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Mercury Remediation using Dow's Experimental XUS-43604.00 Ion-Exchange Resin at Oak Ridge National Laboratory

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ABSTRACT

Mercury contamination is a major concern at Oak Ridge National Laboratory (ORNL), particularly at Building 4501, which housed early research efforts on the COLEX process used at the Y-12 National Security Complex. The greatest concentrations of mercury at Building 4501 are found in Sump I, which represents 80% of the total identifiable mercury discharges at ORNL, generating 900 mg/day (calculations based on previous analysis of Sump I effluent). Currently, Sump I effluent is pumped at 8.2 gal/min to the Process Wastewater Treatment Complex (PWTC) for treatment prior to discharge to White Oak Creek (WOC). The PWTC removes approximately 75% of the dissolved mercury. In order to further reduce mercury discharge to WOC, a mercury treatment system utilizing Dow's experimental XUS-43604.00 ion-exchange resin with thiol active sites will be 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 tests for adsorption limits. The lab-scale column was set up using a peristaltic pump, which pumped untreated Sump I effluent at 3.0 mL/min through a translucent pipe holding 24 mL of resin. Influent and effluent samples were taken twice per week for six weeks. Batch equilibrium tests were conducted in the span of four days with twelve 100 mL samples of $Hg(NO_3)_2$ (mercuric nitrate) spiked tap water. Initial mercury concentrations were 1 mg/L, 10 mg/L, and 100 mg/L with resin masses of 0.3 g and 0.03 g. Control samples and duplicate solutions were also prepared for better accuracy and to determine repeatability. All aqueous samples from both column and batch tests are currently being analyzed using Atomic Absorption Spectroscopy (AAS) for total mercury concentrations. Spent resin samples from both tests have been analyzed for total mercury and mercury leaching using the Toxicity Characteristic Leaching Procedure (TCLP). Total mercury concentrations for the column and batch test resin samples were 17 ppm and 52,500 ppm respectively. TCLP analysis for column and batch tests was assessed at 0.000463 mg/L and 0.326 mg/L respectively. Radionuclide analysis is currently being performed. Data being generated by this project will answer many unknowns when dealing with mercury removal efficiency, resin change-out frequency, and resin disposal costs of the treatment system. Costs will be determined based on the classification of spent resin using radionuclide and TCLP analyses. Possible waste classifications include non-hazardous, hazardous, and mixed waste, which vary significantly in disposal expense.

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1. 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, and 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. 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. 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 will eliminate 99% or approximately 890 mg/day of mercury currently being pumped to the PWTC from Sump I, and will 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 shown in Figure 1. 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).

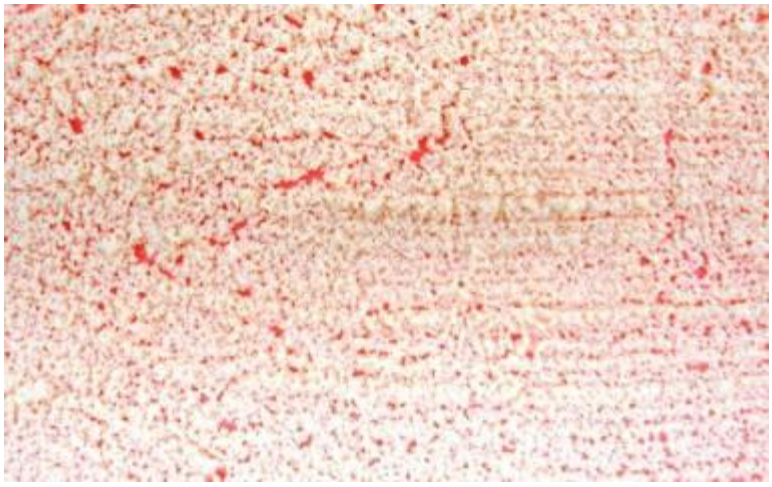

Figure 1. Dow's XUS-46304.00 experimental resin.

Figure 2 displays a variety of photos from the mercury treatment system, which is currently located near Sump I in the basement of Building 4501, awaiting installation. Benefits that come with using the mercury pretreatment system include:

- Reduction of mercury to WOC from Sump I by 99%
- Compliance with state and federal water criteria
- Good faith effort to achieve as low as reasonably achievable (ALARA) cleanup levels
- Lower operating maintenance costs than process modification for enhanced mercury treatment at PWTC

Figure 2. Mercury treatment system located at Building 4501, Sump I.

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 tests. The mercury removal efficiency of the resin allows for preliminary calculations on future amounts of mercury being pumped to WOC after treatment. The absorption limitations provide insight on the resin's life span before needing replacement. Lastly, total mercury, radionuclide, and TCLP analyses were performed on spent resins from the experiments to accurately price disposal costs where non-hazardous, hazardous, and mixed wastes vary significantly in expense.

In the following sections of this document, an executive summary is provided, followed by the research description, which is composed of detailed experimental setup and research pertaining to the column test, batch tests, and disposal costs. The results are then presented and evaluated. Last, the conclusion of this project is presented and includes mercury removal efficiency, approximated change-out frequency, and disposal costs of spent resin which affects the mercury treatment system.

2. EXECUTIVE SUMMARY

The described research work is supported by the Department of Energy (DOE)-Florida International University (FIU) Science & Technology Workforce Initiative, an innovative program developed by the U.S. DOE Office of Environmental Management and FIU's Applied Research Center (ARC) in creating a pipeline of minority students for DOE's future workforce. A DOE Fellow (Charles Castello) was sent to Oak Ridge National Laboratory (ORNL) in Oak Ridge, TN for a 10-week internship in the summer of 2009 (June 1 – August 7, 2009). There, the DOE Fellow was mentored by Mr. Paul A. Taylor in the Nuclear Science and Technology Division (NSTD), Process Engineering Research Group. This internship was coordinated by the Applied Research Center at FIU, the Oak Ridge Institute for Science and Education (ORISE), and the Higher Education Research Experience (HERE) Program.

There are many facets of research and experimentation involved in this project pertaining to the remediation of legacy mercury at ORNL. The main technology utilized to accomplish this goal is ion-exchange resin, which absorbs mercury by exchanging mercury with sodium ions attached to resin beads. Experimentation with Dow's experimental XUS-46304.00 ion-exchange resin has been performed to better understand its characteristics when dealing with Sump I effluent from Building 4501 at ORNL. Specific properties of interest include mercury removal efficiency and adsorption limitations, which respectively aids in the calculation of mercury entering White Oak Creek (WOC) after treatment and resin change-out frequency. Cost analysis of disposal fees for the resin from the mercury treatment system was also studied which is dependent on total mercury, radionuclide, and Toxicity Characteristic Leaching Procedure (TCLP) analyses. Spent resin can fit into three categories: non-hazardous, hazardous, and mixed waste depending on the outcome of total mercury, radionuclide, and TCLP analyses. This is extremely important due to large variations in pricing when dealing with all three classifications for disposal.

3. RESEARCH DESCRIPTIONS

In order to fully grasp the capabilities of Dow's experimental XUS-43604.00 ion-exchange resin with thiol active sites, different types of resins were reviewed followed by the fundamentals of ion-exchange resin. Afterwards, the characterization experiments including column and batch tests are described in detail. A cost analysis was also performed, which is primarily based on disposal costs. The different disposal regulations affecting cost are reviewed followed by the types of expenditures.

3.1 Resin

3.1.1. Types of Resins

There are currently three main types of resins researched for remediation of mercury: (1) polymer sorbents with chelating groups [1] – [2], (2) selective polymeric resins with thiol functions [3] – [5], and (3) polymer resins with amide groups [6] – [8]. Research by Pramanik, et al. [1] deals with a new stable chelating resin that was synthesized by incorporating 2-aminothiophenol into Merrifield polymer through C-N covalent bond and characterized by elemental analysis, infrared (IR), and thermal study. Moawed, et al. [2] studied the use of methylene blue-grafted foam (Me. B-grafted foam) in which ion association complexes are formed between Cd(II), Hg(II), and Ag(I). Various conditions, such as pH, shaking time, maximum capacities, and chromatographic behavior, are examined.

Dujardin, et al. [3] is the first of three research papers referenced that study selective polymeric resins with thiol functions. The focus is on the synthesis of a thiol-supported polymer prepared by hydrolysis of a thioacetate supported resin. Two different techniques were used to create the studied resins: synthesis of a functional monomer and chemical modifications. Work done by Kara [4] immobilized (acetylacetone)-2-thiol-phenyleneimine (H_2L) on an anion-exchange resin (Dowex) to separate and remove mercury from natural water samples and pre-concentrations prior to its determination by cold vapor inductively coupled plasma atomic emission spectroscopy. Various parameters, such as pH, column flow rate, and desorbing agents, are optimized in this study. Lastly, Osteen, et al. [5] experimented with Duolite GT-73, a polystyrene/divinylbenzene resin with thiol (S-H) functional groups, to be used in mercury remediation for Savannah River laboratory wastes in Tank L at the Savannah River Site in South Carolina.

Polymer resin with amide groups is shown in [6], which deals with selective mercury removal by grafting polyacrylamide from N-chlorosulfonamide groups onto crosslinked polystyrene beads using copper-mediated atom transfer radical polymerization (ATRP) methodology. Senkal, et al. [7] researched a glycidyl methacrylate-based resin cross-linked beads with acetamide functions for mercury removal in aqueous solutions. The resulting polymer resin has a mercury sorption capacity of approximately 2.2 mmol/g in non-buffered conditions. Research also by Senkal, et al. [8] 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 is approximately 5.75 mmol/g.

There are many other types of mercury remediation resins, such as the cation exchange resin studied by Anirudhan, et al [9]. This resin contains carboxyl groups via the acrylonitrile (AN) reaction with banana stem (BS) in the presence of ceric ammonium nitrate (CAN) as an initiator. The absorption capabilities for Hg(II) ions from aqueous solutions and chlor-alkali industry wastewater were tested. Research by Rivas, et al. [10] dealt with investigating the binding ability of poly (4-vinylpyridine) hydrochloride resin for Cu(II), Cd(II), Zn(II), Hg(II), Pb(I), Cr(III), and U(VI). Retention of metal ions at different pH, adsorption selectivity of the resin for Hg(II) ions from binary mixtures at pH = 2, and elution behavior of Hg(II) is explored. Bicak, et al. [11] studied the generation of a glycidyl methacrylate-based resin with pendant urea groups to act as a mercury specific sorbent. The resulting polymer resin has a urea group loading of 7.8 mmol/g and shows excellent mercury binding capacity > 6.7 mmol/g, even in the presence of excess chloride ions.

Results from previous research papers dealing in the use of commercially available ion-exchange resins will be compared with results from this project. Research by Chiarle, et al. [12] used Duolite GT-73 ion-exchange resin. Different experiments were performed to determine adsorption efficiency, the effect of pH on the uptake of mercury, and the adsorption kinetics. Andoni, et al. [13] found optimal conditions for removing mercury from water using the PUROLITE S-920 ion-exchange resin. Batch tests were completed using various amounts of HgCl and the S-920 resin. All solutions were shaken at various times including 15, 30, 45, and 60 minutes. Research by Fondeur, et al. [14] tested and compared four different ion-exchange resins: Amberlite GT-73A from Rohn & Haas, Purolite S-920 from Bro-Tech Corporation, Ionac SR-4 from Sybron Chemicals, and SIR-200 from Resin Tech. Batch tests were performed using 45 mL of 200 ppm Hg and 1500 ppm $NaNO_3$ solution in bottles which were placed in a shaker and shook at 400 rpm for 14 days at ambient temperature. Cold-vapor atomic absorption (CVAA) was used to determine mercury concentrations for each solution. Nabi, et al. [15] sorbed Amberlite IRA-400 resin with BromoPhenol Blue (BPB) in order to determine the separation of various metal ions. Distribution coefficients of a number of important metal ions have been determined in various solvent systems in order to explore the separation potential of these materials. Lastly, more research by Nabi, et al. [16] 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 $5x10^{-6}$ mol/g.

3.1.2. Ion-Exchange Mechanism

The mechanics of ion-exchange resin is summarized from Wheaton, et al. [17] 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 and reuse the ion-exchange material, which plays an important role in industrial applications due to its decrease in cost.

There are five key chemical properties of ion-exchange resin: (1) capacity, (2) swelling, (3) selectivity, (4) kinetics, and (5) stability. There are two approaches in 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 and produces unacceptable physical properties.

There are four different resin structures that are utilized in ion-exchange resin: (1) cation-exchange resin, (2) anion-exchange resin, (3) other functional groups, and (4) polymer matrix. Weak acid cation exchange resins are based primarily on acrylic or methacrylic acid that has been crosslinked with a di-functional monomer (generally divinylbenzene). Anion-exchange resin can either be strong-base or weak-base, depending on the active sites. Resins also use other functional groups for the active sites. One in particular is resins with chelating ability and that are 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 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.

3.1.3. Characterization Experiments

Lab-Scale Ion-Exchange Column

The lab-scale ion-exchange column is shown in Figure 3, which was set up using two carboys for untreated (Sump I effluent) and treated waters. The untreated water was pumped through a translucent pipe (inside diameter ≈ ½ in) holding 24 mL of resin using a peristaltic pump (*Masterflex*® Console Drive with Easy-Load® II). The pump speed was set to 1.0, producing an average flow-rate of 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.

The experimental setup began by determining the height vs. volume for the column, which is shown in Table 1. The height of the resin was measured from the lip of the end adapter, where volume below this point is 9 mL. These values were then plotted and shown in Figure 4 where the trend line equation is displayed.

Figure 3. Lab-scale ion-exchange column.

Table 1. Height vs. Volume of Resin in Column

Height (cm)	Volume (mL)
0	9
2.6	14
5.4	19
8.2	24

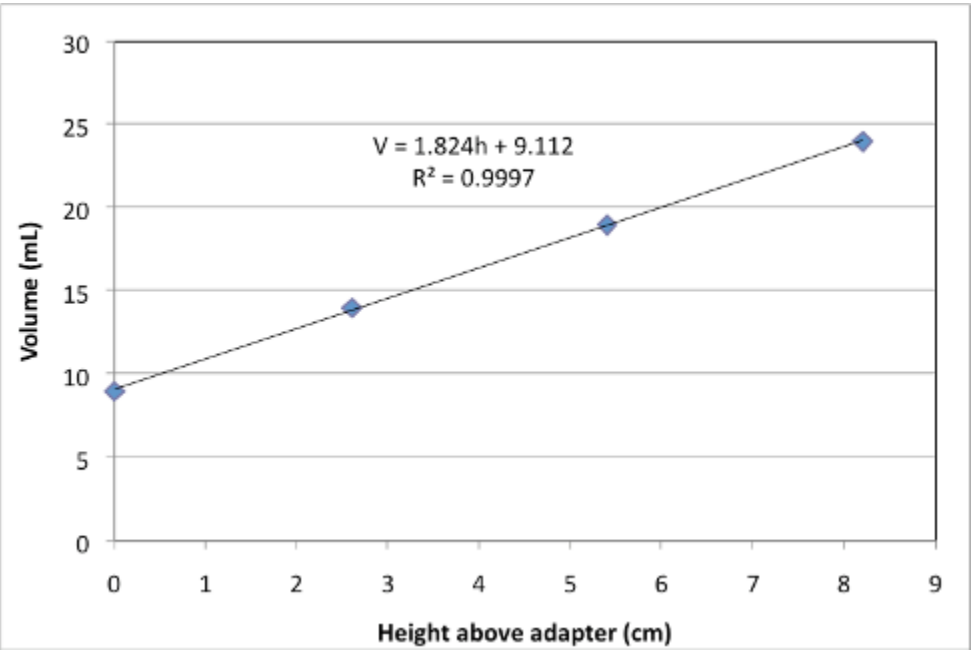

Figure 4. Resin height vs. volume in the lab-scale column.

The trend line equation shown in Figure 4 was used in the first section of Table 2 (S1) to calculate the column diameter and cross-sectional area. The column diameter and cross-sectional area were calculated again (Table 2, S2) by using volume and height values above the adapter lip from Table 3.

Table 2. Column Diameter and Cross-Sectional Area Calculations

S1. From Trendline Equation	
Column ID (cm)	1.52
Area (cm^2)	1.82
S2. From 15 mL and 8.2 cm height:	
Column ID (cm)	1.53
Area (cm^2)	1.83

Table 3. Volume vs. Height Calibration above Adapter Lip

Volume (mL)	5.00	10.00	15.00
Height (cm)	2.60	5.40	8.20

Table 4 shows the flow rates (up flow) and resin heights for differing speed settings on the peristaltic pump utilized in the experiments. Superficial velocity, resin volume, and volume expansion are also calculated. Figure 5 displays the trend where resin expansion increases with increased superficial velocity.

Table 4. Column Flow Rates for Differing Pump Speed Settings

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

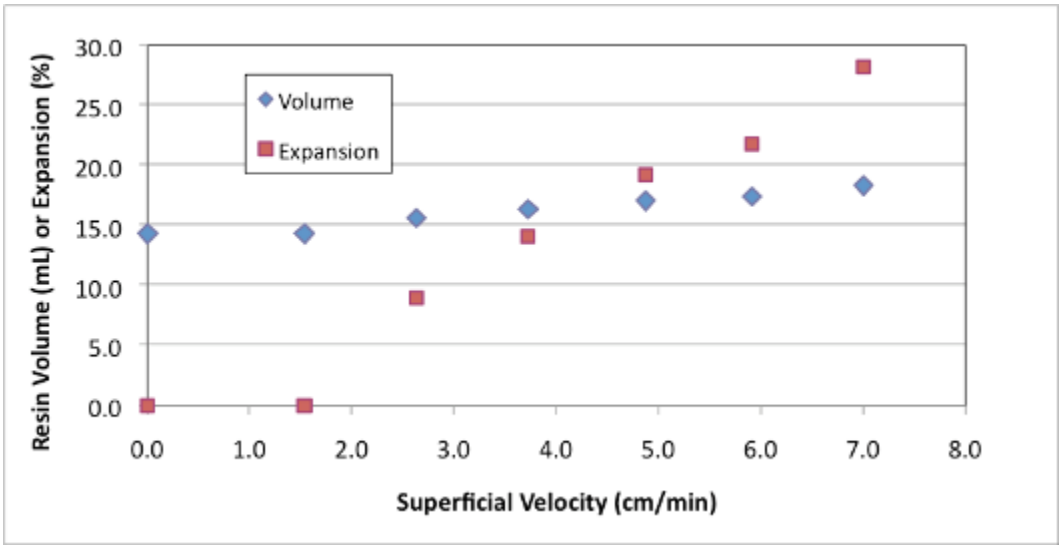

Figure 5. Superficial velocity vs. Resin volume expansion.

Appendix A lists all measured effluent volumes and calculated flow rates for the lab-scale treatment system where approximately 151 L of Sump I effluent 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. All samples from the column experiment are shown in Appendix B. Figure 6 shows the procedure for pumping water from Sump I, where another peristaltic pump was used to pump water into a plastic jug using ½" diameter plastic tubing that was lowered through the grating into the sump.

Figure 6. Pumping of Sump I water using a peristaltic pump.

Batch Equilibrium Tests

Batch equilibrium tests were performed to determine approximate absorption capabilities of Dow's experimental XUS-43604.00 ion-exchange resin. Twelve 250 mL polycarbonate flasks were used with each sample having 100 mL of a mercury solution (mercury (II) nitrate – $Hg(NO_3)_2$ with tap water) and a subset having varying amounts of resin. Table 5 lists the flasks, mercury concentrations, and resin masses. All twelve flasks were placed on a shaker table (Orbit Environ Shaker), shown in Figure 7, for approximately four days in order to obtain equilibrium before being sent to FIU's ARC for mercury analysis to determine the amount of mercury absorbed by the resin. All batch samples are shown in Appendix B. It should be noted that Flasks 1 through 6 are control solutions, without resin, to determine if any mercury was adsorbed by the flasks, for increased accuracy when calculating the resin's absorption. There are also repeated mercury concentrations to test the experiments repeatability.

Figure 7. Batch equilibrium tests on a shaker table.

Table 5. Batch Equilibrium Tests

Flask ID	*Hg* (mg/L)*	*Resin - Target (g)*	*Resin - Measured (g)*
1	10	*Control Solutions*	
2	10		
3	10		
4	1		
5	1		
6	0.1		
7	10	0.3	0.2996
8	10	0.03	0.0307
9	10	0.03	0.0308
10	1	0.3	0.2996
11	1	0.03	0.0295
12	0.1	0.03	0.0303
* Mercury (II) Nitrate - $Hg(NO_3)_2$			

3.2 Cost Analysis

3.2.1. 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) [18], including the TCLP [19], 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 pass 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 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 doesn't meet TCLP and/or exceeds 260 mg Hg/kg of resin, it is considered hazardous.

Table 6 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 radionuclies, the mercury loaded resin can be disposed of at ORNL's sanitary/industrial landfill, where cost isn't 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. Last, 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. All pricing quotes listed above were obtained from previous investigations by Mr. Paul Taylor.

Table 6. Possible Variations of Mercury Loaded Resin Disposal

ORNL Sanitary Landfill	Hazardous Waste Landfill, AL	Perma-Fix at ETTP	
Pass TCLP	Fail TCLP and/or >260 mg/kg		
No-Rad Added - No RCRA	No-Rad Added - RCRA	Radiological - RCRA - Low Hg	Radiological - RCRA - High Hg

3.2.2. Types of Expenditures

There are six primary expenditures, shown in Table 7, 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 8 (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. Excess quantities could be purchased to decrease cost per ft^3, but storage would be an issue. 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. Last, 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 7. Primary Expenditures

1	New Resin
2	New Column
3	Resin Disposal
4	Labor - Changing
5	Labor - Paperwork
6	Resin Characterization

Table 8. Dow Resin Pricing

$635.40	< 80	ft^3
$529.45	80-195	ft^3
$441.25	200-800	ft^3

4. RESULTS AND ANALYSIS

The results from resin characterization will now be discussed and analyzed. Cost scenarios and options for resin disposal based on these results will be explained and reviewed to determine approximations for future expenditures of the mercury treatment system at Building 4501, Sump I.

4.1 Resin Characterization

All aqueous samples from both column and batch tests are currently being analyzed using AAS for total mercury concentrations at FIU's ARC. Spent resin from both experiments was extracted, dried (shown in Figure 8), and sent to ORNL's Radioactive Materials Analytical Laboratory to analyze for the presence of radionuclides, mercury leaching using TCLP, and total mercury.

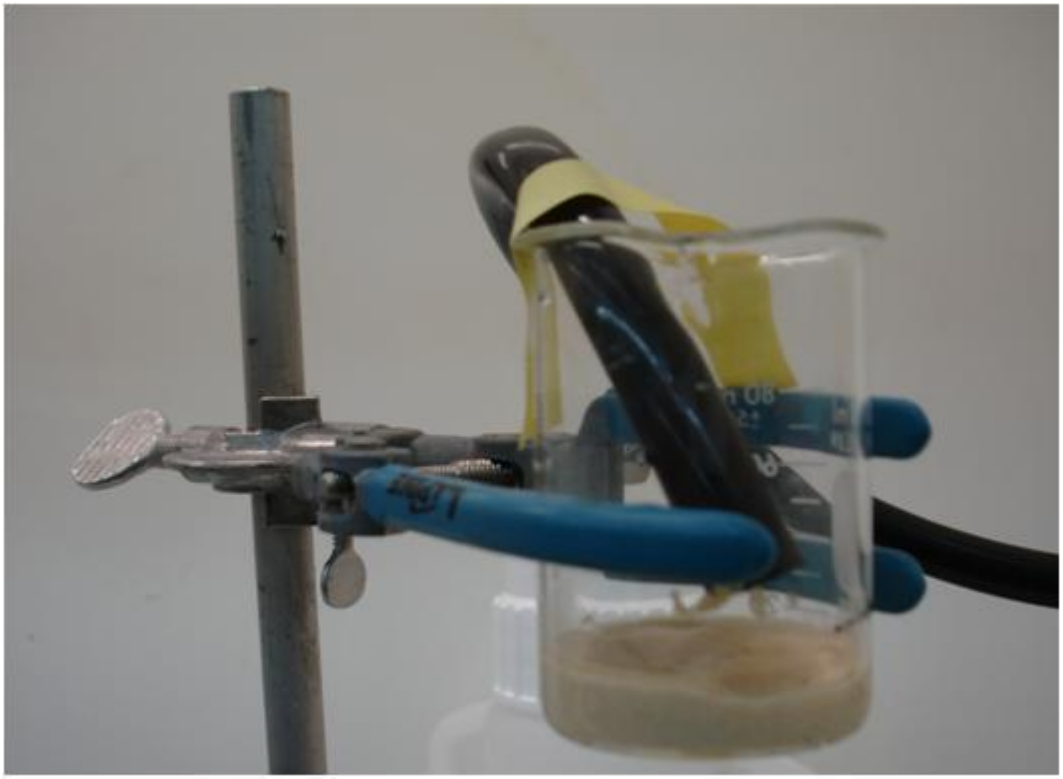

Figure 8. Drying of spent resin.

Currently, TCLP and total mercury results have been returned from ORNL's Radioactive Materials Analytical Laboratory, as shown in Table 9. 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 ppm 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 = 145.996 µg. The average mercury concentration in the water is therefore: 145.996 µg / 154.4 L = 0.946 µg/L = ppb. This is significantly lower than the expected concentration, which was thought to be, from previous mercury analysis, approximately 10 ppb. These calculations, however, are preliminary. Results from the column and batch tests will allow more accurate results for total mercury concentrations in Sump I effluent and sorption characteristics including mercury removal efficiency for Dow's experimental XUS-43604.00 ion-exchange resin. Analysis of radionuclides in spent resins is currently under investigation and results should soon be available.

Table 9. Current TCLP and Total Mercury Results for Spent Resin

	TCLP (mg/L)	*THg (µg/g = ppm)*
Column	0.000463	17
Batch	0.326	52500

4.2 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 Tables 10 and 11, respectively. Each scenario has four options, where each option is a possible combination of regulatory outcomes. It is unclear at this point whether NRA regulation will be met. However, the TCLP regulation should be met in regard to Sump I effluent according to results shown in Table 9. 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 are the optimal solutions where NRA limitations on radionuclides is assumed to be met and 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.

Table 12 displays the pricing differences between all four options in each scenario. By doubling the amount of resin in each column from scenario 1 to scenario 2, the greatest amount of savings is shown in option 1 at 33.03% and the least in option 4. The optimal cost estimate on both scenarios is option 2, where savings from scenario 1 to scenario 2 is 24.18%.

Figures 9 through 13 represent the data in Tables 10 and 11. Figure 9 displays the cost estimation options for scenario 1. The greatest cost in options 3 and 4 are resin disposal due to disposal of mixed (hazardous and radiological) wastes being extremely costly. This is the same case for scenario 2, which is shown in Figure 10. Figure 11 is a comparison between scenarios 1 and 2, where scenario 2 has lower total costs. This is due to decreased change-out frequency because of doubling the amount of resin in each

column, compared with scenario 1. In theory, cost would decrease with greater amounts of resin, though the fiberglass columns being used have an inner volume of 11 ft^3. With the use of two drums of resin, this leaves 1 ft^3, enough for an appropriate contact between Sump I water and resin. Figures 12 and 13 demonstrate expenditures for scenarios 1 and 2, option 2, and how each expense affects the total cost.

Table 10. Cost Analysis, Scenario 1 for Full-Scale Mercury Treatment System

Based on the use of 1 drum (37.4 gal) of resin.	1			2			3			4		
	ORNL Sanitary Landfill			**Hazardous Waste Landfill, AL**			**Perma-Fix at ETTP**					
	Pass TCLP			*Fails TCLP*								
	No-Rad Added - <260 mg/kg			**No Rad Added - >260 mg/kg**			**Radiological - <260 mg/kg**			**Radiological - >260 mg/kg**		
	Cost/Change-Out	*Change-Out/Year*	*Yearly Cost*	*Cost/Change-Out*	*Change-Out/Year*	*Yearly Cost*	*Cost/Change-Out*	*Change-Out/Year*	*Yearly Cost*	*Cost/Change-Out*	*Change-Out/Year*	*Yearly Cost*
New Resin	$3,177.00	6	$19,062.00	$3,177.00	1	$3,177.00	$3,177.00	6	$19,062.00	$3,177.00	1	$3,177.00
New Column	$3,000.00	6	$18,000.00	$3,000.00	1	$3,000.00	$3,000.00	6	$18,000.00	$3,000.00	1	$3,000.00
Resin Disposal	$0.00		$0.00	$668.59	1	$668.59	$4,675.00	6	$28,050.00	$30,000.00	1	$30,000.00
Labor - Changing	$4,160.00	6	$24,960.00	$4,160.00	1	$1,600.00	$4,160.00	6	$24,960.00	$4,160.00	1	$4,160.00
Labor - Paperwork	$0.00		$0.00	$1,600.00	1	$1,601.00	$1,600.00	6	$9,600.00	$1,600.00	1	$1,600.00
Resin Characterization	$3,000.00	1	$3,000.00	$500.00	1	$500.00	$2,000.00	6	$12,000.00	$500.00	1	$500.00
TOTAL ANNUAL COST:			**$65,022.00**			**$10,546.59**			**$111,672.00**			**$42,437.00**

Table 11. Cost Analysis, Scenario 2 for the Full-Scale Mercury Treatment System

Based on the use of 2 drums (74.8 gal) of resin.	1			2			3			4		
	ORNL Sanitary Landfill			**Hazardous Waste Landfill, AL**			**Perma-Fix at ETTP**					
	Pass TCLP			*Fails TCLP*								
	No-Rad Added - <260 mg/kg			**No-Rad Added - >260 mg/kg**			**Radiological - <260 mg/kg**			**Radiological - >260 mg/kg**		
	Cost/Change-Out	*Change-Out/Year*	*Yearly Cost*	*Cost/Change-Out*	*Change-Out/Year*	*Yearly Cost*	*Cost/Change-Out*	*Change-Out/Year*	*Yearly Cost*	*Cost/Change-Out*	*Change-Out/Year*	*Yearly Cost*
New Resin	$6,354.00	3	$19,062.00	$6,354.00	0.5	$3,177.00	$6,354.00	3	$19,062.00	$6,354.00	0.5	$3,177.00
New Column	$3,000.00	3	$9,000.00	$3,000.00	0.5	$1,500.00	$3,000.00	3	$9,000.00	$3,000.00	0.5	$1,500.00
Resin Disposal	$0.00		$0.00	$1,337.18	0.5	$668.59	$9,350.00	3	$28,050.00	$60,000.00	0.5	$30,000.00
Labor - Changing	$4,160.00	3	$12,480.00	$4,160.00	0.5	$800.00	$4,160.00	3	$12,480.00	$4,160.00	0.5	$2,080.00
Labor - Paperwork	$0.00		$0.00	$1,600.00	0.5	$1,600.50	$1,600.00	3	$4,800.00	$1,600.00	0.5	$800.00
Resin Characterization	$3,000.00	1	$3,000.00	$500.00	0.5	$250.00	$2,000.00	3	$6,000.00	$500.00	0.5	$250.00
TOTAL ANNUAL COST:			**$43,542.00**			**$7,996.09**			**$79,392.00**			**$37,807.00**

Table 12. Scenario/Option Differences

	1	2	3	4
Cost Difference:	$21,480.00	$2,550.50	$32,280.00	$4,630.00
Percentage:	33.03%	24.18%	28.91%	10.91%

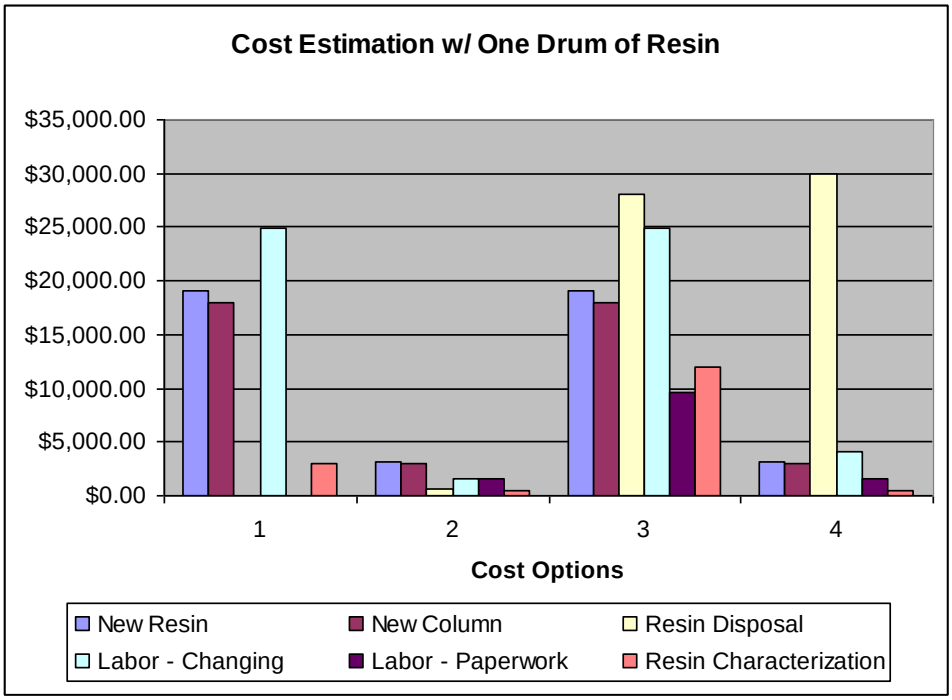

Figure 9. Scenario 1 expenditures.

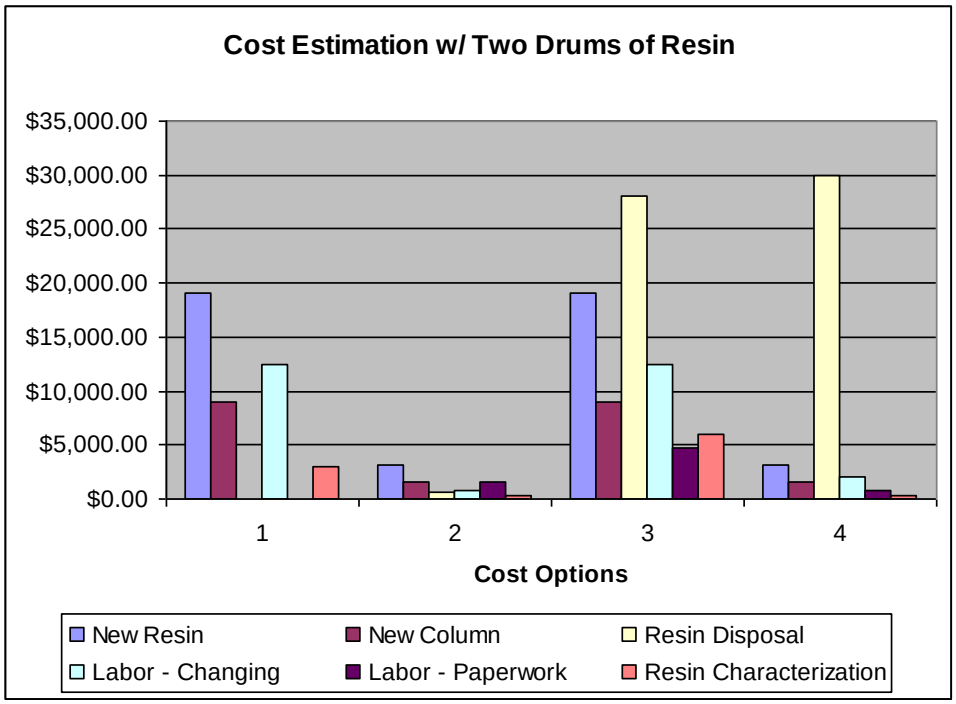

Figure 10. Scenario 2 expenditures.

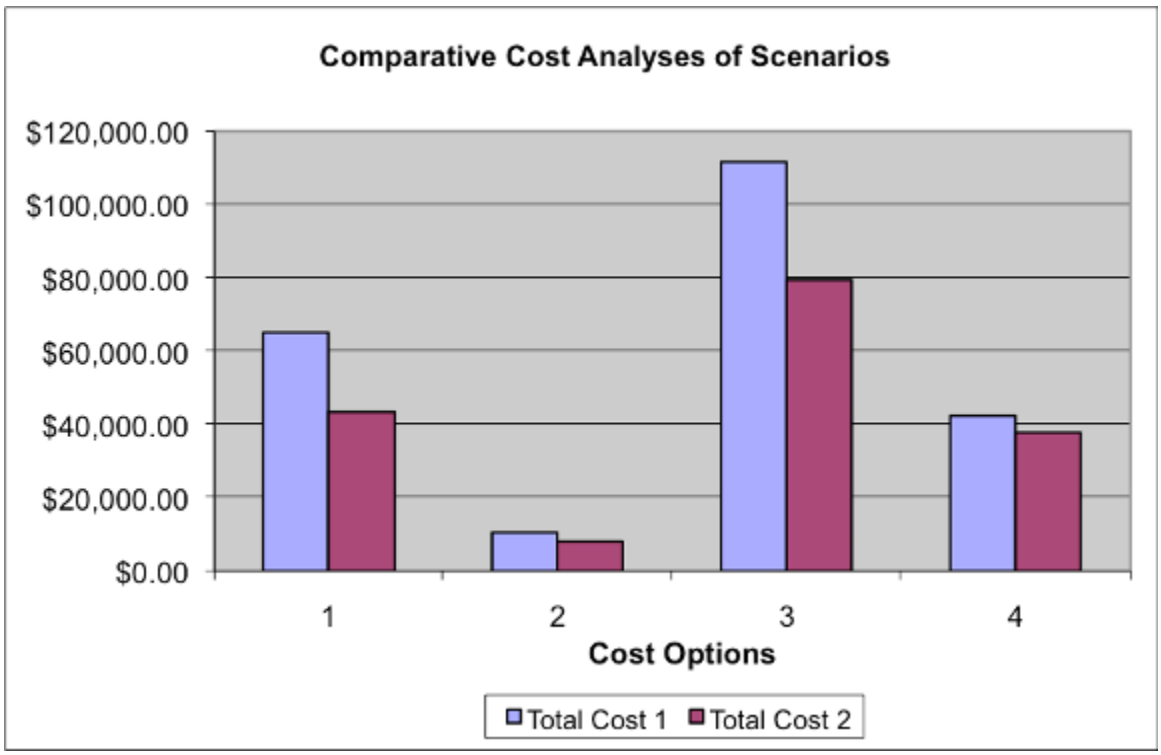

Figure 11. Comparison of both scenarios.

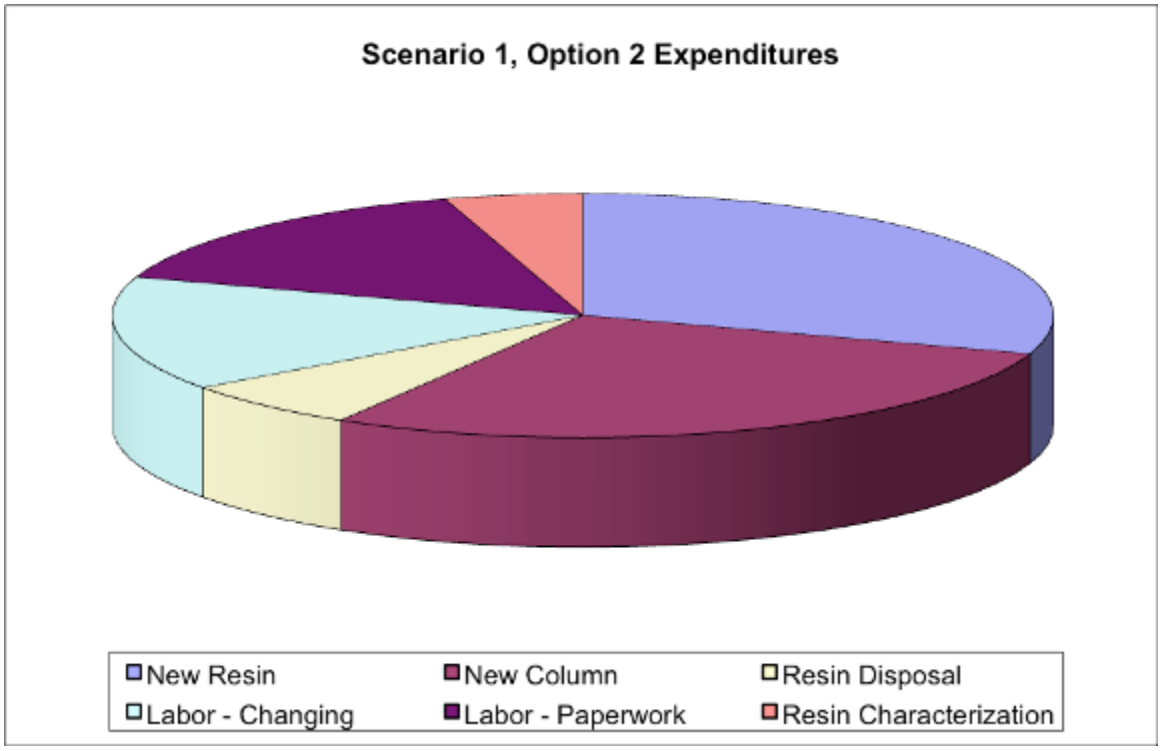

Figure 12. Expenditures of Scenario 1, Option 2.

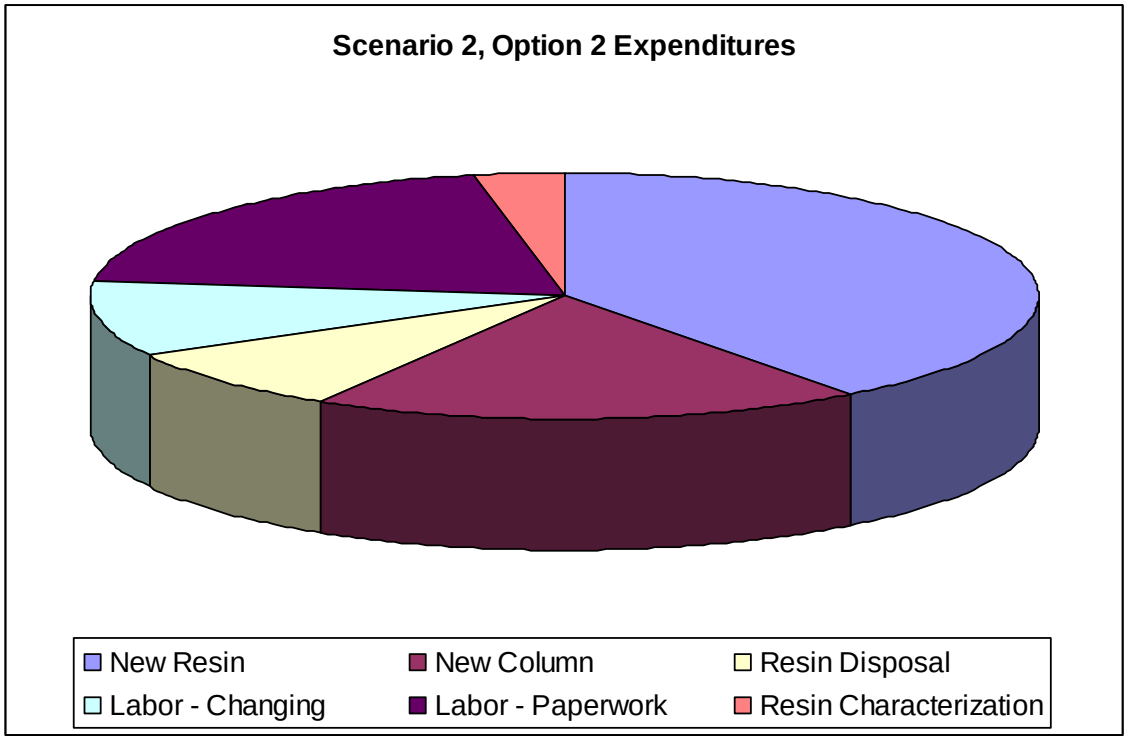

Figure 13. Expenditures of Scenario 2, Option 2.

5. CONCLUSION

The foremost purpose of this project 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. By utilizing this system, approximately 99% of the mercury sent to WOC from Building 4501, Sump I, will be eliminated, which represents 80% of the total identifiable mercury discharges at ORNL.

Without mercury removal efficiency, absorption characteristics, and radionuclide analysis results, disposal costs of spent resin can still be approximated with estimated variables utilized in various options. Mercury removal efficiency is estimated to be 99% based on previous research pertaining to similar resin. The average mercury concentration in Sump I effluent is 10 ppb from previous analysis. Mercury sorption capacity is assumed to be a modest 1.5 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 can't exceed 260 mg/kg and still be considered non-hazardous.

TCLP results shown in Table 9 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. As long as levels of radiological substances do not exceed NRA regulation, which shouldn't occur, scenario 2, option 2, as shown in Table 11 is a probable scenario and is considered the optimal choice in minimizing cost for the mercury treatment system.

6. REFERENCES

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APPENDIX A

Table 13. Measured Flow Rates of Lab-Scale Ion-Exchange Column

DATE & TIME	ELAPSED TIME (DAYS)	EFFLUENT (mL)	ACCUMULATIVE EFFLUENT (mL)	AVG FLOW (mLPD)	AVG FLOW (mLPM)
6/9/09 1:07 PM	0	0	0	NA	NA
6/10/09 8:25 AM	0.80	3,255	3,255	4,048	2.8109
6/11/09 12:10 PM	1.16	4,600	7,855	3,978	2.7628
6/12/09 9:17 AM	0.88	3,440	11,295	3,910	2.7151
6/15/09 9:12 AM	3.00	12,050	23,345	4,021	2.7926
6/16/09 12:55 PM	1.15	5,120	28,465	4,433	3.0788
6/17/09 2:07 PM	1.05	4,600	33,065	4,381	3.0423
6/18/09 11:21 AM	0.88	3,900	36,965	4,408	3.0612
6/19/09 3:02 PM	1.15	5,080	42,045	4,404	3.0584
6/22/09 10:41 AM	2.82	12,345	54,390	4,380	3.0414
6/23/09 9:10 AM	0.94	4,070	58,460	4,345	3.0170
6/24/09 9:17 AM	1.00	4,380	62,840	4,359	3.0270
6/25/09 9:17 AM	1.00	4,380	67,220	4,380	3.0417
6/26/09 10:45 AM	1.06	4,640	71,860	4,373	3.0366
6/29/09 9:21 AM	2.94	12,780	84,640	4,344	3.0170
6/30/09 3:45 PM	1.27	5,460	90,100	4,311	2.9934
7/1/09 10:35 AM	0.78	3,440	93,540	4,384	3.0442
7/6/09 10:04 AM	4.98	9,600	103,140	1,928	1.3391
7/7/09 9:15 AM	0.97	4,180	107,320	4,327	3.0050
7/8/09 8:29 AM	0.97	4,240	111,560	4,380	3.0416
7/9/09 8:40 AM	1.01	4,440	116,000	4,406	3.0600
7/10/09 9:40 AM	1.04	4,600	120,600	4,416	3.0667
7/13/09 9:18 AM	2.98	13,160	133,760	4,409	3.0619
7/14/09 4:24 PM	1.30	5,700	139,460	4,399	3.0547
7/15/09 11:00 AM	0.78	3,420	142,880	4,413	3.0645
7/16/09 3:31 PM	1.19	5,260	148,140	4,427	3.0742
7/17/09 9:15 AM	0.74	3,280	151,420	4,439	3.0827
AVG OR TOTAL	**37.84**	**151,420**	**151,420**	**4,002**	**2.8**

APPENDIX B

Table 14. Collected Samples from Column and Batch Experiments

Date and Time	*Type*	*ID*	*NHO_3 Added*	*Analysis*	*Sent*	*Date Sent*
6/10/09 8:25 AM	Influent	SumpI-In-6-10	2 mL	FIU	Yes	6/15/2009
6/10/09 8:25 AM	Effluent	SumpI-Out-6-10	2 mL	FIU	Yes	6/15/2009
6/15/09 9:12 AM	Influent	SumpI-In-6-15	2 mL	FIU	Yes	6/15/2009
6/15/09 9:12 AM	Effluent	SumpI-Out-6-15	2 mL	FIU	Yes	6/15/2009
6/19/09 3:02 PM	Influent	SumpI-In-6-19	2 mL	FIU	Yes	6/23/2009
6/19/09 3:02 PM	Effluent	SumpI-Out-6-19	2 mL	FIU	Yes	6/23/2009
6/23/09 9:10 AM	Influent	SumpI-In-6-23	2 mL	FIU	Yes	6/23/2009
6/23/09 9:10 AM	Effluent	SumpI-Out-6-23	2 mL	FIU	Yes	6/23/2009
6/26/09 10:45 AM	Influent	SumpI-In-6-26	2 mL	FIU	Yes	6/29/2009
6/26/09 10:45 AM	Effluent	SumpI-Out-6-26	2 mL	FIU	Yes	6/29/2009
6/29/09 9:21 AM	Influent	SumpI-In-6-29	2 mL	FIU	Yes	6/29/2009
6/29/09 9:21 AM	Effluent	SumpI-Out-6-29	2 mL	FIU	Yes	6/29/2009
7/6/09 10:04 AM	Influent	SumpI-In-7-6	2 mL	FIU	Yes	7/13/2009
7/6/09 10:04 AM	Effluent	SumpI-Out-7-6	2 mL	FIU	Yes	7/13/2009
7/10/09 9:40 AM	Influent	SumpI-In-7-10	2 mL	FIU	Yes	7/13/2009
7/10/09 9:40 AM	Effluent	SumpI-Out-7-10	2 mL	FIU	Yes	7/13/2009
7/13/09 9:18 AM	Influent	SumpI-In-7-13	2 mL	FIU	Yes	7/13/2009
7/13/09 9:18 AM	Effluent	SumpI-Out-7-13	2 mL	FIU	Yes	7/13/2009
7/17/09 9:47 AM	Influent	SumpI-In-7-17	2 mL	FIU	Yes	7/21/2009
7/17/09 9:47 AM	Effluent	SumpI-Out-7-17	2 mL	FIU	Yes	7/21/2009
7/17/09 9:47 AM	Batch	Batch1-7-17	2 mL	FIU	Yes	7/21/2009
7/18/09 9:47 AM	Batch	Batch2-7-17	2 mL	FIU	Yes	7/21/2009
7/19/09 9:47 AM	Batch	Batch3-7-17	2 mL	FIU	Yes	7/21/2009
7/20/09 9:47 AM	Batch	Batch4-7-17	2 mL	FIU	Yes	7/21/2009
7/21/09 9:47 AM	Batch	Batch5-7-17	2 mL	FIU	Yes	7/21/2009
7/22/09 9:47 AM	Batch	Batch6-7-17	2 mL	FIU	Yes	7/21/2009
7/23/09 9:47 AM	Batch	Batch7-7-17	2 mL	FIU	Yes	7/21/2009
7/24/09 9:47 AM	Batch	Batch8-7-17	2 mL	FIU	Yes	7/21/2009
7/25/09 9:47 AM	Batch	Batch9-7-17	2 mL	FIU	Yes	7/21/2009
7/26/09 9:47 AM	Batch	Batch10-7-17	2 mL	FIU	Yes	7/21/2009
7/27/09 9:47 AM	Batch	Batch11-7-17	2 mL	FIU	Yes	7/21/2009
7/28/09 9:47 AM	Batch	Batch12-7-17	2 mL	FIU	Yes	7/21/2009