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Mercury Separation from Concentrated Potassium Iodide/Iodine Leachate Using Self-Assembled Mesoporous Mercaptan Support (SAMMS) Technology

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September 1997

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Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

PNNL-11714

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Summary

A study was conducted to demonstrate the effectiveness of a novel adsorber, the Self-Assembled Mesoporous Mercaptan Support (SAMMS) material to remove mercury (Hg) from potassium iodide/iodine (KI/I_2) waste streams. This study included investigations of the SAMMS material's binding kinetics, loading capacity, and selectivity for Hg adsorption from surrogate and actual KI/I_2 waste solutions. The kinetics data showed that binding of Hg by the adsorber material occurs very rapidly, with 82% to 95% adsorption occurring within the first 5 min. No significant differences in the rate of adsorption were noted between pH values of 5 and 9 and at Hg concentrations of ~100 mg/l. Within the same range of pH values, an approximate four-fold increase in initial Hg concentration resulted in a two-fold increase in the rate of adsorption. In all cases studied, equilibrium adsorption occured within 4 h. The loading capacity experiments in KI/I_2 surrogate solutions indicated Hg adsorption densities between 26 to 270 mg/g. The loading density increased with increasing solid:solution ratio and decreasing iodide concentrations. Values of distribution coefficients ($1.3x10^5$ to $>2.6x10^8$ ml/g) indicated that material adsorbs Hg with very high specificity from KI/I_2 surrogate solutions. Reduction studies showed that compared to metallic iron (Fe), sodium dithionite can very rapidly reduce iodine as the triiodide species into the iodide form. Adsorption studies conducted with actual KI/I_2 leachates confirmed the highly specific Hg adsorption properties (K_d $>6x10^7$ to $>1x10^8$ ml/g) of the adsorber material. Following treatment, the Hg concentrations in actual leachates were below instrumental detection limits (i.e., < 0.00005 mg/l), indicating that the KI solutions can be recycled.

This work was funded by the Mixed Waste Focus Area, Office of Science and Technology, U.S. Department of Energy.

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1.0 Introduction

1.1 Purpose and Scope

The U.S.Department of Energy's (DOE's) mixed waste focus area has identified the removal/separation of mercury (Hg) as the number 4 priority among 30 prioritized deficiencies. Over 50,000 m^3 of mixed low-level and transuranic waste-containing Hg have been identified in the DOE complex. Many Hg-bearing DOE wastes are aqueous and nonaqueous liquids, sludges, soils, absorbed liquids, partially or fully stabilized sludges, and debris. The technology deficiency description and target waste streams are described in INEL (1997). So far, no effective treatment technology has been developed for removing the Hg contained in these wastes.

The objective of this study is to demonstrate the effectiveness of the Pacific Northwest National Laboratory (PNNL)[1] developed Self-Assembled Mesoporous Mercaptan Supports (SAMMS) adsorber technology to remove Hg from spent potassium iodide/iodine (KI/I_2) lixiviant. This study was coordinated with a related project at Oak Ridge National Laboratory (ORNL) designed to demonstrate the ability of the KI/I_2 lixiviant to remove Hg from a variety of waste types. The leachates and washwaters generated by ORNL were transferred to PNNL for testing the effectiveness of SAMMS material for removing dissolved Hg from the spent KI/I_2 solutions.

The scope of the PNNL study included investigation of kinetics, loading capacity, and distribution coefficient for Hg adsorption on SAMMS material. All investigations were conducted using both surrogate and actual KI/I_2 solutions of varying ionic strengths and soluble Hg concentrations. Additionally, effective iodine reduction reactions were also investigated.

1.2 Approach

All experiments were conducted in batch equilibrium mode. Factors investigated included soluble Hg concentrations, iodide concentrations, pH, and solution:solid ratios. Except for the kinetic experiments, all others were conducted at a 4-h fixed equilibration time.

1.3 Leaching Process

The KI/I_2 lixiviant process was developed to extract Hg from contaminated soil, sand, and similar materials (Foust 1993). This patented process utilizes solutions consisting of I_2 (0.001 to 0.5M) as the oxidizing agent and the iodide ion (from 0.1 to 1.0M) as a complexing ligand. Depending on Eh-pH conditions, Hg in contaminated solid wastes is known to exist as oxides, sulfides, and elemental form. Additionally, Hg may also exist as solid:solution phases and as the adsorbed phase with clay minerals, aluminum and iron oxides and hydroxides, and organic matter. All these forms are mobilized by the KI/I_2 lixiviant by oxidation and complexation as follows:

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[1]PNNL is operated for DOE by Battelle

mercuric sulfide: $HgS(s) + 4I_2 + 3H_2O = SO_4^{2-} + 6H^+ + 4I^- + HgI_4^{2-}$

elemental mercury: $Hg(l) + I_2 + 2I^- = HgI_4^{2-}$

mercuric oxide: $HgO(s) + 4I^- + 2H^+ = H_2O + HgI_4^{2-}$

adsorbed mercury: $Hg\text{-}X_2\ (s) + 2K^+ + 4I^- = 2KX + HgI_4^{2-}$

As these reactions indicate, the iodide ion forms very strong complexes with divalent Hg ions (log K of 29.8 for HgI_4^{2-} species), resulting in the mobilization of Hg from enhanced solubilities of Hg-bearing solid phases.

This process is used at ORNL to demonstrate the effectiveness of the KI/I_2 lixiviant for removing Hg from a variety of waste types.

1.4 SAMMS Adsorber Technology

The SAMMS materials are a novel class of adsorption substrates currently being developed at PNNL. These materials with specifically designed functional groups have very high specificity and adsorption capacity for Hg and other metallic contaminants of concern. The pores in SAMMS have a very narrow, specifically tailored (15 to 400 Å) pore-size distribution, resulting in very high surface area (>800 m^2/g).

The novel SAMMS materials are synthesized by utilizing the principle of molecular self-assembly in which functional molecules are induced to aggregate on an active surface, resulting in an organized assembly with both order and orientation (Fryxell et al. 1996, Bunker et al. 1994, Tarasevitch et al. 1996). During this process, bifunctional molecules containing hydrophilic and hydrophobic moities adsorb onto an engineered substrate or interface as closely packed monolayers. Such self-assembly of functional molecules is driven by both inter- and intra-molecular forces. The hydrophobic and hydrophilic moities of these functional molecules can be chemically modified to contain specific functional groups to promote covalent bonding between the functional organic molecules and the substrate on one end and the molecular bonding between organic molecules and the metallic ions on the other end. By populating the outer surface with an optimum density of functional groups, an effective means for specifically binding certain metal ions can be established. The metal-loading capacity of such an assemblage is determined by the functional group density that, in turn, is controlled by the available surface area of the underlying inorganic engineered substrate.

The SAMMS materials used in these investigations were synthesized through a coassembly process, using oxide precursors and surfactant molecules (Liu et al. 1995, 1996; Beck et al. 1992; Kresge et al. 1992; LeGrange et al. 1993). The synthetic process consisted of mixing surfactants and oxide precursors in a solvent and reacting the resulting solution under mild hydrothermal conditions. The process consisted of forming ordered liquid-crystalline structures, such as

hexagonally ordered rod-like micelles by the surfactant molecules, followed by the precipitation of oxide materials on the micellar surfaces to replicate the organic templates formed by the rod-like micelles. Calcination of the organic-oxide micelle structures at 500°C removed the surfactant templates, resulting in a high surface area mesoporous oxide structure. Functionalized monolayers, consisting of thiol groups, were formed on the pore surfaces of the mesoporous oxide structure using tris-(methoxy)mercaptopropylsilane in an appropriate solvent (Feng et al. 1997). These thiol functional groups are known to have very high specificity for binding soft cations such as Hg. The SAMMS material used in our investigations consisted of particles 5 to 15 μm in size with pore sizes of 5 nm and 871 m^2/g of surface area. Preliminary binding tests indicted K_d values of $\sim 1 \times 10^8$ ml/g for this SAMMS material (Feng et al. 1997). Dissolved Hg in the form of the HgI_4^{2-} species in spent KI/I_2 lixiviant would be adsorbed covalently by thiol functional groups in SAMMS, resulting in the release of free iodide ions as follows:

$$HgI_4^{2-} + \text{SAMMS} = \text{Hg-SAMMS} + 4I^- + 2H^+$$

In summary, the key features of the current SAMMS technology are the following:

- The large surface areas (>800 m^2/g) of the tailored functional group-bearing mesoporous oxides (SiO_2, ZrO_2, TiO_2) ensure high capacity for loading of soft cation contaminants such as silver and Hg.

- The highly specific molecular recognition capabilities of the interfacial functional groups ensure the high affinity and selectivity for heavy metals without interference from other abundant cations, such as calcium and iron, in waste streams.

- The removal of Hg from both aqueous and organic wastes is feasible.

- The Hg-laden SAMMS materials not only pass the U. S. Environmental Protection Agency's toxicity characteristic leaching procedure (TCLP) tests (EPA 1990) but also have good long-term durability as a waste form because the covalent binding between Hg ions and the functional groups in SAMMS have very good resistance to ion exchange, oxidation, and hydrolysis.

- The uniform and small pore size (15 to 400 Å) of the SAMMS materials prevents bacteria (>2000 nm) from accessing the pore space and mobilizing the covalently bound Hg.

- The SAMMS material can also be used for Hg removal from gaseous Hg wastes and Hg-bearing sludges, sediment, and soils.

2.0 Mercury Binding Behavior of SAMMS Material in Surrogate and Actual Leachates

2.1 Kinetics of Mercury Adsorption Reactions

The kinetics of adsorption reactions are typically evaluated by three different techniques: adsorption, desorption, and isotopic exchange. In adsorption experiments, the rate of adsorption is monitored by the rate of decrease in solution concentration of the adsorbate over a period of time. In the desorption method, the rate of adsorption of a component of interest is measured by the rate of increase in solution concentration of another component that is being desorbed from adsorption sites by the component of interest. In isotopic exchange, an isotope of the adsorbate of interest is used to track the rate of adsorption. This technique is used typically to study adsorption reactions at trace concentrations of an adsorbate.

A set of experiments were designed to study the kinetics of adsorption of dissolved Hg from a matrix solution of 100 mmol/l KI. The binding kinetics were assessed using batch adsorption experiments at four different pH values, ranging from acidic to basic (3, 5, 7, and 9). The rates of adsorption were monitored by measuring the Hg concentration in the solution phase at selected periodic intervals. Because the rate of adsorption is affected by the initial concentration of adsorbate, two sets of kinetic experiments at each pH value were conducted to examine this phenomenon. The initial Hg concentrations in these experiments were set at ~100 and ~370 mg/l, respectively. These concentrations were selected on the basis that this range of Hg concentration may represent the higher range found in KI solution following extraction of actual Hg-bearing wastes. A fixed solid:solution ratio of 1:800 was used in all experiments. The test matrix for the adsorption kinetic studies consisted of 8 experiments with 7 periodic measurements (5, 10, 30, 60, 120, 180, and 360 mins) of Hg concentration in each experiment.

The results of the binding kinetics experiments are listed in Table 2.1, and the solution concentrations and the amount adsorbed per unit mass of SAMMS at each time interval at fixed pH and initial Hg concentrations are displayed in Figures 2.1 through 2.12. The data show that at initial Hg concentrations of ~100 mg/l and at all pH values, ~95% of the final adsorption occurs within the first 5 min (see Figures 2.5 and 2.6). No significant differences in the rate of adsorption (rate of decrease in solution concentration) were observed at pH values of 5, 7, and 9; however, at pH 3, the rate appeared to be lower than that observed at higher pH values. In all cases, adsorption equilibrium seems to have been attained in ~4 h.

In experiments with higher initial concentrations of Hg (360 to 380 mg/l) the rates of adsorption at all pH values were slightly slower than that observed at lower initial Hg concentrations (99.5 to 102 mg/l). On average, ~82% final adsorption occurred within the first 5 min (see Figures 2.7 through 2.12). No significant differences in the rate of adsorption (rate of decrease in solution concentration) were observed at pH values of 3, 5, and 7; however, at pH 9, the rate appeared to be slightly higher than observed at lower pH values. Also in this set of experiments, adsorption equilibrium seems to have been attained in ~4 h.

Table 2.1. Kinetics Data for Mercury Binding by SAMMS Material

pH	Time (min)	Conc. (mg/l)	Adsorbed (mg/g)	pH	Time (min)	Conc. (mg/l)	Adsorbed (mg/g)
3	0	102.0	0.0	3	0	375.0	0.0
3	5	14.2	70.2	3	5	184.0	152.8
3	10	11.9	72.1	3	10	163.5	169.2
3	30	11.0	72.8	3	30	159.0	172.8
3	60	10.1	73.5	3	60	139.0	188.8
3	120	8.3	75.0	3	120	150.0	180.0
3	180	8.3	75.0	3	180	141.0	187.2
3	360	7.8	75.4	3	360	141.0	187.2
5	0	102.0	0.0	5	0	358.0	0.0
5	5	6.1	76.8	5	5	170.5	150.0
5	10	4.2	78.2	5	10	156.0	161.6
5	30	3.7	78.7	5	30	140.0	174.4
5	60	3.0	79.2	5	60	124.0	187.2
5	120	2.7	79.4	5	120	135.0	178.4
5	180	2.6	79.6	5	180	126.0	185.6
5	360	2.1	80.0	5	360	123.0	188.0
7	0	101.0	0.0	7	0	358.0	0.0
7	5	7.0	75.2	7	5	170.5	150.0
7	10	5.2	76.7	7	10	153.5	163.6
7	30	4.5	77.2	7	30	145.0	170.4
7	60	3.5	78.0	7	60	134.0	179.2
7	120	3.5	78.0	7	120	134.0	179.2
7	180	2.95	78.5	7	180	130.0	182.4
7	360	2.6	78.7	7	360	127.0	184.8
9	0	99.5	0.0	9	0	382.0	0.0
9	5	5.9	74.9	9	5	160.0	177.6
9	10	4.5	76.0	9	10	147.0	188.0
9	30	3.7	76.7	9	30	144.0	190.4
9	60	2.8	77.4	9	60	150.0	185.6
9	120	2.6	77.5	9	120	130.0	201.6
9	180	2.6	77.5	9	180	122.0	208.0
9	360	2.0	78.0	9	360	122.0	208.0

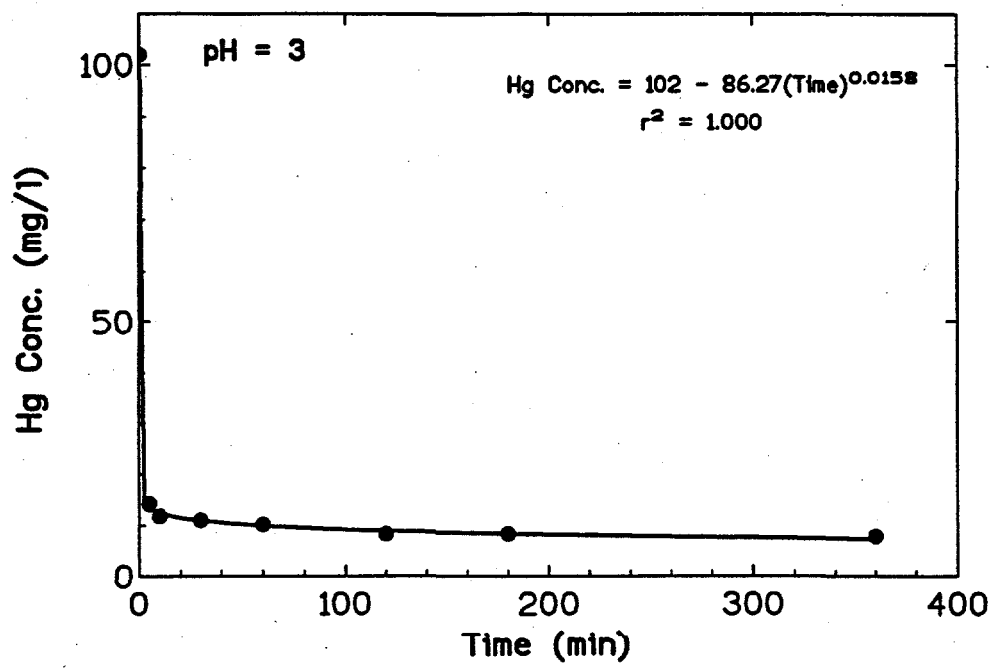

Figure 2.1. Mercury Binding Kinetics at pH 3 and Initial Concentration of ~100 mg/l

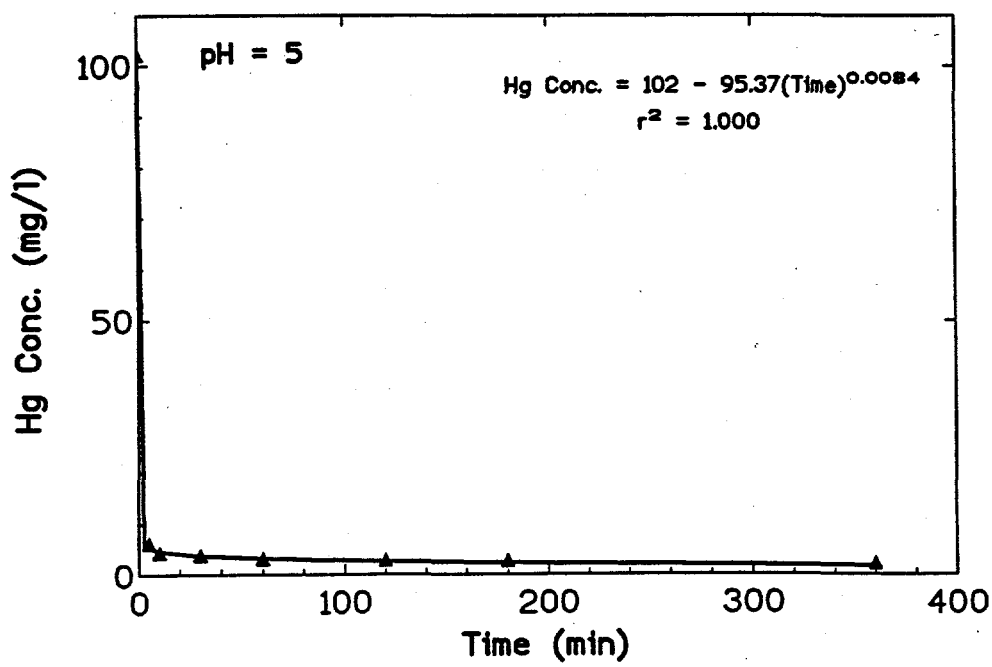

Figure 2.2. Mercury Binding Kinetics at pH 5 and Initial Concentration of ~100 mg/l

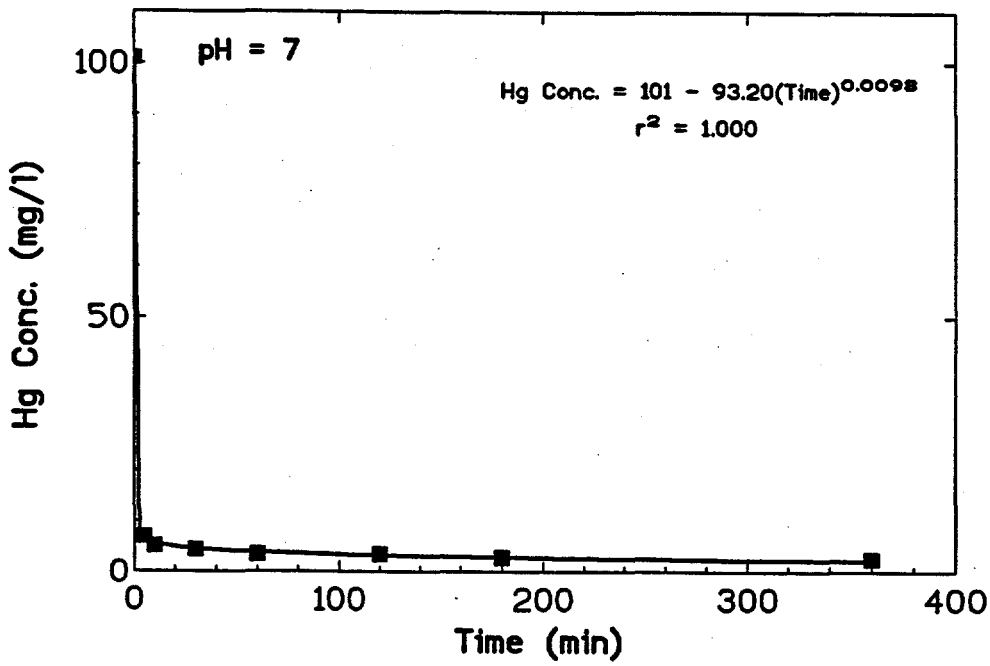

Figure 2.3. Mercury Binding Kinetics at pH 7 and Initial Concentration of ~100 mg/l

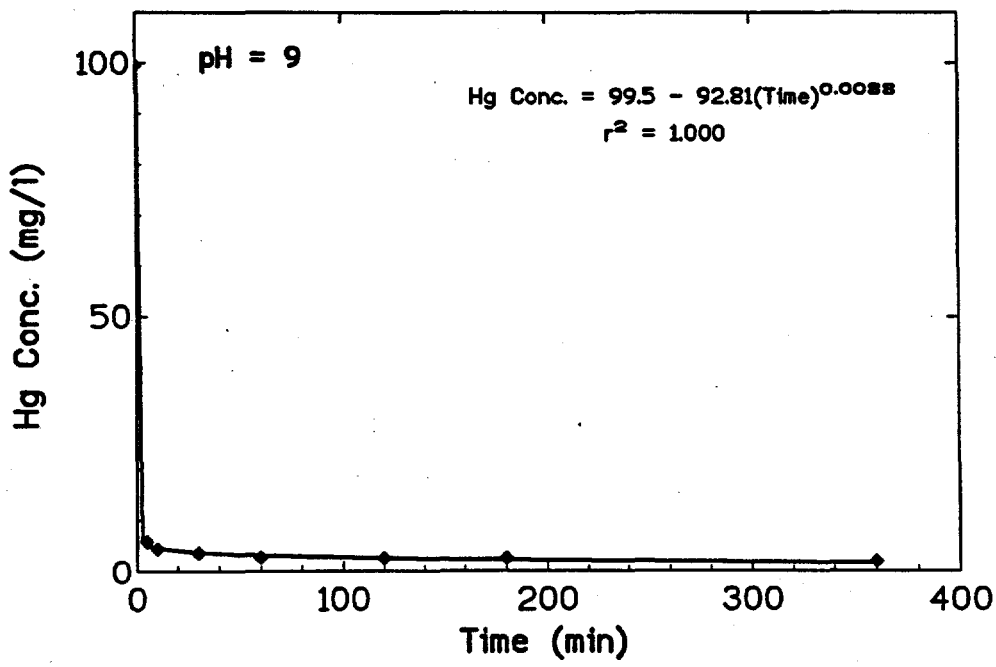

Figure 2.4. Mercury Binding Kinetics at pH 9 and Initial Concentration of ~100 mg/l

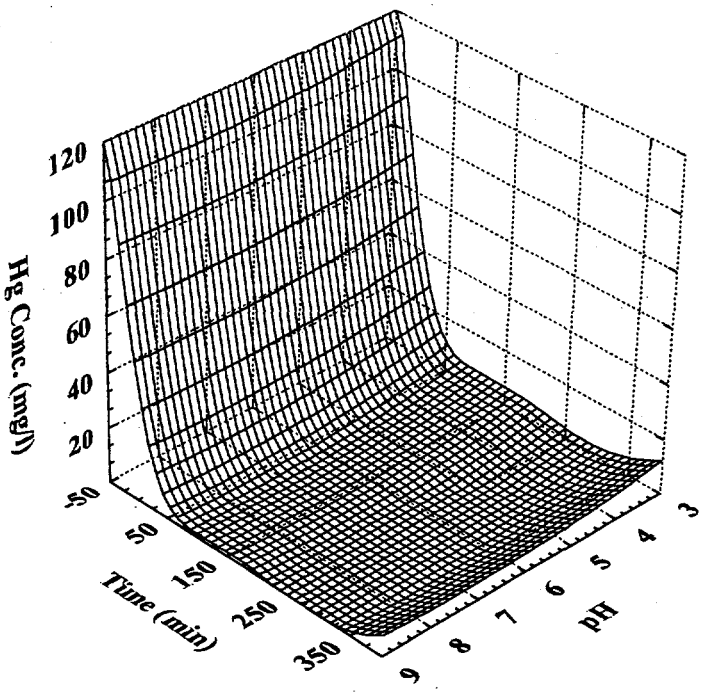

Figure 2.5. Kinetic Response Surface for Removal at an Initial Concentration of ~100 mg/l

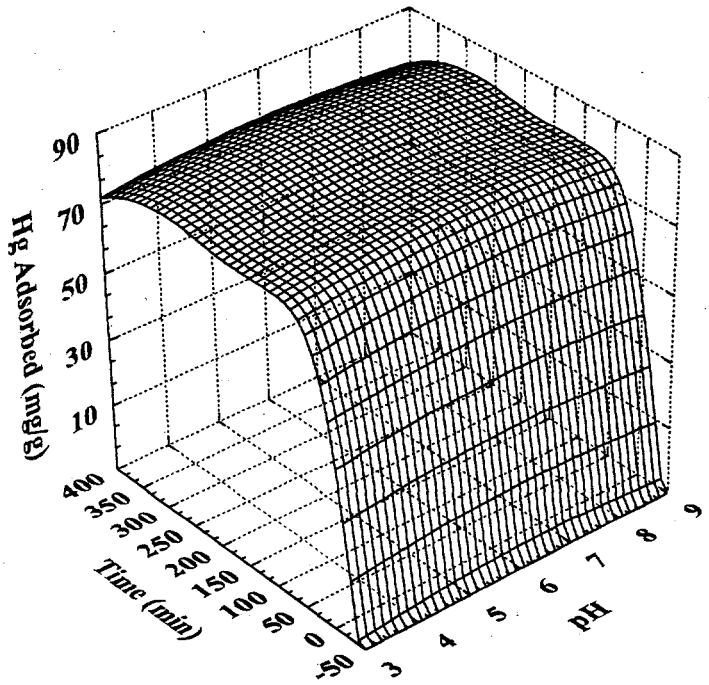

Figure 2.6. Kinetic Response Surface for Loading at an Initial Concentration of ~100 mg/l

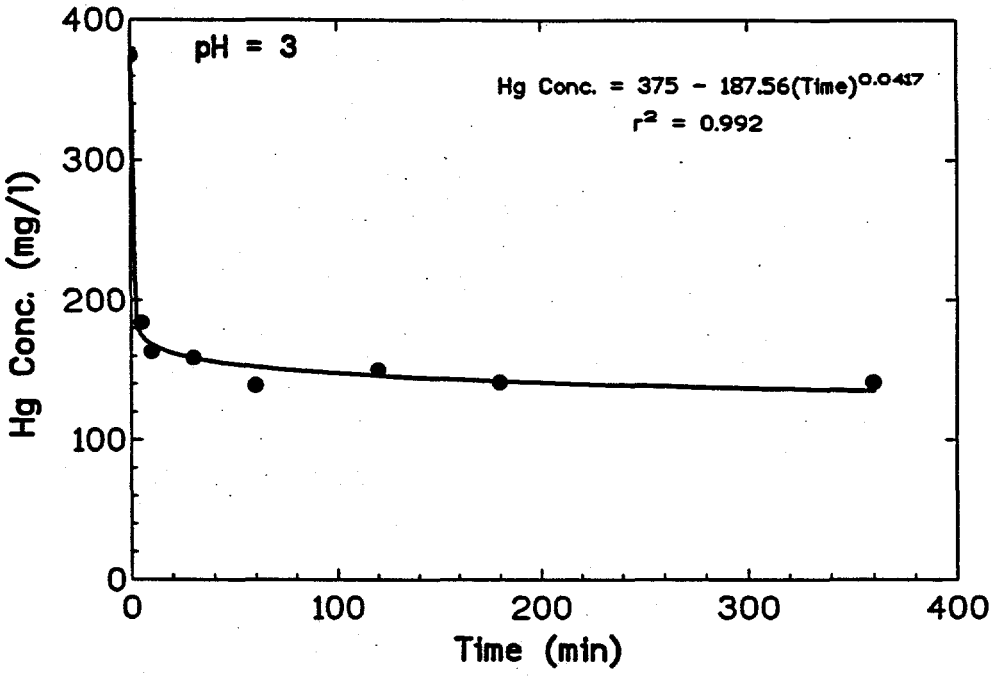

Figure 2.7. Mercury Binding Kinetics at pH 3 and Initial Concentration of ~370 mg/l

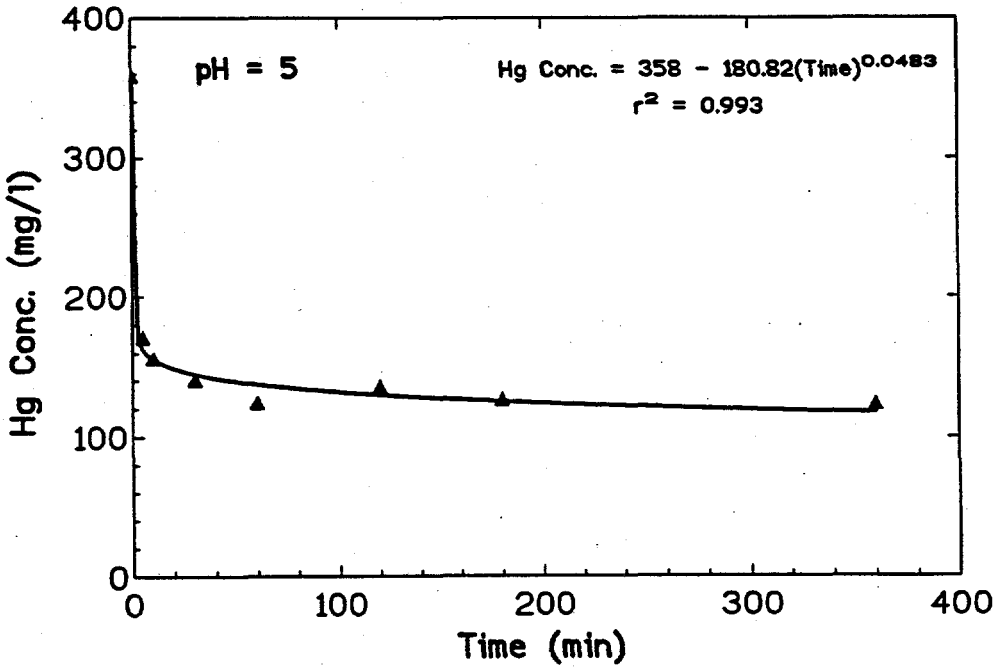

Figure 2.8. Mercury Binding Kinetics at pH 5 and Initial Concentration of ~370 mg/l

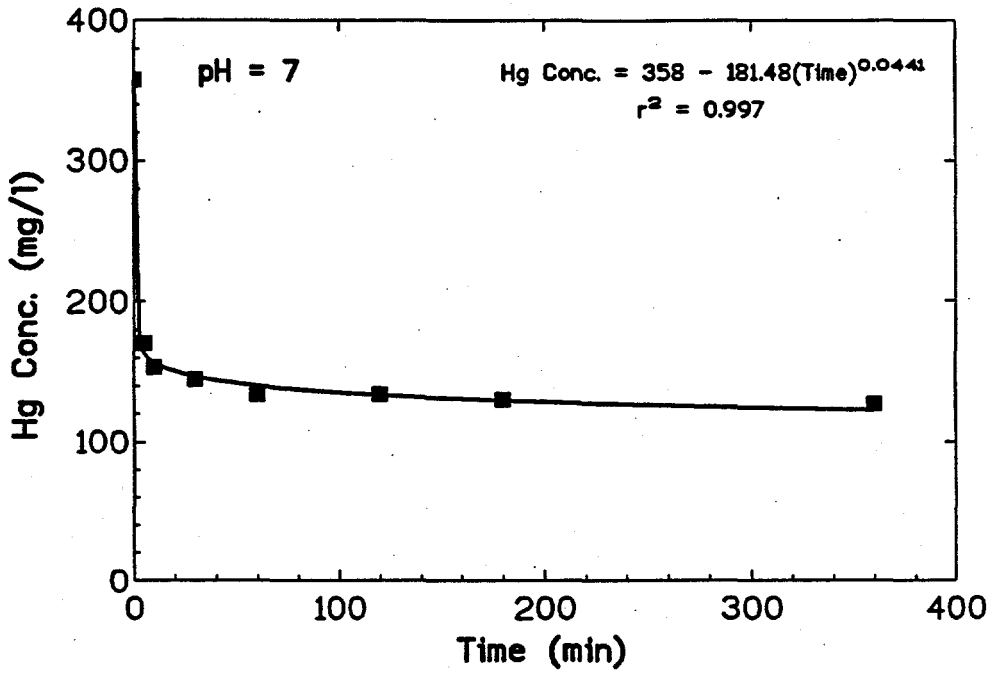

Figure 2.9. Mercury Binding Kinetics at pH 7 and Initial Concentration of ~370 mg/l

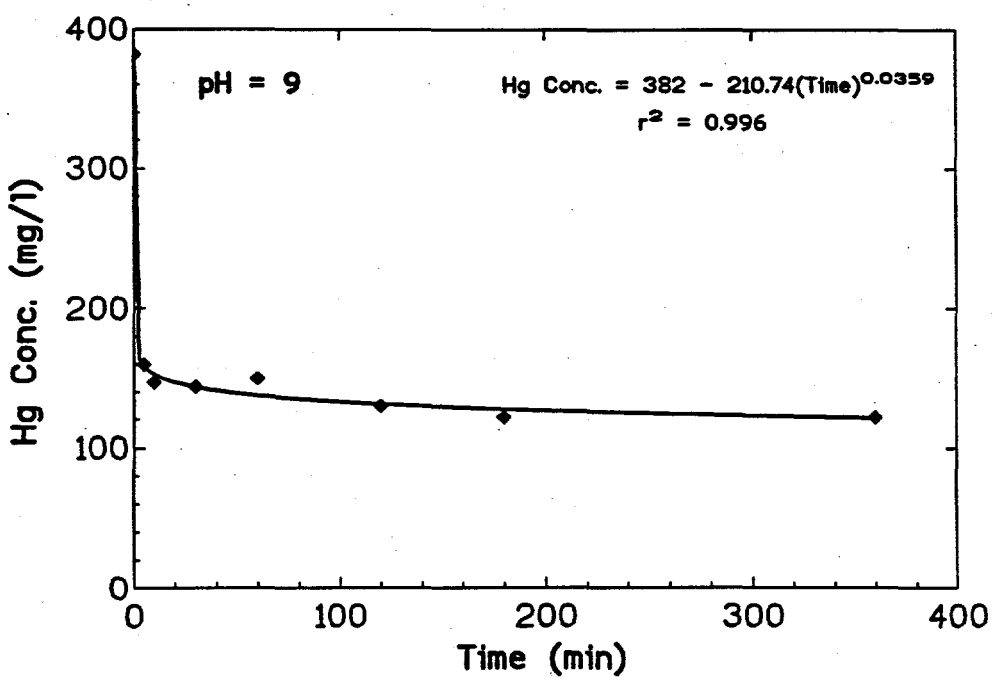

Figure 2.10. Mercury Binding Kinetics at pH 9 and Initial Concentration of ~370 mg/l

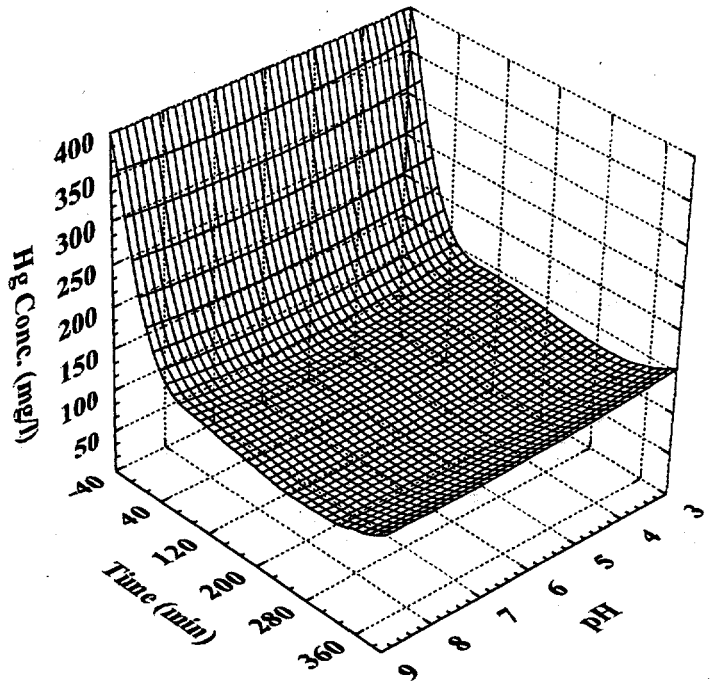

Figure 2.11. Kinetic Response Surface for Removal at an Initial Concentration of ~370 mg/l

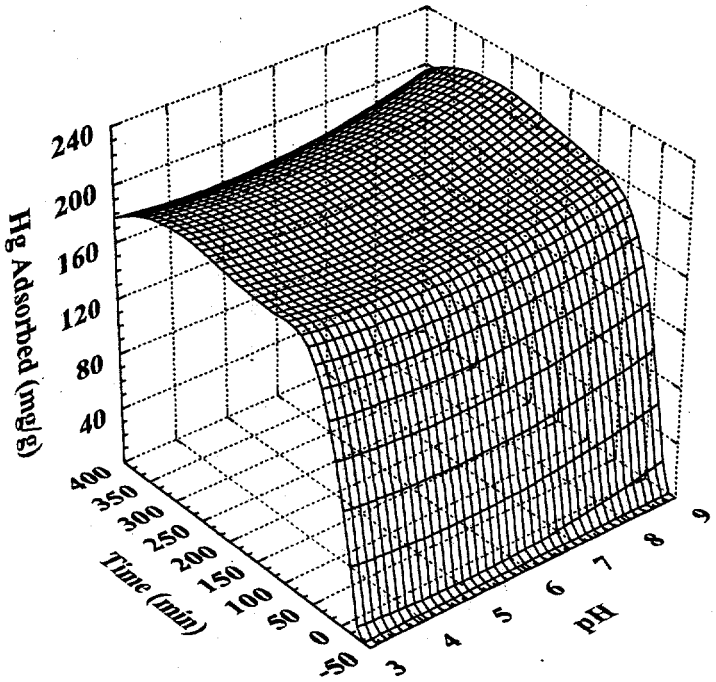

Figure 2.12. Kinetic Response Surface for Loading at an Initial Concentration of ~370 mg/l

The rapid rates of Hg adsorption onto SAMMS materials observed in these experiments are similar to the reaction rates observed previously by coworkers for adsorption on SAMMS in 0.1M $NaNO_3$ solutions with very low initial concentrations of Hg (0.5 and 10 mg/l).

The binding kinetics data collected in these experiments lead to the following conclusions:

- Between the 3 to 9 pH range, ~82% to 95% of final adsorption occurs within the first 5 min, indicating an extremely rapid rate of reaction.

- In experiments with initial Hg concentrations of ~100 mg/l, no significant differences in the rate of adsorption (rate of decrease in solution concentration) were observed at pH values of 5, 7, and 9; however, at pH 3, the rate appeared to be lower than the rates observed at higher pH values.

- In experiments with higher initial Hg concentrations of ~ 370 mg/l, no significant differences in the rate of adsorption (rate of decrease in solution concentration) were observed at pH values of 3, 5, and 7; however at pH 9, the rate appeared to be slightly higher than the rates observed at lower pH values.

- Under tested pH conditions and initial Hg concentrations, adsorption equilibrium seems to have been attained in ~4 h.

2.2 Loading Density and Distribution Coefficient Measurements

2.2.1 Mercury Loading Using Surrogate Waste Stream Solutions

The objective of these experiments was to measure the range of Hg loading on SAMMS material that can be achieved from matrix solutions formulated as surrogates for leachates from actual Hg-containing wastes. The compositions of surrogate solutions were developed on the basis of composition of actual leachate solutions provided by ORNL. According to the ORNL data, the dominant dissolved constituents in the actual Hg-containing waste streams are K^+, I^-, and I_2, with minor amounts of Fe^{2+} and SO_4^{2-}. Based on this information, a series of surrogate solutions were prepared, containing varying concentrations of I, K, and Hg and other minor constituents. These solutions were formulated to represent varying compositions of leachates, washwaters, and combinations of these waste streams. The Hg concentrations used in these experiments ranged from ~100 to 600 mg/l, and the iodide concentrations ranged from ~90 to 600 mmol/l.

Generally, the contaminant loading on an exchange material is affected by several factors, such as the composition of matrix solution (competing ions, ionic strength, and pH), concentration of contaminant, solid:solution ratio, and contact time. In this set of experiments, the effects of the iodide concentrations and solid:solution ratios were tested with a fixed contact time of 4 h. The compositions of the surrogate test solutions used in these experiments are listed in Table 2.2.

Table 2.2. Surrogate Solutions Used in Mercury-Loading Experiments

Constituent	Surrogate Solutions				
	S1	S2	S3	S4	S5
Iodide (mmol/l)	606	410	350	250	90
Sulfate (mmol/l)	20	23	54	54	88
K (mmol/l)	635	440	450	350	265
Fe (II) (mmol/l)	3	3	2	2	0.5
Ca (mmol/l)	--	--	0.1	0.1	0.2
Hg (mg/l)	470	580	260	340	98

The loading experiments were conducted in duplicate (except two very high solid:solution ratio experiments), with surrogate solutions and varying quantities of SAMMS material to achieve ratios ranging from 1:200 to 1:4000. The surrogate solutions were contacted with SAMMS material for 4 h to achieve equilibrium. Following equilibrium, the solutions were separated from the SAMMS material using 0.2-µm syringe filters. The Hg concentrations in the equilibrated solutions were determined by cold vapor atomic adsorption spectroscopy (CVAA) and analyzed for residual Hg concentrations and pH.

The data show that SAMMS loading can range from 26 to 270 mg/l, depending on matrix solutions and solid:solution ratio (Table 2.3). The results indicate that at a fixed solid:solution ratio with sufficient Hg to saturate the adsorption sites, the loading density increases with decreasing iodide concentrations. At both solid:solution ratios (1:200 and 1:800), ~40% reduction in iodide concentrations resulted in ~50% increase in Hg loading by SAMMS. Such increase in loading with decreasing iodide concentrations suggests that I^- may interfere with Hg adsorption through complex formation. A five-fold change in solid:solution ratio (1:800 to 1:4000) at a fixed iodide and initial Hg concentration resulted in an ~50% increase in Hg loading on SAMMS, indicating that increasing solid:solution ratios also increases Hg loading. The highest Hg loading of 270 mg/g of SAMMS was observed when the iodide concentration in the matrix solution was 90 mmol/l at a solid:solution ratio of 1:4000.

These Hg loading data may be compared to previous loading data on SAMMS (solid:solution ratio 1:5000) obtained in matrix solutions consisting of 100 mmol/l $NaNO_3$ with initial Hg concentrations ranging from 0.00024 to 670 mg/l. Loading densities of 83 to 635 mg/g observed in previous experiments indicate that nitrate ions do not influence Hg loading on SAMMS to the same extent that the iodide ions do in these experiments. Data obtained in previous and current experiments under somewhat similar experimental conditions (solid:solution ratio, initial Hg

Table 2.3. Mercury-Loading Data on SAMMS Obtained in Surrogate Solutions Containing Iodide Ions

Replicate	Surrogate Solution	Iodide Conc. (mmol/l)	Initial Hg Conc. (mg/l)	Solid: Solution Ratio	Hg Loading (mg/g) of SAMMS
1	S1	606	470	1:200	26
2	S1	606	470	1:200	28
1	S3	350	260	1:200	41
2	S3	350	260	1:200	41
1	S2	410	580	1:800	78
2	S2	410	580	1:800	70
1	S4	250	340	1:800	105
2	S4	250	340	1:800	113
1	S4	250	340	1:4000	165
1	S5	90	98	1:4000	270

concentration, dominant anion concentrations) show that the presence of iodide ions produces about one-half of the loading density as compared to nitrate ions in matrix solution. These data comparisons suggest that the effect of the iodide ions on Hg loading on SAMMS material (Table 2.4) is mainly due to complex formation with Hg ions. Our data indicate that using actual

Table 2.4. Comparison of Mercury-Loading Data Obtained in Nitrate and Iodide Matrix Solutions

Matrix Solution	Dominant Anion Conc. (mmol/l)	Initial Hg Conc. (mg/l)	Solid: Solution Ratio	Hg-Loading (mg/g) of SAMMS
0.09M KI	90	98	1:5000	270
0.1M $NaNO_3$	100	90	1:4000	547

combined waste streams (containing a mixture of leachate with several sets of wash solutions) would probably result in loading densities approaching ~0.3 g of Hg/g of SAMMS.

2.2.2 Distribution Coefficient Measurements Using Surrogate Waste Stream Solutions

Distribution coefficient is the measure of an exchange substrate's selectivity or specificity for adsorbing a specific contaminant or a group of contaminants from matrix solutions, such as waste streams. The distribution coefficient (sometimes referred to as the partition coefficient at equilibrium) is defined as a ratio of the adsorption density to the final contaminant concentration in solution at equilibrium. This measure of selectivity is defined as

$$K_d = A_{eq} / C_{eq}$$

where K_d is the distribution coefficient (ml/g), A_{eq} is the equilibrium adsorption density (mg of contaminant per gram of adsorbing substrate), and C_{eq} is the contaminant concentration (mg/ml) in contacting solution at equilibrium. The partition coefficient is defined as

$$K_p = A/C$$

where K_p is the partition coefficient (ml/g), A is the adsorption density (mg of contaminant per gram of adsorbing substrate) at any stage before equilibrium is attained, and C is the contaminant concentration (mg/ml) in contacting solution at the same stage as the adsorption is calculated. At equilibrium, the K_p will be equal to K_d.

The K_ds were measured by equilibrating 25- and 100-mg quantities of SAMMS material with 20 ml of contact solution (solid:solution ratios of 1:800 and 1:200, respectively). The contact solution was formulated as a surrogate solution containing ~90 mmol/l of iodide ions. The contact solution compositions and the experimental conditions are listed in Table 2.5. Following 4 h of equilibration, the aliquots of equilibrated solutions were filtered through a 0.2-μm filter and Hg concentrations were measured by CVAA.

The data show that SAMMS material has very high selectivity (very high K_d values) for Hg in iodide containing surrogate solutions (Table 2.6). When solutions containing ~66 mg/l of Hg are contacted with SAMMS material, the equilibrium concentrations of Hg were below detection ($<5x10^{-5}$ mg/l using CVAA). Consequently, the calculations show that SAMMS material has extremely high specificity ($K_d > 2.64x10^8$ ml/g) for dissolved Hg in the tested surrogate solution. The second set of duplicate experiments with solutions containing ~98 mg/l of Hg also showed that SAMMS material has very high specificities (K_d of $1.29x10^5$ and $2.10x10^5$ ml/g) for adsorbing Hg. These data are comparable to those obtained previously by coworkers using matrix solutions consisting of 0.1M $NaNO_3$. Those investigators used a fixed solid:solution ratio of 1:2080 and initial Hg concentrations of 0.487 and 9.70 mg/l, respectively. Following adsorption by SAMMS material, they found equilibrium Hg concentrations in solution of $1x10^{-5}$ and $1.2x10^{-3}$ mg/l with corresponding K_d values of $1.01x10^8$ and $1.68x10^7$ ml/g, respectively. The data obtained from our experiments not only confirm the previous data but indicate that SAMMS

material has very high selectivity (very high K_d and very low equilibrium Hg concentrations) for soluble Hg in waste stream surrogate solutions.

Table 2.5. Experimental Conditions Used for Measuring the Distribution Coefficients

Constituent	K_d Experiment	
	K1	K2
Iodide (mmol/l)	90	90
Sulfate (mmol/l)	88	88
K (mmol/l)	265	265
Fe (II) (mmol/l)	0.5	0.5
Ca (mmol/l)	0.2	0.2
Hg (mg/l)	66	98
Solution Vol (ml)	20	20
Wt. of SAMMS (g)	0.1	0.025
Solid:Solution Ratio (g:ml)	1:200	1:800

Table 2.6. Distribution Coefficients for Adsorption of Mercury by SAMMS Material from Surrogate Solutions

Replicate	Initial Hg Conc. (mg/l)	Final Hg Conc. (mg/l)	Solid:Solution Ratio (g:ml)	K_d (ml/g)
K1- 1	66	$<5x10^{-5}$	1:200	$>2.64x10^{8}$
K1-2	66	$<5x10^{-5}$	1:200	$>2.64x10^{8}$
K2-1	97.5	0.6	1:800	$1.29x10^{5}$
K2-2	97.5	0.4	1:800	$2.10x10^{5}$

2.3 Iodine Reduction Experiments Using Surrogate Waste Stream Solutions

The objective of these experiments was to compare the reducibility of iodine in KI solutions using metallic iron and sodium dithionite. The experiments were conducted on surrogate solutions that were developed on the basis of composition of actual leachate solutions provided by ORNL. According to ORNL data, the dominant dissolved constituents in the actual Hg-containing waste streams are K^+, I^-, and I_2, with minor amounts of Fe^{2+}, and SO_4^{2-}. The removal of Hg from the waste stream can be accomplished in either of two ways: one means is to use metallic iron to reduce iodine to iodide and dissolved Hg iodide complex into elemental Hg; the second method is to reduce iodine into iodide using a reducing agent and later adsorbing Hg from the solution using SAMMS material. In the second method, iodine reduction is a necessary first step because the presence of iodine, which exists as I_3^- ion, deactivates to a significant extent the Hg-adsorbing thiol sites on SAMMS material.

2.3.1 Reductive Reactions of Triiodide Species

Iodine dissolved in KI solutions exists in the form of the triiodide species. This reaction can be represented as

$$I_2 + I^- = I_3^-$$

The reduction of the triiodide species into iodide ions is a two-electron reaction with a redox potential of 0.5338 V.

$$I_3^- + 2e^- = 3I^-$$

The reduction of the triiodide ion into iodide ions with metallic iron with the resultant overall redox potential is represented by

$I_3^- + 2e^- = 3I^-$	0.5338 V
$Fe^o = Fe^{2+} + 2e^-$	0.409 V
$I_3^- + Fe^o = Fe^{2+} + 3I^-$	0.942 V

The reduction of the triiodide species can also be effected by using dithionite (hydrosulfite) ions as reducing agents. The reaction can occur in two steps. The resulting reductive reactions and the related redox potentials can be represented as

$I_3^- + 2e^- = 3I^-$	0.5338 V
$S_2O_4^{2-} + 4OH^- = 2SO_3^{2-} + 2H_2O + 2e^-$	1.12 V
$I_3^- + S_2O_4^{2-} + 4OH^- = 2SO_3^{2-} + 2H_2O + 3I^-$	1.6538 V

$I_3^- + 2e^- = 3I^-$	0.5338 V
$SO_3^{2-} + 2OH^- = SO_4^{2-} + H_2O + 2e^-$	1.84 V
$I_3^- + SO_3^{2-} + 2OH^- = SO_4^{2-} + H_2O + 3I^-$	2.373 V

The overall reductive reaction for the reduction of triiodate species with concomitant oxidation of dithionite ions into sulfate species can be written as

$3I_3^- + 6e^- = 9I^-$	1.601 V
$S_2O_4^{2-} + 8OH^- = 2SO_4^{2-} + 4H_2O + 6e^-$	2.96 V
$3I_3^- + S_2O_4^{2-} + 8OH^- = 2SO_4^{2-} + 4H_2O + 9I^-$	4.561 V

Additionally, any Fe(III) would be reduced to Fe(II) by dithionite ions as follows:

$2Fe^{3+} + 2e^- = 2Fe^{2+}$	1.54 V
$S_2O_4^{2-} + 4OH^- = 2SO_3^{2-} + 2H_2O + 2e^-$	1.12 V
$2Fe^{3+} + S_2O_4^{2-} + 4OH^- = 2Fe^{2+} + 2SO_3^{2-} + 2H_2O$	2.66 V

The reductive experiments were conducted by using the surrogate solutions listed in Table 2.7. Three experiments were conducted with metallic iron powder added in molar equivalents of 1, 9, and 15, respectively. The dithionite experiments were conducted in duplicate by adding 1.5 molar equivalents of sodium dithionite solutions. The dithionite reactions were instantaneous, as indicated by the disappearance of iodine color from solution; whereas, with metallic iron powder, no such immediate reactions were observed. Iron reduction reactions were allowed to proceed for 48 h, the solutions were filtered, and the Hg concentrations in the filtrate were measured to assess any reduction of Hg into elemental forms.

The results show (Table 2.8) that, as expected, in addition to the reduction of the triiodide species, the metallic iron also reduces the divalent Hg species into the elemental forms of Hg. The degree of Hg reduction is proportional to the molar equivalents of metallic iron added to the solution. Adding ~1, 9, and 15 molar equivalents of metallic iron reduced ~33%, 98.5% and 99.8% of divalent Hg, respectively; whereas, the dithionite ions, while effectively reducing triiodide species, did not seem to reduce any divalent Hg species into elemental forms. These data show that metallic iron effectively reduces both the triiodide and dissolved divalent Hg species. However, to effectively remove most of the dissolved Hg from the surrogate solutions, it appears necessary to use an excess molar equivalent (~15) of metallic iron, which produces a large mass of hazardous metallic waste. By comparison, triiodide reduction with dithionite is almost instantaneous without any reduction of dissolved Hg species into elemental form. Consequently, the dissolved Hg from the dithionite-treated solutions can be removed later with SAMMS material and result in a much smaller mass of solid waste as compared to metallic iron reduction treatment.

Table 2.7. Composition of Surrogate Solutions Used in Iodine Reduction Experiments

Constituent	Surrogate Solutions	
	R1	R2
Iodine (mmol/l)	100	10
Iodide (mmol/l)	410	41
Sulfate (mmol/l)	23	11.5
K (mmol/l)	440	220
Fe (II) (mmol/l)	3	1.5
Hg (mg/l)	580	58

Table 2.8. Data from Iodine Reduction Experiments Using Metallic Iron and Sodium Dithionite

Surrogate Solution	Reductive Treatment (molar eq)	Iodine Conc. (mmol/l)	Iodide Conc. (mol/l)	Initial Hg Conc. (mg/l)	Hg Conc. after Reduction (mg/l)
R1	1 Fe^o	100	410	580	390
R1	9 Fe^o	100	410	580	8.3
R1	15 Fe^o	100	410	580	1.3
R2	1.5 S_2O_4	10	41	58	57
R2	1.5 S_2O_4	10	41	58	57

2.4 Mercury Adsorption Experiments Using Actual Leachates

The objective of these experiments was to determine the effect of varying iodide and Hg concentrations in actual leachate (KI/I_2) and washwater mixtures on Hg attenuation characteristics of SAMMS. The composition of the actual leachate and washwater provided by ORNL is listed in Table 2.9. Typically, the leachate and washwater are mixed to combine the waste stream before removing the dissolved Hg. Also, the leached solid waste may be washed successively until all the dissolved Hg in the entrapped leachate is washed out, and the washing solution from each step is combined with the leachate before removal of Hg. Depending on the number of washing steps used, mixing of leachate with wash solutions may result in combined waste stream compositions with different iodide, iodine, and Hg concentrations. To obtain such realistic waste stream solutions, actual leachate was mixed with washwater in varying proportions to achieve combined waste stream compositions that result from a number of washing steps, ranging from 1 to 5. These compositions obtained from mixing actual leachate with washwaters are listed in Table 2.10. For these experiments, the combined waste stream solutions were prepared by initially mixing leachate and washwater followed by dilution to obtain waste stream mixtures that represent leachate combined with two, three, four, and five successive wash solutions. Additionally, some of the leachate-washwater mixtures were spiked with Hg stock solutions to achieve final Hg concentrations that ranged from ~30 to 70 mg/l. Finally, iodine in each of these solutions was reduced by the addition of sodium dithionite stock solution. Following reduction, the final iodide concentrations were computed to range from ~0.148 to 0.44M.

The adsorption experiments were conducted with 20-ml aliquots of actual leachate-washwater mixtures with 200-mg portions of SAMMS material (solid:solution ratio of 1:100) The solutions were contacted with SAMMS material for 4 h to ensure equilibrium. Following equilibrium, the ~5-ml aliquots of solutions were separated from the SAMMS material using 0.2-μm syringe filters. The Hg concentrations in the equilibrated solutions were determined by CVAA.

Table 2.9. Composition of Actual Leachate and First Washwater

Component	Leachate (mmol/l)	Washwater (mmol/l)
KI	400	40
I_2	200	20
$CaSO_4$	40	4
Hg	0.77	0.077

Table 2.10. Composition of Actual Leachate Combined with Washwaters from Successive Washing Steps

Component	Washing Steps				
	1	2	3	4	5
	(mmol/l)				
KI	220	148	111	89	74
I_2	110	74	56	44	37
$CaSO_4$	22	14.8	9.2	7.2	6.1
Hg	0.424	0.285	0.214	0.171	0.143

The results of adsorption experiments with actual leachate waste streams show that SAMMS material is very effective in adsorbing dissolved Hg from the solution phase (Table 2.11). In all cases after SAMMS treatment, the residual Hg concentrations in the waste stream solutions were below the CVAA detection limits (<0.00005 mg/l). Such below-detection concentrations for Hg indicate that the waste streams can be cleaned to several orders of magnitude smaller than U. S. Environmental Protection Agency-specified limits for residual Hg levels for hazardous wastewaters and even below the drinking water standards (40 CFR 141).

These data show that the SAMMS technology is capable of very effectively removing Hg from actual leachate waste streams of varying composition (Hg concentrations ranging from ~30 to 70 mg/l and total iodide of concentrations ~148 to 440 mmol/l) that result from the KI/I_2 extractive process. The calculated K_d values demonstrate that SAMMS material has extremely high specificity (K_d values $>6x10^7$ to $>1x10^8$ ml/g) for Hg in KI/I_2 leachate solutions, indicating that the presence of other major matrix ions, such as K^+ and I^- ,does not diminish the SAMMS material's ability to specifically adsorb soluble Hg species. These data, obtained with actual leachate waste streams, also affirm extremely high SAMMS adsorber specificity for Hg species observed in a previous set of experiments involving surrogate leachates (see Section 2.2). These data effectively demonstrate that using SAMMS technology results in the complete removal of Hg from actual waste streams, thus allowing reclamation and recycling the KI/I_2 leach solution.

Table 2.11. Mercury Adsorption by SAMMS Material from Actual Leachate (KI/I_2) Waste Streams

Total Iodide Conc. after I_2 reduction (mmol/l)	Initial Hg Conc. (mg/l)	Final Hg Conc. (mg/l)	Hg adsorbed (mg/g of SAMMS)	K_d (ml/g)
148	32	<0.00005	32	$>6.44 \times 10^7$
148	72	<0.00005	71	$>1.44 \times 10^8$
178	46	<0.00005	46	$>9.16 \times 10^7$
178	70	<0.00005	70	$>1.41 \times 10^8$
222	31	<0.00005	31	$>6.26 \times 10^7$
222	52	<0.00005	52	$>1.05 \times 10^8$
296	63	<0.00005	64	$>1.26 \times 10^8$
440	52	<0.00005	52	$>1.04 \times 10^8$

3.0 Conclusions

The following conclusions can be made from the experiments conducted and described.

Kinetics of Mercury Binding

- Between the 3 to 9 pH range, ~82 to 95% of final adsorption occurs within the first 5 min, indicating an extremely rapid rate of reaction.

- With initial Hg concentrations of ~100 mg/l, no significant differences in the rate of adsorption (rate of decrease in solution concentration) were observed at pH values of 5, 7, and 9; however at pH 3, the rate appeared to be lower than that observed at higher pH values.

- With higher initial Hg concentrations of ~370 mg/l, no significant differences in the rate of adsorption (rate of decrease in solution concentration) were observed at pH values of 3, 5, and 7; however at pH 9, the rate appeared to be slightly higher than that observed at lower pH values.

- Under tested pH conditions and initial Hg concentrations, adsorption equilibrium seems to have been attained in ~4 h.

Mercury Loading Tests

- Mercury loading on SAMMS material can range from 26 to 270 mg/l, depending on the iodide concentrations and solid:solution ratio. At a fixed solid:solution ratio with sufficient Hg to saturate the adsorption sites, the loading density increases with decreasing iodide concentrations. An ~ 40% reduction in iodide concentrations resulted in an ~50% increase in Hg loading by SAMMS. Such an increase in loading with decreasing iodide concentrations suggests that the I^- ion may interfere with Hg adsorption through complex formation.

- Increasing the solid:solution ratio also increases the Hg loading on SAMMS material. A five-fold change in the solid:solution ratio (1:800 to 1:4000) at a fixed iodide and initial Hg concentration resulted in an ~50% increase in Hg loading on SAMMS. The highest Hg loading of 270 mg/g on SAMMS was observed when the iodide concentration in the matrix solution was 90 mmol/l at a solid:solution ratio of 1:4000.

Distribution Coefficient Measurements

- The SAMMS material has very high selectivity (K_d values ranging from 1.29×10^5 to $>2.64 \times 10^8$ ml/g) for Hg in iodide-containing surrogate solutions.

- The SAMMS material can adsorb Hg with very high specificity even in the presence of other cationic (such as K, Ca, ferrous Fe), anionic (I and SO_4), and their complex species.

Iodine Reduction in KI/I_2 Waste Stream

- Dithionite was very effective in selectively reducing iodine in the KI/I_2 solutions. Reductions with metallic iron were very slow (>24 h) and required excess molar quantities of material to complete the reaction.

- Dithionite reduction of iodine did not cause any concurrent reduction of dissolved Hg, whereas metallic iron reduced both iodine and dissolved Hg, resulting in the formation of elemental Hg.

Mercury Adsorption from Actual KI/I_2 Leachate Waste Streams

- The SAMMS material can reduce Hg concentrations to <0.00005 mg/l in dithionite-reduced KI/I_2 waste stream solutions. The data indicate that KI/I_2 waste streams can be cleaned to several orders of magnitude smaller than specified limits for residual Hg levels for hazardous wastewaters and even below the federal drinking water standards.

- The SAMMS technology is capable of effectively removing Hg from actual KI/I_2 leachate waste streams of varying composition (total iodide concentrations ~148 to 440 mmol/l, Hg concentrations ranging from ~30 to 70 mg/l, and total iodide concentrations of ~148 to 440 mmol/l) that result from the extractive process.

- The K_d values demonstrate that SAMMS adsorber material has extremely high specificity (K_d values $>6x10^7$ to $>1x10^8$ ml/g) for Hg in KI/I_2 leachate solutions, indicating that the presence of other major matrix ions such as K^+ and I^- does not in any way diminish SAMMS ability to specifically adsorb soluble Hg species. These data show that using SAMMS technology results in complete removal of Hg from actual waste streams, thus allowing reclamation and recycling of the KI/I_2 leach solution.

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