg(0) goes to Hg(I) or Hg(II) as indicated in Eq. 5 (*22*). When Fe(III) is complexed, for example, as an amine complex with bispyridyl (Eq. 6) or 1,10-phenanthroline amine (Eq. 7) compounds, the reduction of Fe(III) would become more favorable (*23*). Good aeration would be required for recycling or oxidizing Fe(II) back to Fe(III). If we have too strong of a complexing system for Fe(III) the redox cycle will become less favorable as it will be difficult to convert Fe(II) back to Fe(III) with air. Under less acidic conditions, reduction may be more difficult as Fe(III) can precipitate from solution and the redox reaction becomes less favorable. Under acid conditions the Fe(III) amine complexes are weakened, but the redox reaction with air is more favorable.

$$2\mathrm{Fe(III)} + 2e^- \longrightarrow 2\mathrm{Fe(II)} \qquad 0.771\ \text{Volts}\ (25^0\mathrm{C}) \qquad (5)$$

$[Fe(bipy)_3]^{+3} + e^- \longrightarrow [Fe(bipy)_3]^{+2}$ 1.11 Volts (25^0C)
(6)

$[Fe(phen)_3]^{+3} + e^- \longrightarrow [Fe(phen)_3]^{+2}$ 1.13 Volts (25^0C)
(7)

Table VI. Fe(III) and Ligand Catalyzed Dissolution Studies of Hg(0).

1% Organic Chelator	Acid (M)	Iron Catalyst (mg/mL, M)	Oxidant	Time (hrs)	Result	Comments
none	16	none	O_2/nitrate	15 sec	+	clear, colorless
none	8	none	O_2/nitrate	10 min	+	clear, colorless
none	4	none	O_2/nitrate	16	+	clear, colorless
none	2	none	O_2/nitrate	>24	-	clear, colorless
none	1	none	O_2/nitrate	>24	-	clear, colorless
none	1	0.006	O_2	>24	-	clear, colorless
none	2	0.01	O_2	21	+	clear, colorless
none	2	0.10	O_2	16	+	clear, colorless
DETA	10^{-3}	0.006	O_2	>24	-	orange soln.
TETA	10^{-3}	0.006	O_2	>24	-	orange soln.
DETA	2	0.10	O_2	16	+	clear, colorless
WAB-30	10^{-3}	none	H_2O_2	3	+	cloudy white
WAB-100	10^{-3}	none	H_2O_2	3	+	cloudy white

Conditions: 10 mg of Hg(0), HNO_3, temperature range 50-60^0C, glass conical vial stir bar, - =Bead present, + = Bead gone, >24 hr. means Hg(0) did not dissolve at all;

Thus, with the idea that the WSCP might be a strong binder for Hg(II) and a weak binder for Fe(III), it was thought that Fe(III) could possibly enhance the kinetics of the redox reaction. The experiments summarized in Table VI were undertaken to evaluate this concept. The first section of Table VI summarizes the rate of Hg(0) dissolution (bead disappearance) using varying HNO_3 concentrations under the same stirring and heating conditions used for all the previous survey experiments. Where no Hg(0) dissolution was observed in 1 or 2 M HNO_3, catalytic amounts of Fe(III) were added as $Fe(NO_3)_3$ to determine if any enhancement occurred in the absence of WSCP or other ligands. Rate enhancements were observed in 2 M HNO_3 with 0.01 to 0.1 M Fe(III) as shown in the second section of Table VI. At pH 3, no enhancement was observed even in the presence of the two amine ligands, DETA, TETA, and an orange color was observed, which was thought to be $Fe(OH)_3$. A test result with WAB-30 and WAB-100 WSCP and 2% H_2O_2 at pH 3 is shown for comparison. These polymers greatly increased the rate of Hg(0) bead disappearance, but white milky solid was produced that slowly went into solution as described previously.

We could not use Fe(III) at pH 3 as it hydrolyzed in the solution, so we tested 1% w/v WAB-30, WAB-100, and WAL-40 polymers with 2 M HNO_3 solutions in the presence of 0.1 M

Fe(III), but these WSCP were insoluble at this HNO_3 concentration. These polymers were determined to be insoluble up to pH 0.2. Thus, we were unable to determine the Hg(0) oxidation-enhancing power of the combination of these polymers with Fe(III).

This polymer solubility problem required the development of a WSCP that had better physical properties at low HNO_3 concentration. The polymer, WABOH-30, was developed, tested, and found to have good solubility in this low HNO_3 range. When the 1% w/v WSCP was tested in the presence of Fe(III), a very large rate enhancement for Hg(0) dissolution occurred as indicated by the rapid disappearance of the Hg(0) bead (see Table VII). However, we observed copious amounts of a white milky solid that went into solution at a slower rate than the original Hg(0) bead. This white precipitate had previously been observed (see Table IV) but not in such large quantities as with these reactions. While varying parameters such as [Fe(III)], [WSCP], and [HNO_3], it was observed that we could again eliminate the white solid formation by reducing the [WSCP] 10 fold. At the same time the rate of Hg(0) bead dissolution was enhanced. Other parameter optimization as shown in Table VII indicated that Hg(0) dissolution was better at the lower [Fe(III)] of 0.06 M, and higher [HNO_3] of 2 M, giving dissolution of the Hg(0) bead in a half hour. Again we observed that the use of an orbital shaker was less effective than the use of a stir bar.

Table VII. Fe(III) and WSCP Catalyzed Dissolution Studies of Hg(0).

Organic Chelator	**Acid (M)**	**Iron Catalyst (M)**	**Oxidant**	**Time (hrs)**	**Result**	**Comments**
1% WABOH	1	none	O_2	>24	-	slight cloudiness
1% WABOH	2	none	O_2	>24	-	slight cloudiness
1% WABOH	2	0.10	O_2	5	+	very milky
1% WABOH	1	0.02	O_2	10	+	very milky*
1% WABOH	1	0.06	O_2	2	+	very milky*
1% WABOH	1	0.1	O_2	18	+	very milky*
0.1% WABOH	2	0.06	O_2	0.5	+	slightly cloudy
0.1% WABOH	2	0.02	O_2	2	+	clear, colorless
0.1% WABOH	2	0.06	O_2	24**	+	clear, colorless
0.1% WABOH	1	0.06	O_2	>24	-	clear, colorless*
0.1% WABOH	2	0.06	O_2	2.5	+	clear, yellow, 33 mg Hg(0.041 M)
0.1% WABOH	2	0.06	O_2	4	+	clear, yellow, 54 mg Hg(0.068 M)

Conditions: 10 mg of Hg(0) unless otherwise noted, HNO_3, temperature range 50-60^{0}C, Reaction was in a glass conical vial with triangular magnetic stir bar, - =Bead present, + = Bead gone, >24 hrs. indicates Hg(0) did not dissolve at all; *The solutions got milky fastest with greatest [Fe(III)], as bead disappeared solutions got equally milky. **Used an orbital shaker.

Mercury(II) Binding Studies:

Influence of H_2O_2 on Hg(II) Binding: We performed a Hg(II) binding study using WAB-30 polymer, the polymer most studied thus far, to determine if 2% H_2O_2 significantly altered Hg(II) breakthrough during the ultrafiltration stage. The experiment involved performing ultrafiltration of solutions containing WSCP and several [Hg(II)] in both the presence and absence of H_2O_2. Six replicates were performed and the results with the deviation are presented in Table VIII. With the 1000 ppm Hg(II) solutions a very slight increase in breakthrough was observed in the presence of H_2O_2, but it was not excessive. At the higher concentration of Hg(II) there was considerable Hg(II) breakthrough for both systems as we had exceeded the capacity of the WSCP, but the absolute amount of breakthrough was the same within experimental error. Thus, we have concluded that at least for short contact times, H_2O_2 does not adversely influence the performance of the WSCP. Longer contact studies will need to be performed.

Table VIII. Mercury Breakthrough Studies

Initial [Hg]	Permeate [Hg] Without H_2O_2	Permeate [Hg] With H_2O_2
1000 ppm	1.28(± 0.12)	1.78(± 0.23)
5000 ppm	419(± 34)	411(± 38)

Conditions: 1% w/v WAB-30 polymer, pH 4 with HNO_3, filtered through Centricon-10 unit, stabilized permeate samples in 2% nitric/2% sulfuric acid, diluted and analyzed by FIMS, average of 6 replicates.

Binding Studies of various Polymers: We evaluated a number of different WSCP for their ability to bind Hg(II) as a function of pH. Figure 1 shows a plot of pH versus Hg(II) breakthrough. The plot shows that all of the polymers bound well in the >pH 3 range. Most of the polymers bound well even to pH 1 with two polymers, WAB-100 and WABOH-30, showing some release starting to occur below pH 2. This plot indicates that we can strip the Hg(II) from the WSCP by using a diafiltration process (*24*) at a lower pH range. We need to be aware that some of the polymers studied thus far have poor solubility in the < pH 0.2 ranges. Only WABOH-30 had reasonable solubility at low pH values. Since our goal is to reach 20 ppb Hg(II) in the waste waters, it will be necessary to remove Hg(II) to this low level. A number of the polymers were able to reach the target limit in the higher pH ranges. Uludag et al (*25,26)* have also indicated in their studies that their WSCP is able to readily bind Hg(II), but a solubility study as a function of pH was not reported.

Polymer Capacity Studies: The Hg(II) binding capacity was determined for a number of the WSCP. These experiments were performed at two pH values by adding excess Hg(II) to the polymer and determining the total amount of Hg(II) bound to the polymers by difference. It can be seen that WAB-30 and WAB-100 have the highest and almost equal capacity at pH 7. WABOH-30 has the next highest capacity with WCB-30 trailing. These capacities are quite large compared to common chelating ion exchange material such as Amberlite IRC-718. For example WAB-30 has a Zn capacity of 240 mg metal/gm dry polymer while the resin has a capacity of 30 mg Zn/gm dry polymer (*10*).

Mercury Recovery and Stabilization Approaches: There are a number of approaches to recovering Hg(II) from the WSCP. Hg(II) can be displaced from the WSCP by acid to give Hg(II) in solution as indicated in Figure 1. Sulfide could be used to precipitate HgS directly from the polymer, or Hg(0) could be recovered by electrolytic or chemical reduction from the WSCP. Another possible approach is to sacrifice the WSCP and incorporate it into the final waste form. Since the goal is polymer recycle, this latter option is not viable. Neither Hg(0) or $Hg(II)_{aq}$ is an acceptable waste form, so we did not want to recover the Hg in these final forms. A good final form is as HgS, which passes TCLP.

We decided that we would precipitate the Hg(II) from the concentrate to form the stable waste form of HgS. This form can be buried as is or placed in grout. The two approaches evaluated were direct stripping of Hg(II) from the WSCP with sulfide and dilute HNO_3 diafiltration of the Hg(II) from the WSCP followed by precipitation of the freed Hg(II) with sulfide.

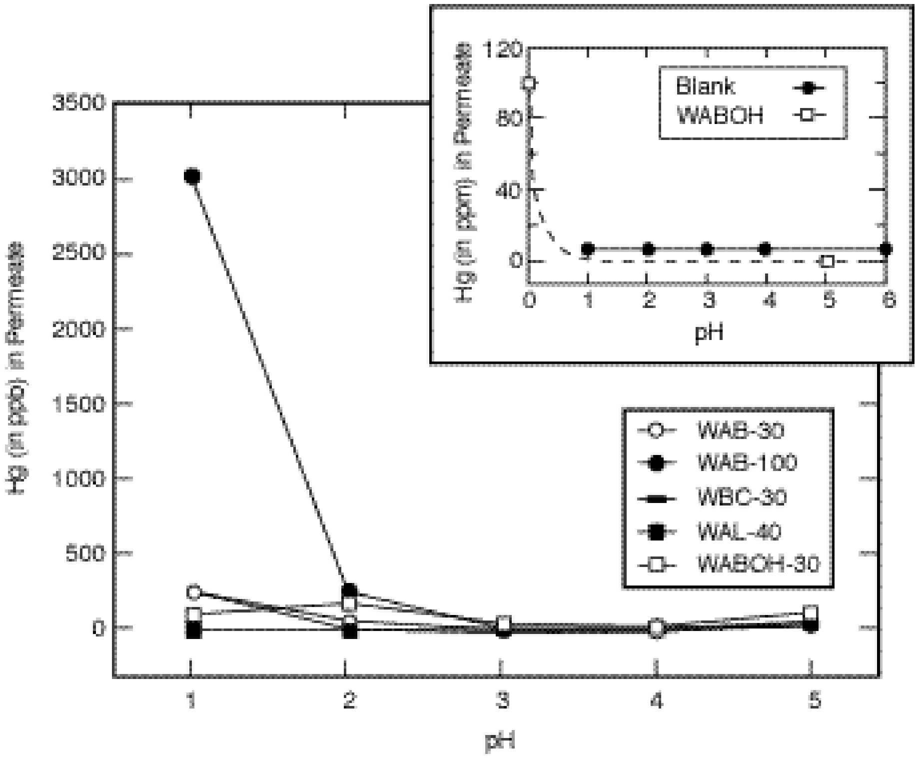


Figure 1. Binding of Hg(II) as a Function of pH. 1% wt/vol WSCP, pH Adjusted with HNO_3, Starting with 10 ppm $Hg(NO_3)_2$ SPEX Standards, Filtered Through Centricon-10 Unit, Permeate Analyzed by FIMS. Insert graph had starting [Hg] of 100 ppm for WABOH-30 and 10 ppm for the blank.

Table IX. Hg(II) Loading Capacities at Two pH Values for Several WSCP

Polymer	pH 7, mg Hg(meq.)/gm WSCP	pH 1, mg Hg/gm WSCP
WAB-30	497(2.5)	------
WAB-100	499(2.5)	221(1.11)
WCB-30	387(2.0)	------
WABOH-30	454(2.3)	114(0.57)

Conditions: At 0.04% w/v WSCP saturated with Hg(II) ions, ultrafiltered using Centracon-10 unit to remove unbound metal, permeate analyzed with FIMS.

Direct Displacement: Studies of direct displacement of Hg(II) with sulfide proved that the success of this approach is doubtful as the polymer caused the HgS to stay solublized as a black, transparent solution. Heating, pH adjustment, acetate treatment, and different precipitating agents could not force HgS to precipitate. In the absence of sulfide, all of the added Hg(II) and polymer passed through a 0.45 µm filter at pH 3, as determined by FIMS analysis. No black HgS was detected on the filter media after filtering through the 0.45µm filter disk in the presence of sulfide, but the permeate was still clear and black. Filtration through several smaller ultrafiltration membranes of 300K or less MWCO filter retained black material on the filter and the permeate was colorless. Thus, the black solution is some form of HgS that is suspended in solution by the polymer and perhaps still attached to it, but it is small enough to pass a 0.45 µm filter but not a 300K MWCO filter.

Table X shows that all the sulfide was bound to Hg(II) as the Hg analysis indicated that at different ratios of sulfide different amounts of Hg(II) remained free. Once an equivalent of sulfide was added, there was no free Hg(II) in solution. The FIMS appears to be unable to measure HgS in solution, probably because the $SnCl_2$ reagent is not capable of reducing HgS to Hg(0), which is the state in which Hg is measured. HgS was completely precipitated as a black solid from dilute HNO_3 in the absence of WSCP. In the absence of any sulfide, all the Hg was accounted for and the two polymers tested (WAB-30 and WCB-30) gave a low and high bias on the FIMS, respectively. Some polymers bias high and some low as shown in Table X. Thus, to recover HgS as the final waste form will require removing the Hg(II) from the polymer in a diafiltration process (*10*,*24*). This process can be performed at pH 0 for the WABOH-30 polymer as indicated from Figure 1. The concentrated Hg(II) solution from the diafiltrate will be precipitated as HgS. Direct precipitation from the polymer was not possible.

Table X. HgS Precipitation Studies in the Presence and Absence of Polymer.

Mole Ratio		ppm Hg in Solution	
$S^{=}$:Hg	H_2O	1% WAB-30*	1% WCB-30*
0:1	101	91	121
0.25:1	46	32	53
0.5:1	4	3	9
1:1	0.3	0	3
2:1	0.03	0	0

Conditions: NaSH as $S^{=}$ source, pH 4 HNO_3, 100 ppm Hg, *Filtered through 0.45 μ filter. Black colloid penetrated membrane. Measured Hg on FIMS.

Stainless Steel Leaching Studies (Pipe simulation): Some final tests were performed to determine if the conditions we had developed for solubilizing Hg(0) beads would aid in the dissolution of Hg(0) from the surfaces of stainless steel materials that represent contaminated pipes such as are found at Oak Ridge. Stainless steel coupons that had been contaminated with Hg(0) were mixed with a leaching solution. The leaching solution included several concentrations of HNO_3 for comparison to the polymer-containing solution. A total of three washings were performed, after which the coupon was dissolved with aqua regia to determine the remaining Hg. The results are summarized in Table XI. The harsh condition of concentrated HNO_3 was very effective at removing Hg(0), releasing 93 to 99% of the Hg(0). Likewise, the mild conditions of 0.1% WABOH-30, pH 2, 0.5% H_2O_2 was able to solubilize 86% of the Hg(0). We were able to remove a substantial amount of Hg(0) even in the presence of only 0.5% H_2O_2. Further testing with adjusting time, temperature, mixing, volume ratios, and H_2O_2 will be needed to raise the Hg removal level, which was already quite high.

Table XI. Hg(0) Decontamination Studies of Stainless Steel Coupons.

Leaching Reagent	Contact 1, % Hg Removed (ug)	Contact 2, % Hg Removed (ug)	Contact 3, % Hg Removed (ug)	% Hg Remaining (ug)	Total % Hg Removed
2 M HNO_3	10.9(85)	5.6(43.9)	7.6(59.8)	75.9(594.6)	24.1
6 M HNO_3	75.4(390)	10(50.9)	7.6(38.9)	6.0(30.7)	93
16 M HNO_3	96.7(1348)	2.4(33.9)	0.27(3.7)	0.63(8.7)	99.4
WSCP/ H_2O_2*	73.9(722.4)	10.1(105.9)	2(19.1)	19(198.4)	86

Conditions: Coated SS was mixed in an ultrasonic bath for 2 hr. *RT, 0.1% WABOH-30, pH 2, 0.5% H_2O_2.

Engineered Pipe Cleaning Unit: From these studies we designed and built a small pipe cleaning apparatus. A diagram of the process is shown in Figure 2. The apparatus has three components, (1) the washing unit which flushes polymer/H_2O_2/dilute HNO_3 through the pipe; (2) the concentration/diafiltration PF unit which collects the Hg/polymer complex concentrate; and (3) the sulfide precipitation unit that converts the Hg(II) concentrate diafiltered from the PF unit to a solid HgS material. The unit will be tested for pipe cleaning and other debris washing as soon as treatability study permits are in place.

CONCLUSIONS

We have successfully found several conditions where Hg(0) can be readily oxidized and solubilized to Hg(II) under mild, selective conditions. We have learned that for the H_2O_2 system (1) if the solution was not properly agitated, no oxidation/dissolution occurred (stir bar worked best, but was erratic); (2) Hg(0) in the presence of H_2O_2, but no polymer, gave no dissolution under our mixing conditions; (3) Hg(0) in the presence of WSCP, but no H_2O_2, did not result in dissolution, (polymers do not act as oxidants); (4) 2% H_2O_2, pH range of 1 to 4 with HNO_3, temp 30-60^oC, and 0.1 to 1% polymer gave Hg(0) dissolution times of 0.5 to 4 hr.; and (5) neither solid chelating resins nor single ligands aided in oxidation/ dissolution of Hg(0) in the presence of H_2O_2.

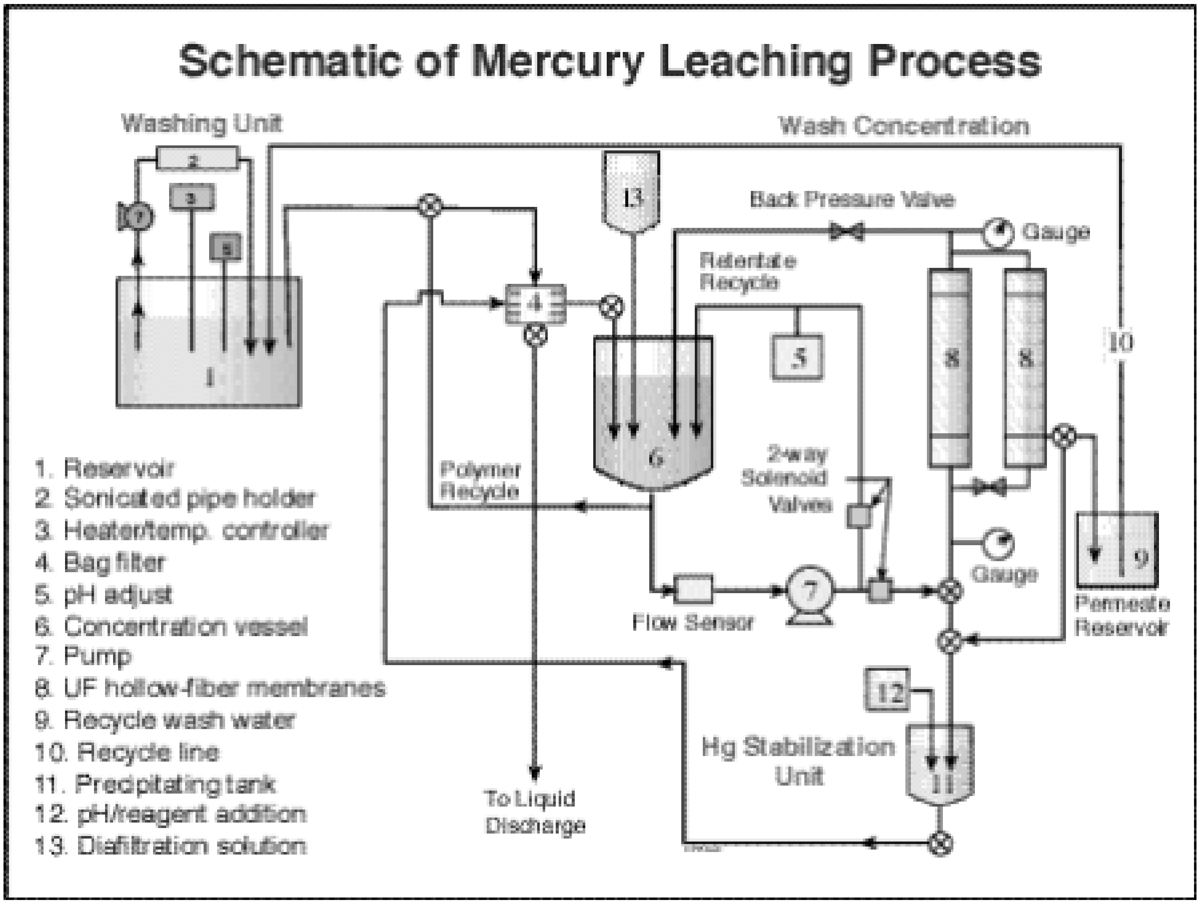


Figure 2. Schematic of the Operation of a Pipe-Washing Unit that Includes an Integrated Flowing Washing System, a Polymer Filtration Concentration Unit, and a Hg Stabilization Unit.

For the Fe(III) catalyzed system we have learned that (1) if the solution is not properly agitated, no oxidation/dissolution occurred (stir bar worked best); (2) Hg(0) in the presence of an Fe(III) catalyst but no polymer gave slow dissolution; (3) 2 M HNO_3, temp 30-60^oC, 0.1 to 1%

polymer, and 0.6 M Fe(III) gave dissolution times of 0.5 to 1 hr; and (5) single chelating ligands did not enhance the oxidation/dissolution of Hg(0) in the presence of Fe(III).

The mechanism of dissolution appears to be complex and may include multiple steps and/or pathways involving Hg(I) and HgO as intermediates. A number of side reactions appeared to be occurring based on observation of the reactions. For example, sometimes we would observe a small amount of orange-yellow solid depositing on the Teflon™ stir bar. It seemed to be HgO as it would dissolve with time or good mixing. Sometimes we observed a white milky solid that would often take a longer period to dissolve than the original Hg(0) bead. It is thought that perhaps it was a Hg(I) species that formed with the WSCP, but it has not yet been identified (*18*). Instead conditions were adjusted to eliminate its formation. Sometimes we observed a black precipitate, which may have been disproportionation of Hg(I) to Hg(0) and Hg(II). We might have been getting peroxide degradation as we sometimes observed bubbles emerging from the Hg(0) surface. All these observations seemed to be affected by polymer, pH, temperature and mixing conditions. Temperature and pH were relatively easy to control, but reproducibly mixing the Hg(0) beads was difficult. To progress to the next phase of a treatibility study will require solving the mixing issue. Some later studies indicated that ultrasonic energy may be the solution to the mixing problem. We will be pursuing the use of ultrasonic cleaners as mixing devices in our next stage of experiments.

It was observed that the polymer did enhance the oxidative dissolution rate. Perhaps the polymer not only shifted the thermodynamic redox equilibrium, but it also aided in the oxidation rate by bringing Hg(0) into closer proximity to the H_2O_2 on the polymer surface or inner structure, allowing for the electron transfer process to be more efficient.

Comparison between Fe(III) catalyzed and H_2O_2 oxidative methods for Hg(0) dissolution can be made. It appears that for both oxidative dissolution methods we have conditions that work equally well as far as attaining a reasonable rate of Hg(0) bead disappearance and minimization of side reactions such as white solid formation. The need for 2 M HNO_3 is still considered harsh conditions for a debris-leaching operation, but it is considerably better than concentrated HNO_3. The defining comparison would be the cost of a process that uses large amounts of HNO_3 and the need for large amounts of base to neutralize the system and the large amounts of secondary wastes that would be generated in the process. This large amount of secondary waste favors the use of the H_2O_2/polymer system. Though the final choice of conditions for the leaching studies was a compromise between the successful conditions determined, cost was the driver behind using the H_2O_2/polymer system for the stainless steel coupon leaching studies. For all further studies for other types of debris that are still ongoing, including incinerable debris, we will use the H_2O_2/polymer/dilute HNO_3 conditions. These conditions were able to readily remove 86 % of Hg(0) from stainless surfaces.

We have demonstrated that there are a number of WSCP that can strongly bind Hg(II) such that when the polymer/Hg(II) complex is ultrafiltered, the permeate can meet the 20 ppm discharge limit. We have shown that Hg(II) can be stripped from one of the WSCP, WABOH-30, at pH 0 and that all these polymers have a high capacity for Hg(II). Permeate from the diafiltration process can be readily precipitated with sulfide to form a stable waste form. Though the complete oxidative stability of the polymer to 2% H_2O_2 has not been proven, we have shown that the breakthrough of Hg(II) was not substantially influenced by the presence of H_2O_2. Longer-term polymer stability studies with H_2O_2 will be undertaken.

After optimizing the dissolution, binding, and stripping chemistry of Hg, we built a debris-washing unit that directs leaching solution to flow through actual pipes. This unit will be used to determine the optimum parameters and obtain an engineering cost analysis of the process. Currently there are not very many technologies that can readily, safely, and efficiently (low temperature, low secondary waste production) leach debris. The preliminary cost analysis of PF is very favorable in comparison with one of the current technologies that uses halogenated leaching agents (*19-21*). Using the data from the process patent (*19*), we have estimated that when the two process units were sized for the same throughput (1) the PF processing time is 6 times faster than the other process; (2) the reagent costs for the other process are 14 times greater that the PF process; (3) the operating costs for the other process are 10 times greater than the PF process; (4) the capital costs are 2 times greater than the PF process; and (5) PF generates little secondary waste and the other process has considerable secondary waste *(27*).

ACKNOWLEDGEMENTS

We would like to thank the Department of Energy (DOE), Office of Industrial Technology for funding the Electroplating Waste Minimization work, which was the foundation for this work, the DOE, Environmental Management (EM-50), Efficient Separations and Processing Crosscutting Program for funding the fundamental mercury work, and the Mixed Waste Focus Area Program (EM-30) for funding some of the applied work.

REFERENCES

1. Roach, Jay A. Mixed Waste Focus Area Department of Energy Complex Needs Report. INEL-95/0555, Nov. 16, **1995**.
2. Warshawsky, A. Chelating Ion Exchangers. in *Ion Exchange and Sorption Processes in Hydrometallurgy,* pp. 166-225, M. Streat, Ed., John Wiley & Sons, New York, **1987**.
3. Kantipuly, C., S. Katragadda, A. Chow and H. D. Gesser, "Chelating Polymers and Related Supports for Separation and Preconcentration of Trace Metals," *Talanta*, 1990, **37**, 491-517.
4. Smith, B. F.; et al., *Chelating Water-Soluble Polymers for Waste Minimization*, **1996**, LA-UR-96-3224.
5. Smith, B. F.; Gibson, R. R.; Jarvinen; G. D.; Jones, M. M.; Lu, M. T.; Robison, T. W.; Schroeder, N. C.; Stalnaker, N. Evaluation of Synthetic Water-Soluble Meta-Binding Polymers with Ultrafiltration for Selective Concentration of Americium and Plutonium. *MARC IV Proceedings, J. Radioanal. Nucl. Chem*., **1998**, *234(1-2),* 219.
6. Smith, B. F.; Gibson, R. R.; Jarvinen; G. D.; Robison, T. W.; and Schroeder, N. C. Preconcentration of Ultra-Low Levels of Americium and Plutonium from Waste Waters by Water-Soluble Metal-Binding Polymers with Ultrafiltration. *MARC IV Proceedings, J. Radioanal. Nucl. Chem*., **1998**, *234(1-2*), 225.
7. Smith, B. F., Robison T. W., Cournoyer, M. E., Wilson, K. V., Sauer, N. N., Lu, M. T., Groshart, E. C., Nelson, M. C. Polymer Filtration: A New Technology for Selective Metals Recovery. *International Technical Proceedings from SURFIN 95*; **1995,** June 26-29, pp 607-616.
8. Geckeler, K.; Lange, G.; Eberhardt, H.and Bayer, E. Preparation and Application of Water-Soluble Polymer-metal Complexes. *Pure and Appl. Chem.* **1980**, *52,* 1883.
9. Geckeler, K.; Volchek, K., *Env. Sci. & Tech*., **1996**, *30*, 727.
10. Smith, B. F.; Robison T. W.; Jarvinen, G. D. Water-Soluble Metal-Binding Polymers with Ultrafiltration: A Technology for the Removal, Concentration, and Recovery of Metal

Ions from Aqueous Streams. ACS Symposium Series volume, *Advances in Metal Ion Separation and Preconcentration*, R. Rogers, A. Bond and M. Dietz Eds, Chapt 20, **1998**.

11. Polymer Filtration™ Technology is commercially available for electroplating and similar applications from PolyIonix Separation Technologies, Inc., a Division of PGI, Dayton, N.J.
12. Standard Potentials in Aqueous Solution, Allen J. Bard, Roger Parsons, and Joseph Jordan, Eds. Marcel Dekker, Inc., New York, **1985**. p. 129.
13. Ibid.. p 282.
14. Ibid., p.54.
15. Ibid., p. 57.
16. Wirth, T. H.; Davidson, N. Mercury(II) Complexes of Guanidine and Ammonia, and a General Discussion of the Complexing of Mercury(II) by Nitrogen Bases. *J. Am. Chem. Soc.*, **1964**, *86*, 4325.
17. Brooks, P.; Davidson, N. Mercury(II) Complexes of Imidazole and Histidine. *J. Am. Chem. Soc.*, **1959**, *26*, 2118.
18. Wirth, T. H.; Davidson, N. Studies of the Chemistry of Mercury in Aqueous Solutions. I. Mercury(I) and Mercury(II) Complexes of Analine. *J. Am. Chem. Soc.*, **1964**, *86*, 4314.
19. Foust, D. F. Extraction of Mercury and Mercury Compounds from Contaminated Materials and Solutions. Pat. No. 5,226,545, July 13, **1993**.
20. Klasson, K. T.; Koran, L. J. Jr.; Gates, D. D.; Cameron, P. A. Removal of Mercury from Solids Using the Potassium Iodide/Iodine Leaching Process. ORNL/TM-13137 Report, Dec. **1997**.

21. Gates, D. D.; Klasson, K. T.; Corder, S. L.; Cameron, P. A.; Petona, J. J; Chao, K. K. Mercury Removal from Liquid and Solid Mixed Waste. Presented at MW'95, Tucson, AZ, February 26- March 2, **1995**.
22. Standard Potentials in Aqueous Solution, Allen J. Bard, Roger Parsons, and Joseph Jordan, Eds. Marcel Dekker, Inc., New York, **1985**. p. 408.
23. Ibid., p. 411.
24. For a general discussion of the ultrafiltration/diafiltration process see: Cheryan, M., *Ultrafiltration Handbook*, **1986**, Technomic, Lancaster, United Kingdom, see also Winston, W. S. and Sirkar, K. K. *Membrane Handbook*, Van Nostrand Reinhold: N.Y., **1992**.
25. Uludag, Y.; Ozbelge, O. H.; Yilmaz, L., *J. of Membrane Sci.* **1997**, *129*, 93-99.
26. Muslehiddinoglu, J.; Uludag, Y.; Ozbelge, H.O.; Yilmaz, L., *J. of Membrane Sci.*. **1998**, *140*, 251-266.
27. Proceedings of the Annual Technical Exchange Meeting of the Efficient Separations and Processing Cross-Cutting Program. pp.1-7, March 17-19, **1998**.