Mercury Remediation using Dow’s Experimental XUS-43604.00 Ion-Exchange Resin at Oak Ridge National Laboratory, Tennessee, USA – 11042

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ABSTRACT

Mercury contamination is a major concern at Oak Ridge National Laboratory, particularly at Building 4501, Sump I. In order to reduce mercury discharge, a mercury treatment system utilizing Dow’s experimental XUS-43604.00 ion-exchange resin with thiol-active sites has been installed at Sump I. Two types of experiments were performed to determine the characteristics of the experimental resin: (1) a column test for removal efficiency and (2) batch equilibrium tests for adsorption limits. Results generated by this research will answer many unknowns when dealing with mercury removal efficiency, resin change-out frequency, and resin disposal costs of the treatment system.

INTRODUCTION

Legacy mercury contamination is an area of concern at the U.S. Department of Energy’s (DOE)’s Oak Ridge National Laboratory (ORNL). A major source of this contamination comes from Building 4501, which housed early research efforts on the COLEX process used at the Y-12 National Security Complex to separate lithium-6 from lithium-7. As a result of this research effort, significant amounts of mercury were released into the building infrastructure, as well as surrounding soil and groundwater. The greatest concentrations of mercury are found at Sump I in Building 4501. The water from Sump I, a mixture of cooling water and groundwater, has historically been a major source of mercury discharge to White Oak Creek (WOC) and represents approximately 80% of the identifiable mercury sources at ORNL. In December of 2007, the groundwater and process water from Sump I was diverted to the Process Wastewater Treatment Complex (PWTC).

Currently, water pumped from Sump I contains approximately 900 mg/day of mercury and is the largest identified point discharge of mercury at ORNL. Based on previous analysis of effluent samples, the PWTC removes approximately 75% of the entering dissolved mercury with the use of Granular Activated Carbon. Based on this historical treatment efficiency, it is predicted that approximately 225 mg/day (25%) of mercury from Sump I now enters WOC in the PWTC effluent [1]. Prior to diverting Sump I water, influent to the PWTC contained approximately 75 mg/day of mercury. This means that mercury loading on the PWTC is increased by more than ten times. Pretreatment of Sump I flow is expected to eliminate 99% or approximately 890 mg/day of mercury currently being pumped to the PWTC from Sump I, and should reduce the amount of mercury entering WOC by approximately 223 mg/day. This substantial reduction in mercury will allow for compliance with state and federal water regulations.

There are two regulatory criteria of interest related to the release of legacy mercury from the ORNL site into WOC. These criteria are: Tennessee criterion for mercury in surface water (< 51 ng/L) and the Environmental Protection Agency (EPA) criterion for methyl mercury in fish tissue (< 0.3 mg/kg). Prior to diverting Building 4501 Sump I water to the ORNL PWTC, both criteria were exceeded in WOC. Following the diversion of that water to the PWTC (where treatment for removal of constituents including mercury occurs before PWTC effluent is released to WOC), monitoring indicates that the Tennessee water-concentration criterion of 51 ng/L is now being met. However, it remains to be seen what level of mercury reduction will be required to achieve 0.3 mg/kg mercury in fish tissue. It is expected that Tennessee will adopt the EPA fish-tissue criterion at some point. In recent discussions with ORNL/DOE, Tennessee regulatory staff have referenced and expressed interest in the fish-tissue criterion relative to ORNL’s situation.

The pretreatment of Sump I water will be managed using a mercury treatment system. This system will use Dow’s experimental XUS-46304.00 ion-exchange resin. This system has been designed and built by MSE Technology Applications, Inc., headquartered in Butte, Montana, which receives Congressionally-directed funding to support DOE’s Office of Environmental Management (EM) Engineering and Technology Program (EM-20).
It is estimated that 99% of mercury will be eliminated from Sump I effluent using Dow’s experimental XUS-46304.00 ion-exchange resin. Characteristics, however, are still unproven or unknown due to the experimental nature of the resin. In order to determine needed attributes such as mercury removal efficiency and absorption limitations, two primary experiments were performed: (1) a column test and (2) batch equilibrium tests. The mercury removal efficiency of the resin allows for preliminary calculations of future amounts of mercury likely to be pumped into WOC after treatment. The absorption limitations provide insight into the resin’s life span before needing replacement. Lastly, total mercury concentration, radionuclide concentrations, and TCLP analyses were performed on spent resins from the experiments to characterize the spent resin and determine disposal costs, since non-hazardous, hazardous, and mixed wastes vary significantly in expense.

In the following sections, background information on resin is provided, followed by the experimental description. Cost analysis is then discussed based on disposal regulations and types of expenditures. The results are then presented and evaluated.

BACKGROUND

In order to fully grasp the capabilities of Dow’s experimental XUS-43604.00 ion-exchange resin with thiol-active sites, the fundamentals of ion-exchange resin are discussed followed by a review of the different types of resins.

Ion-Exchange Mechanism

The mechanics of an ion-exchange resin is summarized from Wheaton, et al. [2], where ion-exchange is the reversible interchange of ions between a solid (resin spheres or granules) and liquid. The ion-exchange method is usually used in water treatment and remediation activities where special uses include chemical synthesis, medical research, food processing, mining, agriculture, and a variety of other areas. A special characteristic of ion-exchange is the ability to use, regenerate, and then reuse the ion-exchange material, which plays an important role in industrial applications as it decreases cost.

There are five key chemical properties of an ion-exchange resin: (1) capacity, (2) swelling, (3) selectivity, (4) kinetics, and (5) stability. There are two approaches to expressing capacity: total capacity, which is the total number of sites available for exchange, and operating capacity, which is a measure of the useful performance obtained with the ion-exchange material when it is operating in a column under a prescribed set of conditions. Swelling is the hydration capacity of the ion-exchanger that is controlled by limits of the polymer network. Selectivity is represented by the selectivity coefficient, which is the ratio between ionic concentrations in solution and resin phases. Kinetics is the speed with which ion-exchange takes place and lastly, stability is based on the susceptibility of attack on either the polymer backbone or active sites that reduces the useful volume-based capacity or produces unacceptable physical properties.

There are four different resin structures that are utilized in an ion-exchange resin: (1) a cation-exchange resin, (2) an anion-exchange resin, (3) other functional groups, and (4) a polymer matrix. Weak acid cation-exchange resins are often based on acrylic or methacrylic acid that has been crosslinked with a di-functional monomer (generally divinylbenzene). An anion-exchange resin can either be a strong-base or weak-base, depending on the active sites. Resins also use other functional groups for the active sites. One in particular is a resin with chelating ability and that is particularly applicable for the selective exchange of various heavy metals from alkaline earth and alkali metal solutions. Lastly, the structure and porosity of an ion-exchange resin are determined principally by the conditions of polymerization of the backbone polymer matrix.

Dow’s experimental XUS-43604.00 ion-exchange resin is built upon a matrix prepared by co-polymerizing styrene and divinylbenzene. Thiol-active sites on the polystyrene and divinylbenzene backbone are used, which exchange sodium or hydrogen with mercury ions, creating mercury sulfide (HgS). This is considered one of the strongest bonds with mercury, making this type of resin appealing in mercury remediation.
Types of Resins

There are currently three main types of resins researched for remediation of mercury: (1) polymer sorbents with chelating groups [3] – [4], (2) selective polymeric resins with thiol functions [5] – [7], and (3) polymer resins with amide groups [8] – [10]. Senkal, et al. [9] researched a glycidyl methacrylate-based resin cross-linked with acetamide functions for mercury removal in aqueous solutions. The resulting polymer resin had a mercury sorption capacity of approximately 2.2 mmol/g in non-buffered conditions. Research also by Senkal, et al. [10] focused on grafting poly (acrylamide) from carboxylic acid groups onto cross-linked polystyrene beads using a redox polymerization method. The mercury sorption capacity under non-buffered conditions was approximately 5.75 mmol/g.

There are many other types of mercury remediation resins [11] – [13]. Bicak, et al. [13] studied the generation of a glycidyl methacrylate-based resin with pendant urea groups to act as a mercury specific sorbent. The resulting polymer resin had a urea group loading of 7.8 mmol/g and showed excellent mercury binding capacity > 6.7 mmol/g, even in the presence of excess chloride ions.

There have also been many studies on commercially available ion-exchange resins [14] – [18]. Research by Fondeur, et al. [16] tested and compared four different ion-exchange resins: Amberlite GT-73A (Rohn & Haas), Purolite S-920 (Bro-Tech Corporation), Ionac SR-4 (Sybron Chemicals), and SIR-200 (Resin Tech). Research by Nabi, et al. [18] dealt with sorption studies of different metal ions on modified anion-exchange resin. Amberlite resin was sorbed with Eriochrome Black T (EBT) to have a maximum uptake of $5 \times 10^6 \mu$mol/g.

EXPERIMENTATION

The characterization experiments including the column and batch tests are described in this section, which gives insight into the capabilities of Dow’s experimental XUS-43604.00 ion-exchange resin. The known characteristics of this resin are shown in Table I [19]. The composition of Sump I effluent is shown in Table II which was taken from water analysis in 1996. From this study, total suspended solids (TSS) of 10.4 mg/L where measured at pH equaled 7.5. The form of mercury has currently not been identified, but likely is ionic due to the chlorine in the tap water (primary constituent of Sump I effluent), which would oxidize any elemental mercury to Hg$^{2+}$.

Table I. Physical and Chemical Properties of Dow’s XUS-43604.00 Ion-Exchange Resin.

<table>
<thead>
<tr>
<th>Property</th>
<th>Measurement</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Exchange Capacity, min</td>
<td>0.7</td>
<td>eq/L</td>
</tr>
<tr>
<td>Water Content</td>
<td>42-65</td>
<td>%</td>
</tr>
<tr>
<td>Volume Median Diameter</td>
<td>500-650</td>
<td>µm</td>
</tr>
<tr>
<td>400-720 µm, min</td>
<td>95</td>
<td>%</td>
</tr>
<tr>
<td>Particle Density</td>
<td>1.06</td>
<td>g/mL</td>
</tr>
</tbody>
</table>
Table II. Composition of Sump I Effluent.

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>37</td>
</tr>
<tr>
<td>Cd</td>
<td>&lt; 0.005</td>
</tr>
<tr>
<td>Cr</td>
<td>&lt; 0.004</td>
</tr>
<tr>
<td>Cu</td>
<td>0.007</td>
</tr>
<tr>
<td>Fe</td>
<td>0.09</td>
</tr>
<tr>
<td>Hg</td>
<td>0.007</td>
</tr>
<tr>
<td>Mg</td>
<td>9.9</td>
</tr>
<tr>
<td>Na</td>
<td>5.4</td>
</tr>
<tr>
<td>Ni</td>
<td>&lt; 0.02</td>
</tr>
<tr>
<td>P</td>
<td>0.4</td>
</tr>
<tr>
<td>Pb</td>
<td>&lt; 0.05</td>
</tr>
<tr>
<td>Si</td>
<td>2.5</td>
</tr>
<tr>
<td>Zn</td>
<td>0.25</td>
</tr>
</tbody>
</table>

The resin for both column and batch equilibrium tests was used in the as-received sodium form. The resin was slurried with water for the column test before adding to the column and then backwashed to remove any air bubbles.

**Lab-Scale Ion-Exchange Column**

The lab-scale ion-exchange column was set up using two carboys for untreated (Sump I effluent) and treated water. The untreated water was pumped through a clear PVC pipe (inside diameter $\approx \frac{1}{2}$ in) with stainless steel encaps and screens, holding 24 mL of resin using a peristaltic pump (*Masterflex®* Console Drive with Easy-Load® II). The average flow-rate was 3.0 mL/min. Flexible rubber tubing (diameter = 1/16 in) was used to connect all components in the system. Influent and effluent samples were taken twice per week for six weeks. All column tests were conducted at room temperature, which averaged 23°C.

The experimental setup began by determining the height vs. volume for the empty column using measured volumes of water (see Table III). The height of the water additions was measured from the lip of the end adapter, and the volume from the bottom screen to the lip was determined to be 9 mL. These values were then plotted and shown in Fig. 1 where the least squares fit equation is displayed.

Table III. Height vs. Volume of Water in Column.

<table>
<thead>
<tr>
<th>Height (cm)</th>
<th>Volume (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>9</td>
</tr>
<tr>
<td>2.6</td>
<td>14</td>
</tr>
<tr>
<td>5.4</td>
<td>19</td>
</tr>
<tr>
<td>8.2</td>
<td>24</td>
</tr>
</tbody>
</table>
Fig. 1. Resin height vs. volume in the lab-scale column.

The least squares fit equation shown in Fig. 1 was used in the first section of Table IV (S1) to calculate the column diameter and cross-sectional area. The column diameter and cross-sectional area were calculated again (Table IV, S2) by using volume and height values above the adapter lip from Table V.

Table IV. Column Diameter and Cross-Sectional Area Calculations.

<table>
<thead>
<tr>
<th>S1. From Least Squares Fit Equation:</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Column ID (cm)</td>
<td>1.52</td>
<td></td>
</tr>
<tr>
<td>Area (cm²)</td>
<td>1.82</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>S2. From 15 mL and 8.2 cm height:</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Column ID (cm)</td>
<td>1.53</td>
<td></td>
</tr>
<tr>
<td>Area (cm²)</td>
<td>1.83</td>
<td></td>
</tr>
</tbody>
</table>

Table V. Volume vs. Height Calibration above Adapter Lip.

<table>
<thead>
<tr>
<th>Volume (mL)</th>
<th>Height (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.00</td>
<td>2.60</td>
</tr>
<tr>
<td>10.00</td>
<td>5.40</td>
</tr>
<tr>
<td>15.00</td>
<td>8.20</td>
</tr>
</tbody>
</table>

Table VI shows the flow rates (up flow) and resin heights (from the lip of the bottom end adapter) for differing speed settings on the peristaltic pump utilized in the experiments. Back wash velocity, resin volume, and volume expansion are also calculated. This information is crucial to determine the flow rate needed to expand the full-scale bed, backwash the resin, and remove any accumulated particulates without losing any resin. The particle size of Dow’s experimental XUS-43604.00 ion-exchange resin is 0.57 mm [19]. Fig. 2 displays the trend where resin expansion increases with increased backwash velocity.
Table VI. Column Flow Rates for Differing Pump Speed Settings.

<table>
<thead>
<tr>
<th>Pump Setting</th>
<th>Flow Rate (mL/min)</th>
<th>Superficial Velocity (cm/min)</th>
<th>Resin Height (cm)</th>
<th>Resin Volume (cm$^3$)</th>
<th>Volume Expansion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0</td>
<td>0.0</td>
<td>2.9</td>
<td>14.3</td>
<td>0.0</td>
</tr>
<tr>
<td>1.0</td>
<td>2.8</td>
<td>1.5</td>
<td>2.9</td>
<td>14.3</td>
<td>0.0</td>
</tr>
<tr>
<td>1.5</td>
<td>4.8</td>
<td>2.6</td>
<td>3.6</td>
<td>15.6</td>
<td>9.0</td>
</tr>
<tr>
<td>2.0</td>
<td>6.8</td>
<td>3.7</td>
<td>4.0</td>
<td>16.3</td>
<td>14.1</td>
</tr>
<tr>
<td>2.5</td>
<td>8.9</td>
<td>4.9</td>
<td>4.4</td>
<td>17.0</td>
<td>19.2</td>
</tr>
<tr>
<td>3.0</td>
<td>10.8</td>
<td>5.9</td>
<td>4.6</td>
<td>17.4</td>
<td>21.8</td>
</tr>
<tr>
<td>3.5</td>
<td>12.8</td>
<td>7.0</td>
<td>5.1</td>
<td>18.3</td>
<td>28.2</td>
</tr>
</tbody>
</table>

Fig. 2. Superficial velocity vs. resin volume expansion.

For the treatment test, the Sump I water was pumped down through the resin. Approximately 151 L of the water was treated in a span of roughly 38 days, with an average flow rate of 2.8 mL/min. Influent and effluent samples were collected twice a week for mercury analysis in order to monitor the performance of the system.

**Batch-Equilibrium Tests**

Batch equilibrium tests were performed to determine approximate absorption capabilities of Dow’s experimental XUS-43604.00 ion-exchange resin. These tests were conducted at much higher mercury concentrations than what is found in Sump I effluent to determine the apparent resin capacity for mercury. Twelve 250 mL capped polycarbonate flasks were used with each sample having 100 mL of a mercury solution (mercury (II) nitrate – Hg(NO$_3$)$_2$ in tap water) and a subset having varying amounts of resin. Tap water was used in the surrogate due to Sump I water being primarily tap water (once-through cooling water) and groundwater, which is rainwater that seeps through the soil. Batch equilibrium tests were also conducted at room temperature, which averaged 23°C. Table VII lists the flasks, mercury concentrations, and resin masses. All twelve flasks were placed on a shaker table (Orbit Environ Shaker), for approximately four days in order to obtain equilibrium. Previous batch tests with other mercury sorbents at ORNL have shown that four days is more than enough time to reach equilibrium. It should be noted that Flasks 1 through 6 were control samples without resin, to determine mercury losses on flask walls and caps to accurately account the resin’s absorption capacity. There were also repeated mercury concentrations to test the experiment’s reproducibility.
Table VII. Batch Equilibrium Tests.

<table>
<thead>
<tr>
<th>Flask ID</th>
<th>Hg(^a) (mg/L)</th>
<th>Resin - Target (g)</th>
<th>Resin - Measured (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>Control Samples</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>10</td>
<td>0.3</td>
<td>0.2996</td>
</tr>
<tr>
<td>8</td>
<td>10</td>
<td>0.03</td>
<td>0.0307</td>
</tr>
<tr>
<td>9</td>
<td>10</td>
<td>0.03</td>
<td>0.0308</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>0.3</td>
<td>0.2996</td>
</tr>
<tr>
<td>11</td>
<td>1</td>
<td>0.03</td>
<td>0.0295</td>
</tr>
<tr>
<td>12</td>
<td>0.1</td>
<td>0.03</td>
<td>0.0303</td>
</tr>
</tbody>
</table>

\(^a\) Mercury (II) Nitrate - Hg(NO\(_3\))_2

COST ANALYSIS

A cost analysis was performed, which was primarily based on disposal costs. The different disposal regulations affecting cost were reviewed followed by the types of expenditures.

Disposal Regulations

A major expense in operating and maintaining the mercury treatment system will be disposing of the mercury loaded resin, due to a variety of regulations that affect the required disposal techniques. Primary regulations affecting the disposal of loaded resin from the mercury treatment system are: the EPA’s Resource Conservation and Recovery Act (RCRA) [20], including the TCLP [21], and the DOE’s No-Radionuclides Added (NRA) Policy. TCLP is a method which tests the amount of mercury that may leach from the loaded resin. According to TCLP regulations, the loaded resin would be non-hazardous if no more than 0.2 mg/L of mercury is present in the leach solution. The NRA policy specifies that waste being disposed of from DOE sites as non-radiological will not contain measurable quantities of radionuclides (e.g. Cs-137, Co-60, etc.) that are not naturally occurring in the disposed materials. Previous analysis on Sump I effluent found: Cs-137 = 49 pCi/L, Co-60 = 0.06 pCi/L, gross alpha = 1.4 pCi/L, and gross beta = 57 pCi/L. If the resin adsorbs radionuclides from the water, it would not qualify as NRA. Lastly, RCRA states that waste exceeding 260 mg/kg of mercury in the resin is classified as hazardous. If waste does not meet TCLP and/or exceeds 260 mg Hg/kg of resin, it is considered hazardous.

Fig. 3 displays all three of these regulations, all possible combinations, and where mercury loaded resin could be disposed of for each option. If the resin is not hazardous and meets the waste acceptance criteria (WAC) for radionuclides, the mercury-loaded resin can be disposed of at ORNL’s sanitary/industrial landfill, where direct disposal cost is not incurred. If the resin is hazardous and NRA passes, the spent resin can be sent to a hazardous waste landfill in Alabama, which costs $7.00/kg of waste. Lastly, if the resin is a mixed waste (hazardous and radioactive), it could be sent to Perma-Fix at East Tennessee Technology Park (ETTP) in Oak Ridge, TN. If mercury levels are below 260 mg/kg, disposal costs would be $125.00/gal of waste. If above 260 mg/kg, disposal costs would be $30,000.00/drum of waste. The steep increase in pricing when mercury is above the RCRA threshold is due to the RCRA requirement for mercury extraction and recovery from the waste. There is also the possibility that the mercury loaded resin could be sent to ORNL’s sanitary/industrial landfill if TCLP and RCRA regulations are met and radionuclide levels are low, even if it fails NRA regulations. All pricing quotes listed above were obtained from previous investigations by Mr. Paul Taylor.
Types of Expenditures

There are six primary expenditures, shown in Table VIII, for replacing and disposing of the resin from the mercury treatment system. Pricing for new resin as of July 14, 2009 is displayed in Table IX (pricing obtained from communications with The Dow Chemical Company) where 37.4 gal (5 ft$^3$) or 74.8 gal (10 ft$^3$) of resin will be bought per change-out. A new Pentair Water-Structural Fiberglass Column (d$_i$=22" h=50") will also be needed for every change-out, each of which costs $3,000. New resin and fiberglass columns will have to be installed during each change-out due to the difficulty of removing mercury-loaded resin from the column. It would be much more manageable and economical to replace the entire column rather than spend the additional labor costs for withdrawing resin from the column. Resin disposal costs will vary based on TCLP, NRA, and RCRA classifications and resin volume. Labor costs per change-out are $130 on average per hour for an estimated 32 hours. Labor costs for the paperwork associated with disposing the resin are $100 on average per hour, where 16 hours are needed for each change-out. This charge, however, is not needed for disposal at ORNL’s Sanitary/Industrial Landfill. Lastly, resin characterization is needed at particular intervals, which are dependent on meeting specific regulations. The cost of characterization is generally higher when trying to prove the resin is below RCRA’s 260 mg/kg threshold and passes TCLP. Column, labor, and resin characterization costs were obtained from previous investigations by Mr. Paul Taylor.

Table VIII. Primary Expenditures.

<table>
<thead>
<tr>
<th></th>
<th>New Resin</th>
<th>New Column</th>
<th>Resin Disposal</th>
<th>Labor - Changing</th>
<th>Labor - Paperwork</th>
<th>Resin Characterization</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table IX. Dow Resin Pricing.

<table>
<thead>
<tr>
<th>Price</th>
<th>Range</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>$635.40</td>
<td>&lt; 80  ft$^3</td>
<td></td>
</tr>
<tr>
<td>$529.45</td>
<td>80-195 ft$^3</td>
<td></td>
</tr>
<tr>
<td>$441.25</td>
<td>200-800 ft$^3</td>
<td></td>
</tr>
</tbody>
</table>

The measured total mercury concentration in the combined resin samples from the batch tests was higher than expected based on the target mercury concentrations for the starting solutions, which indicates that the actual mercury concentrations were higher than planned.

RESULTS AND ANALYSIS

Resin Characterization

All aqueous samples from both column and batch tests were analyzed using a Shimadzu Atomic Absorption Spectrophotometer (AA-6701) with a Shimadzu Mercury Vaporizer Unit (MVU-1A) for total mercury concentrations. Spent resin from both experiments were extracted, dried, and sent to ORNL’s Radioactive Materials Analytical Laboratory to analyze for the presence of radionuclides, mercury leaching using TCLP, and total mercury.

Results for the collected influent samples from the column test are shown in Table X. Total mercury was quantified for each of the nine samples three times and averaged. The average total mercury concentration of the Sump I effluent from all samples is: 1.062 µg/L±0.01. Effluent samples taken from the column test were also analyzed to determine the mercury removal efficiency when compared with results generated from the influent samples. However, concentrations of the collected effluent samples from the column test were lower than 1 µg/L, the detection limit of the total mercury analysis techniques being utilized in these experiments. Therefore, further analysis is required using more sensitive methods.

Table X. Total Mercury Analysis of Column Test Samples.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Conc. #1 (µg/L)</th>
<th>Conc. #2 (µg/L)</th>
<th>Conc. #3 (µg/L)</th>
<th>Avg. (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-10</td>
<td>0.05</td>
<td>0.05</td>
<td>0.04</td>
<td>0.05±0.004</td>
</tr>
<tr>
<td>6-12</td>
<td>0.69</td>
<td>0.71</td>
<td>0.67</td>
<td>0.69±0.022</td>
</tr>
<tr>
<td>6-15</td>
<td>0.80</td>
<td>0.78</td>
<td>0.79</td>
<td>0.79±0.011</td>
</tr>
<tr>
<td>6-19</td>
<td>1.32</td>
<td>1.34</td>
<td>1.33</td>
<td>1.33±0.011</td>
</tr>
<tr>
<td>6-23</td>
<td>1.37</td>
<td>1.37</td>
<td>1.35</td>
<td>1.36±0.008</td>
</tr>
<tr>
<td>7-6</td>
<td>1.23</td>
<td>1.30</td>
<td>1.30</td>
<td>1.28±0.039</td>
</tr>
<tr>
<td>7-10</td>
<td>1.30</td>
<td>1.30</td>
<td>1.28</td>
<td>1.29±0.010</td>
</tr>
<tr>
<td>7-13</td>
<td>1.29</td>
<td>1.28</td>
<td>1.28</td>
<td>1.28±0.008</td>
</tr>
<tr>
<td>7-17</td>
<td>1.50</td>
<td>1.47</td>
<td>1.48</td>
<td>1.48±0.015</td>
</tr>
</tbody>
</table>

Total mercury analysis results for batch tests are shown in Table XI where each average mercury concentration is a result of using three separate measurements. The total mercury on the sorbent was calculated based on the average total mercury concentrations in the control solutions which are shown in Table XII, total mercury in the water after contact with the resin, and the resin mass. The Hg isotherm has been plotted in Fig. 4. However, results from flask #12 were not used due to the negative value which was likely caused by the low Hg concentration. The data points in Fig. 4 produced an almost straight line, which suggests that the maximum capacity of the sorbent has not yet been approached. Further batch tests are needed to determine the point of saturation.
Table XI. Total Mercury Analysis of Batch Tests Samples.

<table>
<thead>
<tr>
<th>Flask ID</th>
<th>Hg (mg/L)</th>
<th>Resin - Target (g)</th>
<th>Resin - Measured (g)</th>
<th>Average Hg - Water (mg/L)</th>
<th>Hg - Sorbent (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>Control Solutions</td>
<td></td>
<td>113.47</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>Control Solutions</td>
<td></td>
<td>114.24</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>100</td>
<td>Control Solutions</td>
<td></td>
<td>121.13</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>Control Solutions</td>
<td></td>
<td>1.14</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>Control Solutions</td>
<td></td>
<td>1.20</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1</td>
<td>Control Solutions</td>
<td></td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>100</td>
<td>0.3</td>
<td>0.30</td>
<td>7.61</td>
<td>36.27</td>
</tr>
<tr>
<td>8</td>
<td>100</td>
<td>0.03</td>
<td>0.03</td>
<td>24.86</td>
<td>297.77</td>
</tr>
<tr>
<td>9</td>
<td>100</td>
<td>0.03</td>
<td>0.03</td>
<td>24.95</td>
<td>296.51</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>0.3</td>
<td>0.30</td>
<td>0.0230</td>
<td>0.38</td>
</tr>
<tr>
<td>11</td>
<td>10</td>
<td>0.03</td>
<td>0.03</td>
<td>0.0041</td>
<td>3.95</td>
</tr>
<tr>
<td>12</td>
<td>1</td>
<td>0.03</td>
<td>0.03</td>
<td>-0.0001</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Table XII. Average Total Mercury Concentrations of Control Solutions (Batch Tests).

<table>
<thead>
<tr>
<th>Hg (mg/L)</th>
<th>Average (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>116.28</td>
</tr>
<tr>
<td>10</td>
<td>1.17</td>
</tr>
<tr>
<td>1</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Fig. 4. Hg isotherm.

TCLP and total mercury results are shown in Table XIII for resin samples from both column and batch tests. The batch tests used high mercury concentrations in the starting solution in order to get high loading on the resin. Resin from the various flasks was combined in order to get enough resin to perform the TCLP test. The TCLP result for
the column test, which utilized Sump I effluent, shows mercury leaching from spent resin at 0.000463 mg/L, well below the RCRA regulation of 0.2 mg/L to classify the waste as non-hazardous. The total mercury result of 17 µg/g for the column test allows for preliminary calculations of the current mercury concentration in Sump I effluent. This was calculated by using the dried weight of the resin from the column, which is 8.588 g and the amount of treated effluent, 151.4 L. The total amount of mercury in the column was calculated as 8.588 g * 17 µg/g = 146 µg. Assuming that essentially all of the mercury was removed from the solution, the average initial mercury concentration in the water was therefore: 146 µg / 154.4 L = 0.946 µg/L. This calculated concentration is lower than the expected concentration, which was thought to be, from previous mercury analysis, approximately 10 µg/L. A possible reason behind the mercury concentration being an order of magnitude below the expectation is that mercury may be adsorbing to experimental materials such as the column and tubing. This however was not experimentally evaluated and these calculations are preliminary. Analysis of radionuclides in spent resins produced no measurable amount of radionuclides on the spent resins where detection limits at ORNL’s Radioactive Materials Analytical Laboratory were Gross Alpha < 0.008 Bq/g and Gross Beta < 0.01 Bq/g. This result eliminates the possibility of classifying the spent resin from the mercury treatment system as mixed waste.

Table XIII. Current TCLP and Total Mercury Results for Spent Resin.

<table>
<thead>
<tr>
<th></th>
<th>TCLP (mg/L)</th>
<th>THg (µg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column</td>
<td>0.000463</td>
<td>17</td>
</tr>
<tr>
<td>Batch</td>
<td>0.326</td>
<td>52500</td>
</tr>
</tbody>
</table>

The column test also produced a color change in the resin after six weeks of operation. A subset of resin beads changed to a reddish-brown color. This could be due to particulates forming from Sump I effluent over time.

Cost Scenarios and Options

The cost analysis performed has two scenarios using 37.4 gal and 74.8 gal of resin per column, which are shown in Table XIV through Table XVI. Each scenario has four options, where each option is a possible combination of regulatory outcomes. It is understood at this point that NRA and TCLP regulations should be met in regard to Sump I effluent according to results shown in the previous section. The RCRA regulation of mercury loading above or below 260 mg/kg can be controlled by the change-out frequency based on the flow-rate and mercury concentration in the Sump I water. For the scenarios where the mercury concentration is > 260 mg/kg, it is assumed the resin will last one year, but this has not yet been proven. It is shown in the cost analyses that option 2 of both scenarios is the optimal solution where the RCRA limit on mercury (260 mg/kg) is being surpassed. The outcome of TCLP is of no concern at this point due to the waste being classified as hazardous. This is because of the total mercury concentration of the resin surpassing the 260 mg/kg regulatory mark. The optimality of option 2 is due to the lower frequency of change-outs, limiting costs of resin, columns, labor, and resin characterization.

It was surprising that fully loading the resin with mercury and sending the waste to the Hazardous Waste Landfill in Alabama would be less expensive than minimizing the loaded mercury to RCRA’s 260 mg/kg regulatory limit where no disposal fee would be incurred from ORNL’s Sanitary Landfill. The benefit of fully loading the resin with mercury would be decreasing the change-out frequency, thereby eliminating the added costs of more frequent change-outs. Fig. 4 demonstrates the cost division of the optimal solution (scenario 2, option 2) where disposal fees at the Hazardous Waste Landfill in Alabama is a small portion of the total cost.
Scenario 2, Option 2 Expenditures

Fig. 4. Expenditures of Scenario 2, Option 2.

Table XIV. Cost Analysis, Scenario 1 for Full-Scale Mercury Treatment System (Options 1 and 2).

<table>
<thead>
<tr>
<th>Based on the use of 1 drum (37.4 gal) of resin.</th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>ORNL Sanitary Landfill</td>
<td>Hazardous Waste Landfill, AL</td>
<td></td>
</tr>
<tr>
<td><strong>Pass TCLP</strong></td>
<td><strong>Pass TCLP</strong></td>
<td></td>
</tr>
<tr>
<td>No-Rad Added - &lt;260 mg/kg</td>
<td>No Rad Added - &gt;260 mg/kg</td>
<td></td>
</tr>
<tr>
<td>Cost/Change-Out</td>
<td>Change-Out/Year</td>
<td>Yearly Cost</td>
</tr>
<tr>
<td>New Resin</td>
<td>$3,177.00</td>
<td>12</td>
</tr>
<tr>
<td>New Column</td>
<td>$3,000.00</td>
<td>12</td>
</tr>
<tr>
<td>Resin Disposal</td>
<td>$0.00</td>
<td>12</td>
</tr>
<tr>
<td>Labor - Changing</td>
<td>$4,160.00</td>
<td>12</td>
</tr>
<tr>
<td>Labor - Paperwork</td>
<td>$0.00</td>
<td>12</td>
</tr>
<tr>
<td>Resin Characterization</td>
<td>$3,000.00</td>
<td>1</td>
</tr>
<tr>
<td><strong>TOTAL ANNUAL COST:</strong></td>
<td><strong>$127,044.00</strong></td>
<td><strong>$19,493.18</strong></td>
</tr>
</tbody>
</table>
Table XV. Cost Analysis, Scenario 1 for Full-Scale Mercury Treatment System (Options 3 and 4).

<table>
<thead>
<tr>
<th></th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Based on the use of 1 drum (37.4 gal) of resin.</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Perma-Fix at ETTP</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Radiological - &lt;260 mg/kg</td>
<td>Radiological - &gt;260 mg/kg</td>
</tr>
<tr>
<td></td>
<td>Cost/Change-Out</td>
<td>Change-Out/Year</td>
</tr>
<tr>
<td>New Resin</td>
<td>$3,177.00</td>
<td>12</td>
</tr>
<tr>
<td>New Column</td>
<td>$3,000.00</td>
<td>12</td>
</tr>
<tr>
<td>Resin Disposal</td>
<td>$4,675.00</td>
<td>12</td>
</tr>
<tr>
<td>Labor - Changing</td>
<td>$4,160.00</td>
<td>12</td>
</tr>
<tr>
<td>Labor - Paperwork</td>
<td>$1,600.00</td>
<td>12</td>
</tr>
<tr>
<td>Resin Characterization</td>
<td>$2,000.00</td>
<td>12</td>
</tr>
<tr>
<td><strong>TOTAL ANNUAL COST:</strong></td>
<td></td>
<td>$223,344.00</td>
</tr>
</tbody>
</table>

Table XVI. Cost Analysis, Scenario 2 for the Full-Scale Mercury Treatment System (Options 1 and 2).

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Based on the use of 2 drums (74.8 gal) of resin.</strong></td>
<td>ORNL Sanitary Landfill</td>
<td>Hazardous Waste Landfill, AL</td>
</tr>
<tr>
<td></td>
<td>Pass TCLP</td>
<td>Fails TCLP</td>
</tr>
<tr>
<td></td>
<td>No-Rad Added - &lt;260 mg/kg</td>
<td>No-Rad Added - &gt;260 mg/kg</td>
</tr>
<tr>
<td></td>
<td>Cost/Change-Out</td>
<td>Change-Out/Year</td>
</tr>
<tr>
<td>New Resin</td>
<td>$6,354.00</td>
<td>6</td>
</tr>
<tr>
<td>New Column</td>
<td>$3,000.00</td>
<td>6</td>
</tr>
<tr>
<td>Resin Disposal</td>
<td>$0.00</td>
<td>6</td>
</tr>
<tr>
<td>Labor - Changing</td>
<td>$4,160.00</td>
<td>6</td>
</tr>
<tr>
<td>Labor - Paperwork</td>
<td>$0.00</td>
<td>6</td>
</tr>
<tr>
<td>Resin Characterization</td>
<td>$3,000.00</td>
<td>1</td>
</tr>
<tr>
<td><strong>TOTAL ANNUAL COST:</strong></td>
<td></td>
<td>$84,084.00</td>
</tr>
</tbody>
</table>
Table XVII. Cost Analysis, Scenario 2 for the Full-Scale Mercury Treatment System (Options 3 and 4).

<table>
<thead>
<tr>
<th>Based on the use of 2 drums (74.8 gal) of resin.</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Perma-Fix at ETTP</strong></td>
<td><strong>Fails TCLP</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Radiological - &lt;260 mg/kg</strong></td>
<td><strong>Radiological - &gt;260 mg/kg</strong></td>
<td></td>
</tr>
<tr>
<td>Cost/Change-Out</td>
<td>Change-Out/Year</td>
<td>Yearly Cost</td>
</tr>
<tr>
<td>New Resin</td>
<td>$6,354.00</td>
<td>6</td>
</tr>
<tr>
<td>New Column</td>
<td>$3,000.00</td>
<td>6</td>
</tr>
<tr>
<td>Resin Disposal</td>
<td>$9,350.00</td>
<td>6</td>
</tr>
<tr>
<td>Labor - Changing</td>
<td>$4,160.00</td>
<td>6</td>
</tr>
<tr>
<td>Labor - Paperwork</td>
<td>$1,600.00</td>
<td>6</td>
</tr>
<tr>
<td>Resin Characterization</td>
<td>$2,000.00</td>
<td>6</td>
</tr>
<tr>
<td><strong>TOTAL ANNUAL COST:</strong></td>
<td><strong>$158,784.00</strong></td>
<td><strong>$75,614.00</strong></td>
</tr>
</tbody>
</table>
CONCLUSION

The primary purpose of this research is to characterize Dow’s experimental XUS-43604.00 ion-exchange resin, which includes mercury removal efficiency, adsorption capabilities, mercury leaching using TCLP, and its reaction to radionuclides. With this valuable information, mercury concentrations that reach WOC from Building 4501, Sump I, can be determined in addition to cost estimates for spent resin disposal of the mercury treatment system.

Without mercury removal efficiency and absorption characteristics, disposal costs of spent resin can still be approximated with estimated variables utilized in various options. Mercury removal efficiency was estimated to be 99% based on previous research pertaining to a similar resin. Mercury sorption capacity was calculated to be 0.52 mmol/g at this low influent concentration for Dow’s experimental XUS-43604.00 ion-exchange resin. There are four cost analysis options based on the resulting radionuclide and TCLP analyses: (1) non-hazardous, (2) hazardous, (3) mixed waste – low mercury concentration, and (4) mixed waste – high mercury concentration. Low mercury concentration is defined by the RCRA, which states that mercury cannot exceed 260 mg/kg and still be considered non-hazardous.

TCLP results, shown in Table XIII from column experiments, illustrate that the RCRA leaching requirement of 0.2 mg/L from the spent resin is being met. This, however, is irrelevant if the resin is loaded to its maximum limit (above 260 mg/kg), thereby classifying the spent resin as hazardous, even if it passes TCLP. Results also indicate that there were no measurable amounts of radionuclides on the spent resins. Therefore, sending the waste to the Hazardous Waste Landfill in Alabama (scenario 2, option 2, as shown in Table XVI), is a probable scenario and is considered the optimal choice in minimizing cost for the mercury treatment system.

ACKNOWLEDGEMENTS

Special thanks to the U.S. Department of Energy for their continued support.

REFERENCES