

RECOVERY OF MERCURY FROM CONTAMINATED PRIMARY AND SECONDARY WASTES

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Abstract

ADA is developing a novel process for removing and recovering mercury from contaminated groundwater and aqueous wastes at DOE sites. The technology will apply to the mercury-contaminated groundwater, primary liquid wastes in DOE's inventory, and the mercury-contaminated secondary liquid wastes that will result from cleanup as well as decontamination and decommissioning activities. This process is also suitable for treating industrial mercury-contaminated water, such as that generated by dental clinics and chlor-alkali plants.

ADA's process is based on the highly efficient sorption of mercury by noble metals. Contaminated liquid flows through a packed bed that contains microporous sorbent particles on which a noble metal has been finely dispersed. When the sorbent is loaded with mercury to the point of breakthrough, the flow of contaminated liquid is switched to a fresh sorbent bed. The spent bed is regenerated by heating, first to drive off residual water and then to drive off the mercury. A small flow of purge gas carries the desorbed mercury to a mercury recovery unit. The end result is mercury suitable for recycle for commercial use (if not radioactive) or for disposal (if radioactive). The regenerated sorbent is then returned to the sorption process with no loss in sorption efficiency.

In bench-scale tests using mercuric chloride in water at concentrations between 0.5 mg/l to 50 mg/l, ADA has demonstrated three key components that are needed for a practical, regenerable sorption process for removing and recovering dissolved mercury from liquid streams: 1) sorbents have been found that have a high capacity for dissolved, ionic mercury, 2) ionic mercury is removed at greater than 99% efficiency, and 3) the spent sorbent is thermally regenerable.

Laboratory tests and field tests using water from the East Fork Poplar Creek in the Y-12 weapons plant at Oak Ridge, TN, show that the ADA sorbent reduces the mercury concentration in the water from 1000 nanograms per liter (part per trillion or ppt) to less than 1 ppt. The field test unit uses two columns in series, each four inches in diameter and two feet long. This field test will continue through several cycles of sorption and regeneration to allow development of life-cycle costs for the treatment system. Future efforts will also include the development of sorbents capable of removing mercury at flow rates higher than those used in standard water treatment facilities.

Introduction

ADA is developing a novel mercury capture technology that involves a highly efficient, regenerable sorbent. The main attributes of this process are mercury **re**moval, mercury **re**covery, sorbent **re**generation, and sorbent **re**-use, and as a consequence, ADA has adopted the name “Mercur-RE” to describe the process. The Mercur-RE process has the following advantages:

- Mercury removal efficiencies in liquids exceeding 99.9%, including both oxidized and elemental mercury,**
- Mercury removal to one ppt in DOE wastewater field tests,**
- Elimination of mercury-contaminated solid or liquid secondary wastes in the cleanup process, and**
- Removal of mercury from the biosystem.**

The promise of the Mercur-RE process to meet the needs of a range of applications, such as removal of mercury from groundwater, industrial wastewater, and decontamination and decommissioning process water, derives from its ability to capture all common forms of mercury and from the variety of physical configurations in which the technology can be deployed.

Program Objective

The objective of the program described in this paper is to develop and demonstrate a novel process for recovering mercury from contaminated primary and secondary liquid wastes found and expected to be generated in the DOE complex. The technology will treat mercury-contaminated groundwater at DOE sites, primary liquid wastes already in DOE’s inventory, and mercury-contaminated secondary liquid wastes that will result from many of the processes and activities planned for treating the mercury-contaminated solids, soils, debris, and aqueous wastes in DOE’s inventory.

The goal at the end of the program is to have demonstrated, to the satisfaction of the DOE end user, an operating unit on a mercury-containing liquid stream at a DOE site. Based on our previous work, the program began at the Advanced Development stage (Stage 4) and will proceed through Engineering Development (Stage 5) and Demonstration (Stage 6). The Stage 4 work under the Base Contract emphasized the manufacturing and testing of kilogram batches of superior sorbent, devising regeneration operating conditions, modeling the sorption and regeneration process, and testing a small sorption unit operation at a field site. The Stage 5 effort will involve the development of high mass transfer sorbent configurations, devising scale-up rules for both the sorption and regeneration processes and applying these scale-up rules to field prototype units. A small field sorption unit is currently being tested at a DOE site, and scale-up of this unit is anticipated. In Stage 6, the experience and know-how gained in the previous stages will allow the design and operation of a complete sorption/regeneration unit at a selected DOE site.

Technical Approach

ADA's process is based on the highly efficient sorption of mercury on a specialty sorbent. Contaminated liquid flows through a packed bed that contains the microporous sorbent particles. When the sorbent is loaded with mercury to the point of breakthrough, the flow of contaminated liquid is switched to a fresh sorbent bed. The spent bed is regenerated by heating, first to drive off residual water and then to drive off the mercury. A small flow of purge gas carries the desorbed mercury to a mercury recovery unit.

Project Description

There are two subcontractors associated with the project: the University of North Dakota, Energy and Environmental Research Center (EERC) and the Oak Ridge National Laboratory (ORNL). ADA Technologies was responsible for synthesizing reproducible sorbents, testing these sorbents, developing sorption/regeneration models, and developing an efficient mercury collector for use during regeneration. The last two tasks were accomplished with the aid of EERC. EERC was responsible for much of the process development on surrogate wastes, as well as the fabrication and operation of the field unit. ORNL tested the three best sorbents on various DOE wastes, and supported operation of the field test unit.

This project consisted of three tasks:

- Task 1 – Produce Pilot Scale Quantities of Sorbent
- Task 2 – Develop Regeneration Methods
- Task 3 – Integrate Sorption and Regeneration Units

The following paragraphs explain the objectives and results of each of these tasks.

Results

Task 1. Produce Pilot Scale Quantities of Sorbent

The main objective of this task was to develop the ability to routinely and inexpensively make kilogram quantities of sorbent with favorable properties. Small batches of sorbent were first tested using mercuric chloride in water, then the three best were tested using a surrogate waste. The best sorbent from the surrogate testing was then tested on actual DOE wastewater. Finally, large (10-kg) batches of sorbent were made with the same sorption properties.

The equilibrium sorption capacity of sorbents were measured using mercuric chloride in distilled water. Ten solutions ranging from 0.5 mg/l to 50 mg/l at equilibrium were used in the isotherm tests. Reproducible sorption behavior from batch-to-batch was considered the key test for satisfactory synthesis of the sorbents. We also measured the size of the noble metal crystallites in

the sorbent, via x-ray diffraction line broadening. All of the duplicate batches of sorbent prepared at ADA showed reproducible crystallite sizes and reproducible sorption behavior using mercuric chloride in water.

Many of the isotherm tests were performed at high mercury concentrations in anticipation of treating highly mercury-contaminated wastes. Additional data were required at the ultra-low concentrations in order to treat Outfall 200 wastewater at the Y-12 plant at Oak Ridge, TN. The sorbents tested at the low concentrations were C-N-X, C-E100-Alpha1 and C-E33-Beta5. Dr. Ralph Turner of Frontier Geosciences (Seattle, WA) performed a set of isotherms using a surrogate of the Non-Radioactive Wastewater Treatment Plant (NRWTP) waters. In these tests, the resulting solution concentration was 0.49 ppt in one sample for sorbent C-N-X. The final solution concentration for sorbent C-E33-Beta5 was 8-15 ppt. One data point out of four samples was high (81 ppt), and may have been caused by contamination of the sample. **The final concentrations for sorbent C-E100-Alpha1 were 0.47 and 0.49 ppt.**

The mercury sorption capabilities were very similar for the three sorbents tested using surrogate Outfall 200 wastewater (C-E100-Alpha1, C-E33-Beta5 and C-N-X). All three were capable of removing >99.9% of the mercury present in the surrogate wastewater. All three sorbents removed mercury to below 1 ppt when five grams of sorbent were used to treat 100 ml of water. All three sorbents removed mercury to below 12 ppt at 0.5 g sorbent. **Only C-E100-Alpha1 removed mercury below 12 ppt at 0.05 g sorbent.** Figure 1 shows the isotherm results for mercuric chloride in distilled water and surrogate water using sorbent C-E100-Alpha1. This figure shows the loading of mercury on the sorbent as related to concentration.

Isotherm tests using sorbent C-E100-Alpha1 on Outfall 200 wastewater were performed in July, 1997. These tests were performed by ORNL personnel, and the samples were analyzed at Frontier Geosciences. **Four samples showed equilibrium levels of mercury below 4 ppt, one of which was at 0.24 ppt.** The duplicates and spiked samples showed quantitative recoveries, indicating that the series of tests was representative and accurate. Figure 2 shows the results of all the isotherm tests for sorbent C-E100-Alpha1 in terms of the distribution coefficient (the ratio of the mass loading on the sorbent to the concentration of mercury in the solution at equilibrium).

Four 10 kg batches of sorbent were synthesized at ADA and analyzed with XRD. These were batches C-N-Beta1-B1, C-N-Beta1-B2, C-N-Beta1-B3 and C-E100-Alpha1. The three Beta1 sorbents had crystallite diameters of 33.0, 33.3 and 33.9 nm. These results are well within the 25% variation and the 60 nm upper limit desired. The Alpha1 batch had a crystallite diameter of 17.6 nm, which is very close to the 1 kg batches (23.7 and 15.9 nm). The three 10 kg batches of Beta1 sorbent also showed excellent reproducibility in the isotherm tests. These results show that the 10 kg sorbent batches had reproducible physical and sorption properties.

The conclusions from the laboratory tests in Task 1 are the following: at least one ADA sorbent removes mercury to 1 ppt in actual wastewater; there is very little difference in sorption behavior between HgCl_2 in water, surrogate waste and actual waste; the noble metal crystallite sizes are small; and 10 kg batches can be manufactured reproducibly.

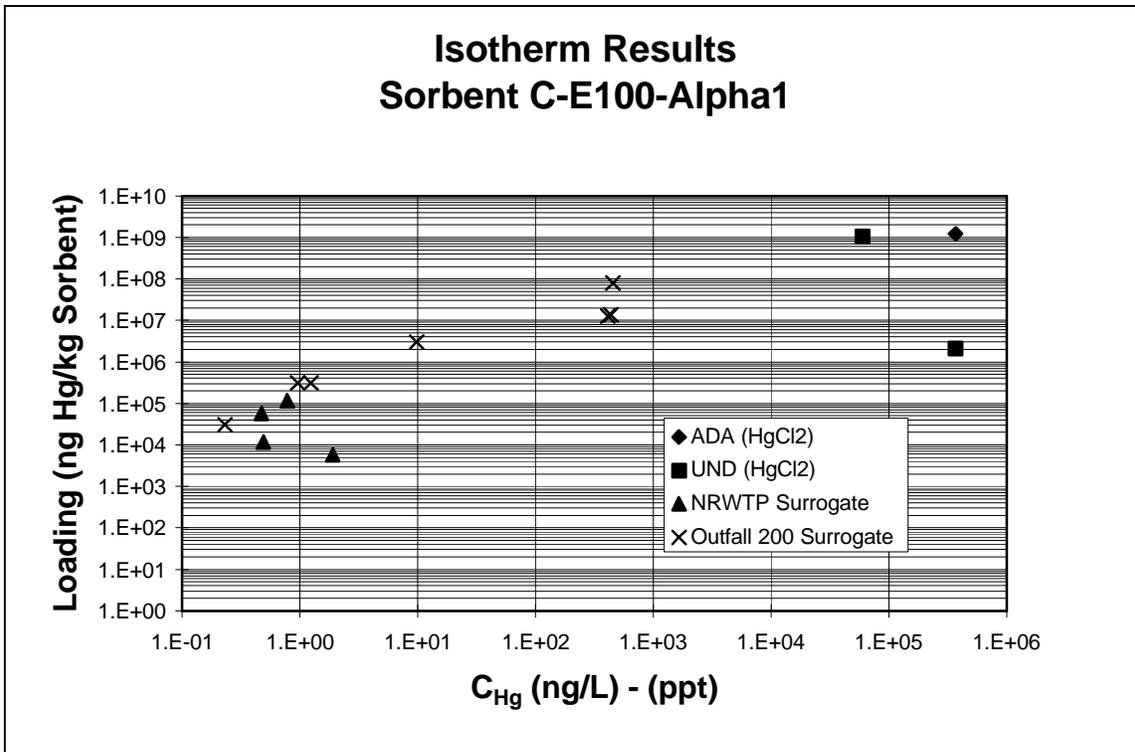


Figure 1. Isotherm Results using C-E100-Alpha1

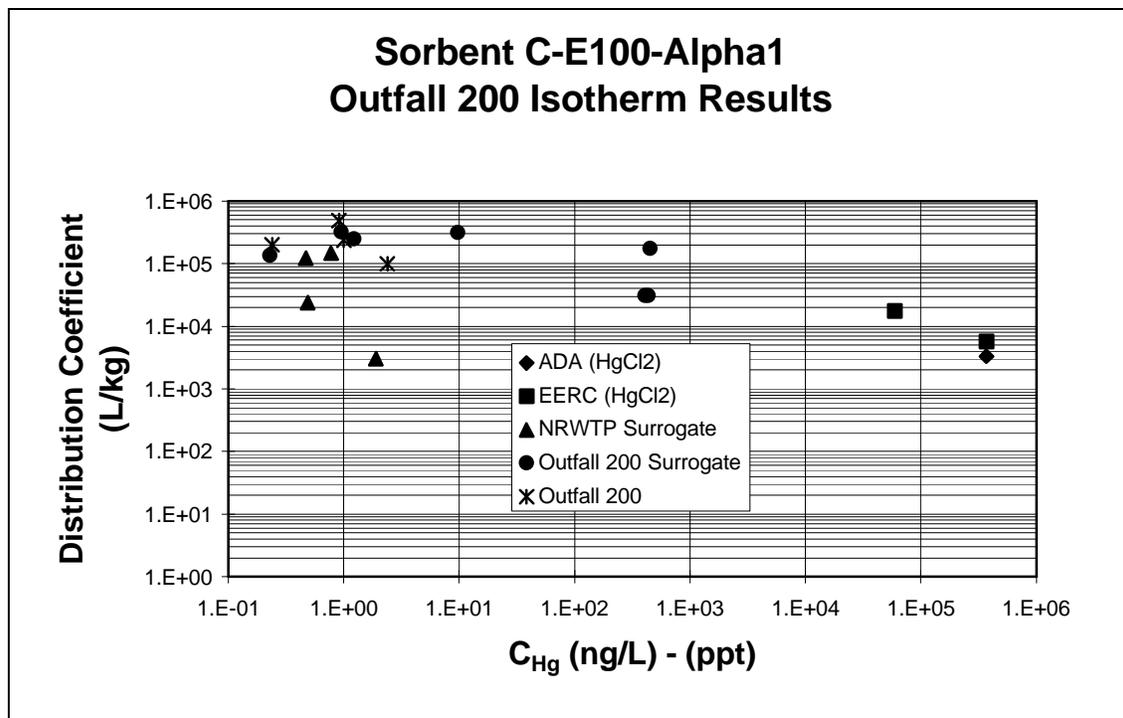


Figure 2. Isotherm Results Including Actual Wastewater

Task 2. Develop Regeneration Methods

The objective of this task was to devise practical methods to regenerate the sorbents. Specific objectives included determining time and temperature required to remove water and mercury from sorbents and methods for capturing the mercury evolved during regeneration.

Packed-bed desorption studies were performed at both ADA and UND-EERC on sorbent loaded with mercuric chloride. In the ADA studies, a small amount of purge gas flowed through the bed during desorption. The mercury concentration in this purge gas was monitored with ADA's mercury analyzer (Durham, et al., 1997) so that we could determine the time required for complete desorption. In the UND-EERC studies, the sorbent was heated for a specified time at a specified temperature, then analyzed for residual mercury.

Eight regeneration tests were performed at ADA on two different sorbents (C-E100-Alpha1 and A-BVI-Alpha1). In these tests, three samples of each sorbent were weighed, placed in a 10,000 µg/l solution of mercuric chloride, and placed on a shaker table for 24 hours (standard isotherm procedure). The samples were filtered, and the solution was submitted for mercury analysis. The sorbent was packed in a quartz tube which was placed in a tube furnace. Dry nitrogen was passed through the bed of sorbent as the temperature in the furnace was increased to 370°C. The mercury concentration in this purge gas was monitored to determine when all of the mercury was removed.

After regeneration, the sorbent was weighed again and placed in another 100 ml of mercuric chloride solution. This procedure was repeated four times. Sorbent C-E100-Alpha1 was regenerated at 370°C, and required at least 48 hours for complete desorption. Sorbent A-BVI-Alpha1 was regenerated at 550°C, and even at these elevated temperatures, 96 hours were required for complete removal of the sorbed mercury.

The isotherm results for before and after the regenerations are shown in Figure 3. The sorbent C-E100-Alpha 1 performed very well after each regeneration (99.9% uptake). Sorbent A-BVI-Alpha1 performed well before regeneration (99.99% uptake) but deteriorated after the first regeneration.

Regeneration tests were also performed at UND-EERC on sorbent C-E100-Alpha1. These tests showed that complete mercury removal occurs between 26 and 52 hours at 370°C, which compares favorably with the ADA desorption time of 48 hours.

The conclusions from the laboratory tests in Task 2 are: 1) sorbent C-E100-Alpha1 shows the same sorption behavior after four regeneration cycles, and 2) the desorption time for this sorbent is on the order of 48 hours.

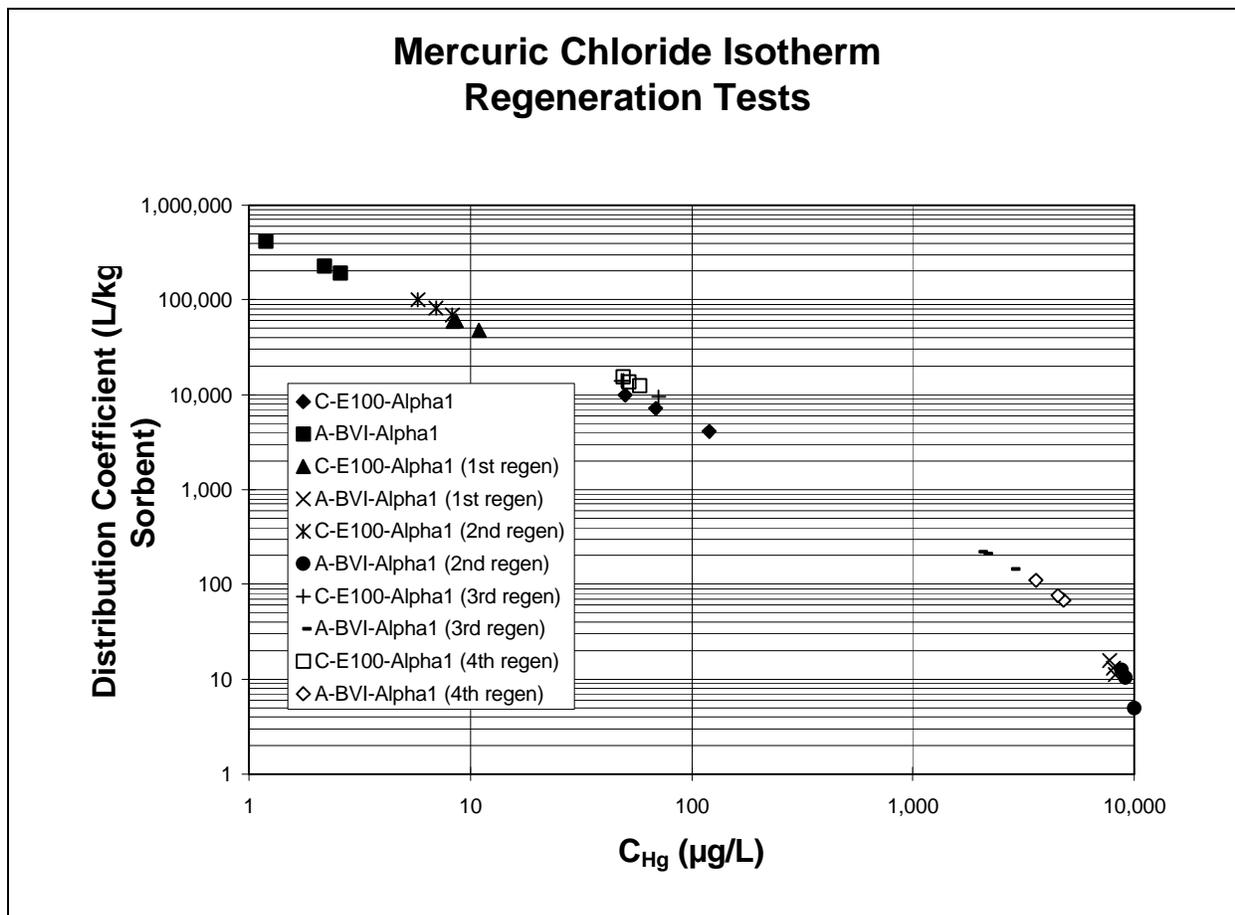


Figure 3. Isotherm Results from Regeneration Tests

Task 3. Integrate Sorption and Regeneration Units

The objectives of this task were to 1) install and test a small field sorption unit, with regeneration capabilities, at Outfall 200 in the Y-12 plant at Oak Ridge, TN, and 2) to develop models for the sorption and regeneration processes.

The design for the field-scale sorption-regeneration unit was developed by UND-EERC. The field unit consists of three beds of sorbent. Two beds are used in series at all times, and the third bed is held in reserve or undergoing regeneration. The sorbent columns are 28-inch long stainless steel tubes with a 4-inch inner diameter. The sorbent bed depth is 24 inches. A diaphragm pump draws the water from the stream, through a one-micron filter, and into the sorption unit. The flow of water is upwards through the sorbent beds. The valve configuration allows the operator to switch the flow of liquid through different beds. When the first column shows breakthrough of mercury above acceptable levels, the flow is switched so that the second and third columns treat the water while the first column is being regenerated.

During September, 1997, the field sorption unit was transported to Y-12 in Oak Ridge, TN, and all connections made. After we leak-checked the system on September 4, water was allowed to flow through the empty columns overnight. Samples were taken on September 5 at multiple points to determine if mercury was being sorbed by the walls of the columns and tubing. No losses were found. Next, two kilograms of sorbent were added to each of the three columns. The vessels were filled with water, and the sorbent was allowed to degas over the weekend.

The flow of Outfall 200 water through the columns began on September 8 at 8 am. The flow rate was 500 cc/minute (six bed volumes per hour). Samples were taken every day for the first week then every other day the second week. Twice-weekly sampling began in the third week. An increase in concentration at 2500 bed volumes was probably caused by heavy rainfall in the previous two days; a surge in creek and outfall mercury concentrations after rain events has been documented in previous work at Y-12. The system recovered from this mercury surge.

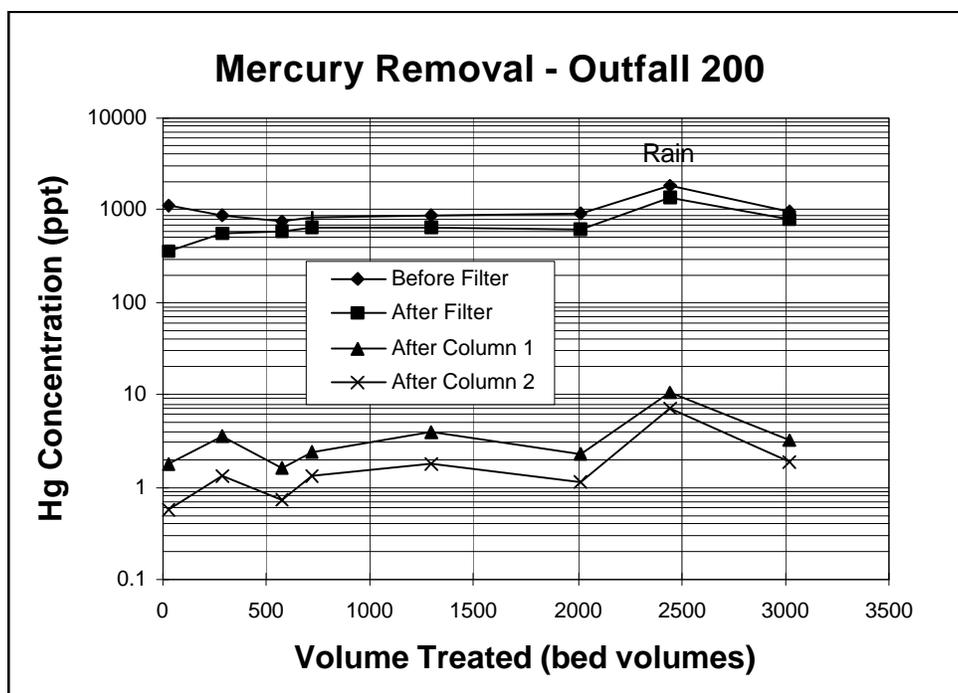


Figure 4. Results from Field Test at Outfall 200

Regeneration of the mercury-containing columns will be performed at a regeneration station. This station could be placed on the same platform as the three-column field test unit, but considering the electrical requirements and the infrequency of regeneration, the regeneration unit will initially be placed in a laboratory at ORNL. The mercury-containing column will be wrapped in heat tape and preheated air will be sent through the sorbent bed. The starting temperature for regeneration will be 105°C to drive off the water. This water will be captured in a condenser and sent through a sorbent bed to remove any vaporized mercury which was transported with the water. After drying of the sorbent in the column, the temperature will be increased to a maximum of 370°C and the gas sent through a mercury capture unit. The captured mercury will be disposed of by ORNL.

ADA is currently investigating sorption and regeneration models for the treatment system. These models will aid in predicting breakthrough in the field tests and will aid in scale-up of the system.

Two models are being investigated. One of these is an early mechanistic model proposed by Hougen and Marshall (1947). This model assumes a linear isotherm where mass transfer through the fluid phase is the controlling factor. An analytical solution to the applicable differential equations is available for an initially clean bed and for constant flow into the bed. The second model being investigated (Rosen, 1952, 1954) considers the diffusion of the solute within the sorbent particle pores along with the fluid film resistance around the sorbent particle. A linear isotherm is used to describe the equilibrium between the liquid and solid phases. An analytical expression is possible under certain conditions.

We applied these models to the conditions of the Y-12 field test wherein we have two two-foot-long vessels in series each four inches in diameter and flowing 500 cc/min of water (six bed volumes per hour in each bed). Figure 5 gives the results of the Rosen model (the more realistic of the two models) using a inlet concentration of 1000 ppt and a breakthrough concentration of 10 ppt. The Rosen model predicts that regeneration of the first column will be required at about 100 days (7200 bed volumes) from the start of the field test. At this time, the outlet concentration of mercury from the second column should reach 10 ppt.

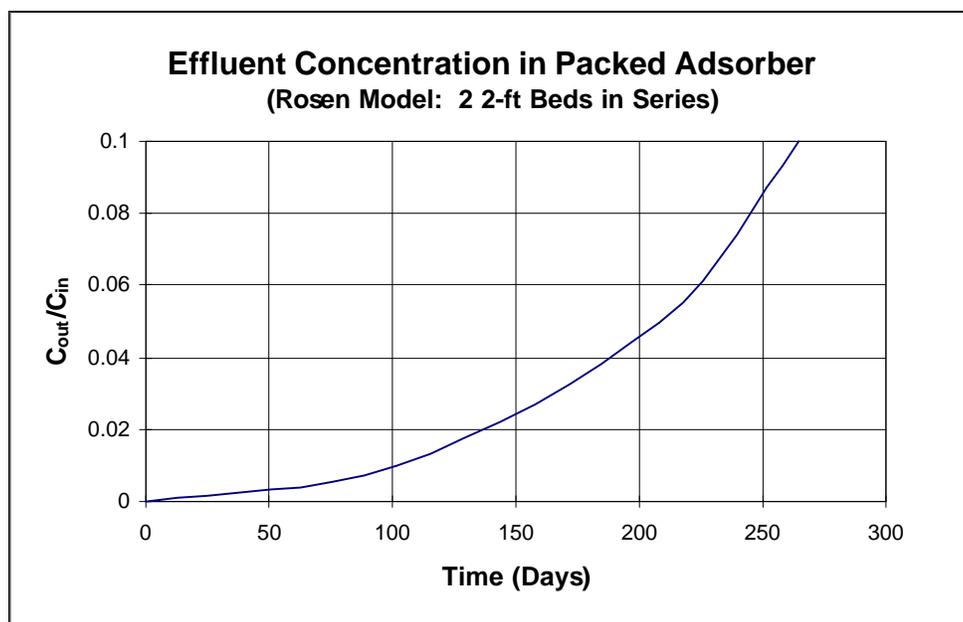


Figure 5. Predicted Breakthrough Time for Outfall 200 Test Skid

Application

ADA's regenerable sorbent performs well at both high and ultra-low mercury concentrations. For that reason, the sorption process should be applicable to a wide range of contaminated aqueous waste streams including creek water, such as at the Y-12 plant, scrubber liquor generated during

the scrubbing of mercury-containing off-gas, and D&D wash solutions used to wash mercury-contaminated equipment. The sorption process has been proven on a small scale in the field using Outfall 200 wastewater, achieving very low (1-2 ppt) treatment levels. Recovery of the mercury from the sorbent for subsequent disposal and the re-use of the sorbent are especially attractive features in situations where the mercury is considered radioactive.

Future Activities

The field test at Outfall 200 is scheduled to continue operation through the end of September, 1998. During this time, breakthrough curves will be determined on actual creek water, and several regenerations should be accomplished. Because of the low levels of mercury required in the East Fork Poplar Creek, it will be important to achieve increased mass transfer rates for economical application of the sorbent. This work has been proposed for further funding so that the Y-12 plant can meet its restriction of 12 ppt discharge from the East Fork Poplar Creek by the year 2000.

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