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**Fabrication and Testing of Engineered
Forms of Self-Assembled Monolayers
on Mesoporous Silica (SAMMS)
Material**

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September 1998

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under Contract DE-AC06-76RLO 1830

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Available to DOE and DOE contractors from the
Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831;
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Available to the public from the National Technical Information Service,
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Summary

A number of engineered forms such as flexible extrudates, beads, and rods were fabricated using thiol-SAMMS (Self-Assembled Monolayers on Mesoporous Silica) and tested for their mercury adsorption capacities. The flexible extrudate form had a mercury adsorption capacity of 340 mg/g but was found to be structurally unstable. A structurally sound bead form of thiol-SAMMS was fabricated with 5, 10, 25, and 40% by weight clay binder (attapulgite) and successfully functionalized. A structurally stable but non-optimized rod form of thiol-SAMMS was also fabricated. Bench-scale processes were developed to silanize and functionalize mesoporous silica beads made with attapulgite clay binder. Contact angle measurements were conducted to assess the degree of surface coverage by functional groups on mesoporous silica materials. Adsorption data indicated that optimum mercury adsorption by SAMMS material (about 700 mg/g) was found to occur when functional group density approached about 80% surface coverage. Optimized thiol-SAMMS material had a significantly higher mercury loading capacity (560 mg/g) compared to the commercial GT-73 exchange material (300 mg/g). Mercury adsorption measurements on bead forms of thiol-SAMMS containing 5, 10, 25, and 25% by weight binder material indicated that it may be cost-effective to maximize the binder content of SAMMS beads. Adsorption data indicated that the mercury adsorption performance of the rod form of thiol-SAMMS may be improved if rod diameter, porosity, and composition are optimized. Flow tests conducted with disc forms of thiol-SAMMS indicated a high mercury loading capacity (700 mg/g) and no breakthrough during a total flow of 800 bed volumes of solution. Flow tests through both conditioned and unconditioned GT-73 exchanger material columns showed early breakthrough of mercury (<100 bed volumes). Flow-through measurements with unconditioned thiol-SAMMS beads showed early breakthrough with both mercury concentrations (<1 mg/l and 80 mg/l) tested. Such early breakthrough may have been due to a number of causes such as air entrapment within beads, lack of preconditioning, and too large a bead size. These factors need to be evaluated to improve the mercury adsorption performance of bead forms in flow-through mode.

Acknowledgments

This work was funded by the Mixed Waste Focus Area, Office of Science and Technology, U.S. Department of Energy. We appreciate the consistent encouragement provided by Jim Buel, Joe Perez, Nick Lombardo, Bill Kuhn, Jud Virden, Bill Bonner, Bruce Bunker, Rod Quinn, and John Sealock support for the development of SAMMS technology. We thank Rosalind E. Schrempf for her efficient editorial assistance.

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1.0 Introduction

1.1 Target Problem

At the U.S. Department of Energy (DOE) Oak Ridge Site, an estimated 2.5 million pounds of mercury has been lost to soil and surface water, and 3000 ft³ of mercury is contained in plant sumps. The headwaters of Upper East Fork Poplar Creek (UEFPC) are within the DOE Y-12 plant boundary and discharge 7 million gallons per day to Lower East Fork Poplar Creek. UEFPC is contaminated with low levels of mercury. A mercury reduction program at the Oak Ridge Site has achieved point source reduction, and mercury treatment systems are placed such that the concentration of mercury in surface water is declining. However, the Site has been unable to meet the National Pollution Discharge Emission Standard (NPDES) permit requirement that treatment to 0.012 mg/l be achieved at the UEFPC by April 27, 2000. Exceeding the anticipated limit would require monitoring methyl mercury in edible portions of fish present in contaminated streams of the UEFPC. If the concentration of methyl mercury exceeds 1 mg/kg, the public must be protected from ingesting fish.

Large amounts of mercury-contaminated oil also exist at various DOE sites. To date, no efficient technology has been demonstrated for removing mercury from organic liquids.

1.2 Technology Description

The self-assembled monolayers on mesoporous silica (SAMMS) material is based on self-assembled mesoporous mercaptan support materials (Liu et al. 1998, Feng et al. 1997). Molecular self-assembly is a unique phenomenon in which functional molecules aggregate on an active surface, resulting in an organized assembly having both order and orientation (Bunker et al. 1993, Whitesides 1996). The mesoporous support material used for this purpose consists of stable oxides such as SiO₂, ZrO₂, and TiO₂, which have controlled porosities and high surface areas (>1000 m²/g) (Beck et al. 1992, Kresge et al. 1992). By populating the surfaces of the mesoporous oxide with alkylthiols (which are well known to have a high affinity for mercury), SAMMS provides a highly effective and selective means for scavenging mercury with a high mercury loading capacity (up to 0.7 g Hg/g of SAMMS). SAMMS also provides an extremely narrow pore size distribution, which can be specifically tailored from 15 Å to 400 Å, thereby minimizing biodegradation from microbes and bacteria. Due to their inherent stability, spent SAMMS materials can be disposed of as stable waste forms.

1.3 Technology Benefits

The objective of this project was to develop appropriate engineered forms for SAMMS materials and to test the mercury removal capacities of these forms. SAMMS materials have the potential to remove mercury from oil effectively. SAMMS can reduce mercury concentrations in water to below 0.012 mg/l as required by the NPDES permit. Because SAMMS provides high mercury loading and stable waste forms, both the secondary wastes generated and costs of remediation will be reduced.

2.0 Fabrication and Testing of Engineered Forms of Thiol-SAMMS

2.1 Fabrication of Flexible Extruded Form of Thiol-SAMMS

Fabrication of a flexible extruded engineered form of mesoporous material was initially attempted by using a polysaccharide gelling agent. The starting material consisted of mesoporous substrate that had been functionalized with thiol groups. This thiol-SAMMS material was prepared in a slurry form containing a dissolved polysaccharide that gels in the presence of specific multivalent ions. A typical recipe contained 2.5 g SAMMS, 49.2 g H₂O, and 0.75 g polysaccharide. The slurry was mixed and sonicated for 10 min. The slurry was extruded from a pressurized container through a narrow orifice (2-mm diameter) into a gelling salt solution. The gelled, flexible extrudate, typically a few mm wide, was washed for >3 h in flowing water to remove impurity cations and then evaluated for mercury treatment. This engineered SAMMS had a mercury loading of about 340 mg/g. Additional tests indicated that this material had poor structural stability and therefore had a tendency to disintegrate when immersed in solutions.

2.2 Fabrication of Mesoporous Material Spheres with 10% Clay Binder

The goal of this experiment was to develop a method for fabricating a more stable engineered form of SAMMS material. The following method describes how spherical forms of structurally stable thiol-SAMMS material were fabricated.

First, a 3 wt% solution of ammonium alginate polymer (Superloid alginate, Kelco Division of Merck, Inc.) was prepared. The solution was prepared a day ahead to obtain a homogeneous solution by allowing the alginate polymer to dissolve completely.

Next, a second solution was prepared by mixing 42.9 g of 1 M NH₄OH into 403 g of deionized water in a large plastic beaker. While stirring, 10.8 g of attapulgite clay (MIN-U-GEL MB, Floridin Co., Quincy, FL) was sifted into this solution to form a slurry. This slurry was sonicated for 1 min using a horn-sonicator. The next step consisted of adding 56.7 g of concentrated (~29% NH₃ assay) ammonium hydroxide and stirring the slurry for a few seconds.

The prepared slurry was poured into a 2-liter polyethylene jar. A known volume (~45% of the volume of the container) of high-density alumina milling spheres was added to this slurry followed by the addition of 97.6 g of mesoporous silica (65Å pore size) material. This mixture was ball-milled at 120-140 rpm for 40 h.

Following this treatment, the slurry was decanted into a 2-liter plastic Mason jar and a weight of 3% alginate solution (equivalent to 0.1447 times the weight of the decanted slurry) was added using a spatula to stir this mixture. Next, the jar was capped, and the slurry-alginate mixture was mixed vigorously for 2 min by using a paint-shaker.

The mixture was de-aired by vacuum until the entrapped air was released from the solution. The de-aired slurry was loaded into a pressure vessel fitted with many 16-gauge needles, and the vessel was pressurized until the slurry began to flow out as droplets. A large plastic container holding a volume of gelling solution (1M CaCl_2 solution) was placed with the tips of the needles positioned about 1 cm from the surface of the solution, and the extrusion process continued until all the slurry was forced out in the form of spheres.

Following the extrusion process, the gelling solution was drained off, and the spheres were washed for 16 h. A final washing/rinsing was conducted with deionized water, and the spheres were spread out in a monolayer on 25- or 30-mesh brass sieves and dried at 40° C in a forced-air convection oven for 20 h.

Next, the dried spheres were loaded into ceramic (aluminosilicate) boats and calcined at 550° C for 1 h. The heating and cooling rates used for this step were 5° C/min and 15° C/min, respectively. The final step consisted of functionalizing these spheres with self-assembled monolayers of thiol functional groups.

About 300 g of these thiol-SAMMS spheres (10% binder) were delivered to Oak Ridge National Laboratory for conducting mercury adsorption experiments.

2.3 Fabrication of SAMMS Spheres with Optimization of Clay Binder Content

The objective of this study was to fabricate mesoporous beads with different concentrations of a clay binder and to evaluate these beads for optimal stability and mercury adsorption performance.

The method used to fabricate these beads was identical to the previously described method except that the clay content of the bead slurry ranged from 5 to 40% by weight. A series of bead slurries was prepared that contained 5, 10, 25, and 40 wt % attapulgite clay as binder material. The slurry mixtures were pH adjusted and sonicated to yield a maximum solids content extruded into bead forms. These beads were first dried at 40° C and calcined at 650-700°C.

The crushing strength for single beads from these formulations exceeded 1 kg, indicating that these beads would provide durable engineering support. The surface areas of calcined beads ranged from 450 to 460 m^2/gm , indicating that large numbers of surface sites were available for functionalization. The final step consisted of functionalizing these spheres with self-assembled monolayers of thiol functional groups.

2.4 Fabrication of Rod Form of Thiol-SAMMS

A quantity of SAMMS material was sent to Mobil Corporation to be fabricated into rod-shaped engineered forms. According to Mobil, this engineered form was not optimized for characteristics such as rod diameter, pore size, and composition. These rod forms were tested without any pretreatment for their mercury adsorption characteristics.

3.0 Silanization and Functionalization of the Bead Form of SAMMS

3.1 Silanization Chemistry for Beads

Silanization of the alginate/attapulgit/mesoporous silica beads required a fundamentally different strategy than does silanization of simple mesoporous silica powders. A different strategy was needed because the beads are less robust than the powders and residual impurities are present from the gelation process.

Because bead forms are structurally less robust than powders, long-term stirring of the beads was considered counterproductive since abrasion would eventually pulverize them. Therefore, an entirely different treatment process was considered for stirring the beads as passively as possible. This passive mixing requirement eliminated the choice of toluene as the deposition solvent since the first step in the process is the hydration of the mesoporous silica surface and water is immiscible with toluene. Such immiscibility would cause some beads to be over-hydrated and others to be unhydrated. (This is not a problem in the powder synthesis because the powders are vigorously stirred during the hydration step).

Toluene was considered an excellent choice for silanization of the powders since its low polarity enhances siloxane's affinity for the hydrated silica surface, thereby enhancing the hydrolysis reaction rate. Therefore, the solvent chosen for silanation of the beads must be miscible with water.

It was still desirable to use a solvent of moderately low polarity to enhance the association (hydrogen bonding) of the siloxane with the hydrated silica surface (e.g., alcohols might be a poor choice due to their high polarities and strong hydrogen-bonding capabilities).

In addition, the beads still contained significant amounts of calcium ion (from the gelation step), which binds strongly to silica surfaces and precludes the binding of siloxanes to that portion of the silica surface. We found that this residual calcium can be mobilized by adding acetic acid to the hydration mixture. Therefore, it was decided that the solvent chosen must be not only miscible with acetic acid (which is not difficult since almost all solvents are) but should also solubilize calcium acetate, thus freeing up the silica interface for subsequent deposition of the monolayers.

Once hydration of the silica surfaces is completed and the surfaces are freed of calcium ion contamination, monolayer deposition can occur by hydrolysis of the surface-associated siloxane, followed by condensation of the resultant tris(hydroxy)silane onto the silica surface. To complete this process within a convenient timeframe in the laboratory, the reaction would require temperatures above 80°C.

To drive the silanation reaction to completion, it was necessary to remove the methanol and water by-products from the reaction mixture at the end of the reflux period. Among the number of ways to achieve this objective, the most convenient method appeared to be either a routine distillation or an azeotropic distillation step. The solvent used to achieve optimum silanation of the beads needed to

possess the following characteristics: 1) must be miscible with water, 2) of modest polarity, 3) non-hydrogen bonding, 4) miscible with acetic acid, 5) able to solubilize calcium acetate, 6) have a boiling point above 80°C, and 7) allow for the removal of both methanol and water by distillation. Among the solvents examined, 1,4-Dioxane appeared to satisfy all of the above criteria.

3.2 Procedure for Mesoporous Bead Functionalization

We added 3.0 ml of water to 125 ml of dioxane and 5.0 ml of glacial acetic acid. This solution was swirled for complete mixing and then 16.6 g of beads (surface area of 485 m²/g) containing 10% attapulgite clay was added, and the mixture was allowed to stand overnight at ambient temperature to allow water to percolate uniformly throughout the beads' pore structure. The following day, 18 ml of mercaptopropylsilane (MPS) was added, and the mixture was swirled gently to disperse the silane. The reaction mixture was then heated to reflux for 4 h. The methanol and water were removed after the reflux step by replacing the reflux condensor with a still head and distilling the methanol off, followed by distilling off the dioxane/water azeotrope. The beads were then collected by filtration, washed twice with 2-propanol and twice with dichloromethane, air-dried overnight, and then dried under vacuum for 2 days. The recovered beads weighed 24.9 g, which corresponds to approximately 91% monolayer coverage (based on available surface area) or a loading density of approximately 2.45 mmole/g.

4.0 Optimization of the Thiol Functional Group Density and Mercury Loading Capacity of Thiol-SAMMS Material

The mercury adsorption capacity of thiol-SAMMS material depends on the functional group density. The degree of surface coverage that can be attained on mesoporous material substrate may range from 20 to 100% (Feng et al. 1997). Hydrolyzed mesoporous silica material with no SH-functional group coverage (0%) is hydrophilic. However, the hydrophobicity of mesoporous silica material increases (decrease in hydrophilicity) with increasing surface coverage by the SH-functional groups. Therefore, the degree of surface coverage on mesoporous silica material can be determined by measuring the wetting contact angle that reflects the hydrophobicity of the surface.

4.1 Contact Angle Measurements

A series of wetting contact angle measurements was conducted on silica-based mesoporous material samples functionalized with thiol groups. The degree of surface coverage ranged from 20 to 100%. The contact angle measurements were conducted on 0.25 g of powder samples that had been compressed into

disc forms at 22.9 kg/cm² pressure. A static contact angle measurement of a hydrolyzed glass surface was used to calibrate the measurements. All measurements were conducted at room temperature using water as the wetting agent.

The results of contact angle measurements (Figure 1) indicated that, even at low surface coverage (20%), the surface became less hydrophilic and more hydrophobic in nature. Increasing surface coverage increased the contact angle (increased hydrophobicity). Even though the overall functional relationship appeared to be nonlinear, the relationship seems to attain linearity when the surface coverage exceeded about 80%.

Figure 1. Relationship Between Contact Angle and the Degree of Surface Coverage by Thiol Groups

4.2 Mercury Adsorption Capacity as a Function of Thiol Functional Group Density

A set of mercury loading tests was conducted using SAMMS materials containing different degrees of thiol functional group coverage (0 - 100%). The data were generated to establish an optimum range of surface coverage at which mercury adsorption capacity would be maximum.

The mercury adsorption data for SAMMS material with different degrees of functional group coverage showed that the loading increased with increasing surface coverage and attained a maximum value of about 700 mg/g (Figure 2). The data showed that the loading curve reaches a plateau at a surface coverage of about 80%. Any additional coverage beyond this limit does not significantly enhance mercury adsorption by thiol-SAMMS. These data indicated that the optimum mercury adsorption can be achieved at 80% surface functionalization with thiol-groups. The data imply that smaller quantities of the chemical

Figure 2. Relationship Between Mercury Adsorption Capacity and the Degree of Surface Coverage by Thiol Groups

(tris(methoxy)mercaptopropylsilane) can be used to functionalize SAMMS, leading to a reduction in manufacturing costs. Additionally, at 80% coverage the hydrophobicity of SAMMS material appears to be low enough to achieve maximum mercury adsorption. The method developed from these tests can be applied to optimization studies involving coverage of different functional groups on various mesoporous silica substrates.

4.3 Mercury Adsorption Tests on Optimized Thiol-SAMMS and GT-73 Exchanger

A set of tests was conducted by the 3M Company to compare the mercury adsorption characteristics of optimized thiol-SAMMS (80% surface coverage) with Duolite GT-73, a commercial exchange material. These experiments were conducted with acidic solutions (pH: 3.6) containing 190 mg/l of mercury in the form of HgCl_2 .

The results of these tests showed that the optimized thiol-SAMMS material achieved an average mercury loading density of about 560 mg/g (Table 1). These data are consistent with adsorption data previously generated at Pacific Northwest National Laboratory (PNNL). Comparatively, the GT-73 exchanger attained an average mercury loading of about 300 mg/g. These data indicated that the optimized thiol-SAMMS can adsorb significantly more mercury than the commercial material. It is also important to note that the mercury loading capacity of optimized thiol-SAMMS material increases significantly in less acidic contact solutions (Feng et al. 1997). Therefore, optimized thiol-SAMMS would be expected to attain a higher mercury loading capacity under more moderate pH conditions.

Table 1. Comparison of Mercury Loading Between Thiol-SAMMS and GT-73 Exchanger

Substrate	Mass (mg)	Hg removed (mg/g)	Loading (mg/g)	Kd (ml/g)	Hg Removed (%)
SAMMSa	14.7	8.64	588	12777	76
SAMMSb	15.5	8.52	550	11452	75
SAMMSc	17.0	9.12	536	14118	80
GT-73a	15.6	4.80	308	2797	42
GT-73	18.4	5.94	323	3548	52
GT-73c	15.8	4.20	266	2215	37

5.0 Mercury Adsorption Tests on the Engineered Form of Thiol-SAMMS

5.1 Mercury Adsorption Tests on Bead Form of Thiol-SAMMS

A set of batch adsorption tests was conducted to evaluate the effects of different binder (attapulgite clay) content (5, 10, 25, and 40% by wt) on mercury adsorption capacities of the bead form of thiol-SAMMS. The binder content of thiol-SAMMS beads was expected to influence the effective surface area, resulting in differing mercury adsorption capacities. The beads used in this experiment were fabricated as described in Section 2.3.

The batch experiment consisted of equilibrating about 0.2 g of SAMMS beads in 40 ml of 0.1M NaNO_3 solution containing about 2000 mg/l of mercury in the form of $\text{Hg}(\text{NO}_3)_2$. The bead-solution mixture was equilibrated overnight, and mercury concentrations in the filtrates were measured by using cold vapor atomic absorption spectrometry. Triplicate tests were conducted for each binder content.

The data showed that, on average, beads with 10% binder content had the highest adsorption capacity (260 mg/g) as compared to beads made with other binder contents (Table 2). It was observed that beads made with 25% and 40% binder material had mercury loading capacities that were about 11% and 19% less than for beads made with 10% binder material. Therefore, it would be more economical to fabricate beads with a higher binder content (25 - 40% by wt) without a significant reduction in mercury loading capacities.

Table 2. Mercury Loading Capacities of Thiol-SAMMS Beads with Different Binder Content

Replicate	Binder content of thiol-SAMMS Beads (Percent by Weight)	Mercury adsorbed (mg/g of SAMMS)
1	5	256
2	5	228
3	5	159
1	10	233
2	10	275
3	10	276
1	25	220
2	25	259
3	25	218
1	40	221
2	40	221
3	40	193

5.2 Mercury Adsorption by the Rod Form of Thiol-SAMMS

The objective of these tests was to determine the mercury loading capacities of thiol-SAMMS fabricated in the rod form. The matrix solution used in these experiments consisted of 0.1 M NaNO_3 containing 1700 mg/l of mercury in the form $\text{Hg}(\text{NO}_3)_2$. About 40 ml of solution was equilibrated with varying amounts of thiol-SAMMS rod material to achieve solution:solid ratios of about 350, 360, and 445. Following a 12-h equilibration, the solutions were filtered and analyzed for mercury concentrations using cold vapor atomic absorption spectrometry. All loading tests were conducted in triplicate.

The adsorption data indicated that, depending on the solution:solid ratio, the rod form A of thiol-SAMMS had mercury adsorption capacities ranging from 236 to 340 mg/l (Table 3). In comparison, the rod form B had adsorption capacities ranging from 160 to 315 mg/l. This test indicated that on average, the rod form A had about 23% higher mercury adsorption capacities than rod form B. As expected, the highest adsorption capacities for both rod forms were achieved at high solution:solid ratio (445). On average, the rod form A of thiol-SAMMS appears to have a higher mercury adsorption capacity (~300 mg/g) as compared to the best-performing bead form of thiol-SAMMS (10% binder content, ~260 mg/g). Additional tests are needed to examine whether optimization of such factors as rod diameter, porosity, and composition would improve the mercury adsorption capacities of the rod form of thiol-SAMMS.

Table 3. Mercury Loading Capacities of the Rod Form of Thiol-SAMMS

Rod Form	Soln/solids	Solution Vol (ml)	SAMMS Wt(mg)	Initial Hg mg/l	Final Hg mg/l	Hg adsorb mg/g	Kd ml/g
A	443	40	90.30	1700	930	341	367
A	444	40	90.00	1700	960	329	343
A	442	40	90.43	1700	930	341	366
B	442	40	90.34	1700	1010	306	302
B	443	40	90.30	1700	1010	306	303
B	444	40	90.08	1700	990	315	318
A	362	40	110.40	1700	860	304	354
A	362	40	110.38	1700	860	304	354
A	363	40	110.29	1700	800	326	408
B	362	40	110.54	1700	920	282	307
B	364	40	110.34	1700	1080	225	208
B	348	40	110.10	1700	1100	218	198
A	347	40	115.06	1700	996	245	246
A	347	40	115.10	1700	993	246	247
A	347	40	115.22	1700	1020	236	231
B	347	40	115.21	1700	1110	205	185
B	347	40	115.25	1700	1240	160	129
B	347	40	115.22	1700	1230	163	133

5.3 Flow Tests on Engineered Forms of Thiol-SAMMS

5.3.1 Flow Tests on the Empore Disc Form of Thiol-SAMMS

The objective of this test was to examine the mercury adsorption performance of thiol-SAMMS powder that had been fabricated into an engineered form. This engineered form consisted of thiol-SAMMS powder made by PNNL that was embedded into discs (Empore disc) by the 3M company using one of their proprietary processes.

Flow-through experiments were conducted using the Empore disc form of thiol-SAMMS. Previous data have shown that the SAMMS materials become more hydrophobic as the functional group density approaches 80% surface coverage. These data also indicate that preconditioning with methanol would improve the wetting behavior (hydrophilicity) of SAMMS with high surface coverages. Such preconditioning of SAMMS improves its adsorption characteristics by allowing the adsorbate better access to the functional groups on the surface.

For comparison, flow-through experiments were also conducted on a commercial mercury adsorbent, Duolite GT-73 exchange resin manufactured by Rohm and Haas Company. Two experiments were conducted using each adsorbent, one with methanol preconditioning and the other without any preconditioning treatment. The flow-through experiments were conducted with solutions of deionized water containing 120 - 170 mg/l of mercury at a fixed flow rate of 5 ml/min. The tests were continued until a total of ~800 bed volumes of solution had passed through each material.

The results showed that for the duration of the experiment, no breakthrough occurred with preconditioned SAMMS material, whereas early breakthrough (<100 bed volumes) was observed for both preconditioned and unconditioned GT-73 resins (Figure 3). The data showed that even the unconditioned SAMMS materials performed much better than the conditioned GT-73 materials. From the breakthrough data, the mercury loading capacity for SAMMS material embedded in Empore was calculated as 700 mg/g (SAMMS). These mercury loading capacity data for Empore-embedded SAMMS are similar to the mercury loading capacity observed for free SAMMS material. Such adsorption performance indicated that fabricating SAMMS material into the Empore engineered form does not in any way diminish its mercury adsorption capacity.

Figure 3. Breakthrough Curves for SAMMS and GT-73 Resin

5.3.2 Flow Tests on the Bead Form of Thiol-SAMMS

The objective of this test was to examine the mercury adsorption performance of thiol-SAMMS powder that had been fabricated into a bead form. The fabrication of this bead form and its functionalization with thiol groups has been previously described.

Two flow tests were conducted, one with low mercury concentration (<1 mg/l) and another at a higher concentration (~ 80 mg/l). The test solutions were prepared with deionized distilled water spiked with appropriate concentrations of mercury in the form of mercuric nitrate. Appropriate weights of thiol-SAMMS beads without any preconditioning were packed into glass columns, and the solution flow was controlled at a constant rate by using intravenous (IV) pumps. The experimental conditions used for these flow tests were as follows.

For the low mercury concentration tests, the bed volume was 4.43 ml, the flow rate was fixed at 325 bed volumes/day (residence time 3.3 min), and the influent mercury concentration was 520-860 ppb. For the high mercury concentration tests, the bed volume was 4.43 ml, the flow rate was fixed at 112 bed volumes/day (residence time 9.5 min), and the influent mercury concentration was fixed at 80 mg/l.

The data showed that in the low mercury concentration test, the breakthrough fraction (the ratio of effluent concentration to the influent concentration) ranged from about 0.05 to 0.6 during a total flow of about 8800 bed volumes of solution (Figure 4). Significant degassing of the SAMMS beads was observed during this test. The variations in breakthrough fractions are probably related to two factors. The first is changes in influent concentration. The data indicated that the breakthrough fraction showed a decline following a change in influent concentration. The second factor appears to be the entrapment and random release of air bubbles within the bead bed that results in changes of contact surface between solution and adsorbing material. Such changes would affect the adsorption by limiting the contact between the adsorbent and the adsorbate. This test indicated that preconditioning of the SAMMS beads is necessary to eliminate the problem of changing contact surface due to degassing and bubble entrapment.

The results of the test conducted at a higher mercury concentration (80 mg/l) indicated that a breakthrough fraction of 0.5 was attained at about 120 bed volumes (Figure 5). In this flow test, the column was agitated frequently to release the entrapped bubbles and ensure that the solution-solid contact surface was maintained at a constant level and the influent mercury concentration remained constant at 80 ppm. Therefore, significant variations in breakthrough fraction was not observed in this test.

The tests at both high and low mercury conditions suggest that the performance of the thiol-SAMMS beads needs to be improved. The earlier-than-expected breakthrough might be attributed to the fact that the engineered form was not optimized. For example, the bead size may have been too large. The test also indicated that preconditioning of SAMMS beads with methanol and prior degassing may eliminate the problem of degassing during the flow-through test.

Figure 4. Breakthrough Curve for Low Mercury Concentration Flow Test Using Thiol-SAMMS Beads

Figure 5. Breakthrough Curve for High Mercury Concentration Flow Test Using Thiol-SAMMS Beads

6.0 Conclusions

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

6.1 Fabrication and Testing of Engineered Forms of Thiol-SAMMS

- Flexible extruded forms of SAMMS made by using a polysaccharide gelling agent had a mercury loading capacity of about 340 mg/g. These forms, however, had poor structural stability and tended to disintegrate when immersed in solution for extended periods of time.
- Mesoporous material beads with 5, 10, 25, and 40% by weight clay binder (attapulgite) were fabricated, and the calcined beads were successfully functionalized with self-assembled monolayers of thiol groups. These beads were structurally stable (1 kg crushing strength per bead) and had surface areas ranging from about 455 m²/g.
- Rod forms of SAMMS material were fabricated by the Mobil Corporation. These rod forms have not been optimized as to the rod diameter, pore size, and composition.

6.2 Silanization and Functionalization of the Bead Form of SAMMS

- Mesoporous silica beads made with attapulgite clay binder can be successfully silanized.
- It is possible to functionalize silanized mesoporous silica beads.

6.3 Optimization of Thiol Functional Group Density and Mercury Loading Capacity

- Contact angle measurement provides a measure of the degree of surface coverage by functional groups.
- Optimum mercury adsorption by SAMMS material (about 700 mg/g) was found to occur when functional group density approached about 80% surface coverage.
- A comparison of mercury adsorption performance indicated that optimized SAMMS material (80% surface coverage) attained an average adsorption density of about 560 mg/g, whereas GT-73, a commercial ion exchanger achieved an average adsorption density of 300 mg/g.

6.4 Mercury Adsorption Tests on the Engineered Form of Thiol-SAMMS

- Batch adsorption tests on thiol-SAMMS beads containing 5, 10, 25, and 40% binder material showed that beads containing 10% binder on average had the highest mercury loading capacity (260 mg/g). Beads with 25 and 40% binder material had loading capacities that were about 11 and 19% lower than the loading capacity of beads with 10% binder. These measurements indicated that it may be cost-effective to maximize the binder content of SAMMS beads.
- Batch adsorption tests on the rod form of thiol-SAMMS indicated mercury loading capacities that ranged from 160 to 340 mg/g. These rod forms, if optimized as to rod diameter, porosity, and composition may show enhanced mercury loading capacities.
- Flow tests conducted with thiol-SAMMS material in the form of Empore discs (fabricated by the 3M Company) indicated a mercury loading capacity of 700 mg/g. No breakthrough of mercury was detected from preconditioned thiol-SAMMS material column during a total flow of 800 bed volumes of solution. By comparison, early breakthrough of mercury (<100 bed volumes) was observed from both preconditioned and unconditioned GT-73 exchanger columns.
- Flow tests conducted on unconditioned thiol-SAMMS beads showed early breakthrough at both mercury concentrations (<1 mg/l and 80 mg/l). Such early breakthrough may have been due to a number of causes such as air entrapment within beads, lack of preconditioning, and too large a bead size. These factors need to be evaluated to improve the mercury adsorption performance of bead forms.

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