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**Development of Ultrafiltration
and Inorganic Adsorbents:
January-March 1977**

John W. Koenst, Jr.

June 24, 1977

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Miamisburg, Ohio
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Abstract

Ultrafiltration media with and without the assistance of bone char filters were evaluated to determine their effectiveness in removing radionuclides from contaminated solutions. Precipitants, resin, adsorbents, and inorganic adsorbents were studied to determine their effectiveness in decontaminating solutions. A study of the effects of radiation on ultrafiltration media was initiated. An ultrafiltration media pilot plant was ordered and is being installed.

Introduction

The objective of this program is to develop and demonstrate separation methods for removing radionuclides from liquid process waste streams. As part of this program, Mound Laboratory will develop lower cost alternatives for use in the nuclear processing industry; evaluate the processes within the nuclear fuel cycle which contribute to low-level and intermediate-level waste; and determine the feasibility of ultrafiltration, reverse osmosis, inorganic adsorbents, and other separation concepts as additions to process design to reduce the generation of this type of waste. In the initial phase of this program, a membrane pilot plant will be purchased from a commercial membrane manufacturer. After the pilot plant is installed, it will be checked out on nonradioactive feed in order to obtain initial flux and rejection data for comparison to data obtained later in the program. After completion of the nonradioactive tests, the membrane pilot plant will be tested on combined radioactively contaminated feed emanating from showers, laboratory drains, janitorial sinks, and decontamination solutions, as well as a laundry waste stream containing alpha-contaminated wastes. These combined waste streams contain only alpha contamination (U and

Pu). However, as part of this program, gamma activity will be added to the waste stream. These wastes will be representative of those streams found at fuel re-processing plants, as well as various ERDA processing facilities such as Mound, LASL, Hanford, and Rocky Flats.

For the second part of the program, various adsorbents will be tested to evaluate their respective capacities for removing radionuclides. As part of this program a technique for screening adsorbents developed at Mound Laboratory will be used.

Concurrently, a column system has been designed and is being built to test the several promising adsorbents chosen from the laboratory tests. The engineering tests will determine various design parameters (i.e., loading rates, bed capacity, throughput rates, residence times, feed velocity, and bed height). At the conclusion of this part of the program, data from the several most promising adsorbents will be utilized to design a pilot plant. Mound Laboratory will work closely with industry and other ERDA facilities in the definition of typical waste compositions and the final process design.

Work Accomplished

Bench scale experiments using hollow fiber ultrafiltration (U.F.) modules were continued [1]. Caustic waste containing high concentrations of plutonium was run through U.F. modules after it had been passed through bone char columns. The solution had an initial concentration of approximately 10^7 dis/min/ml. After bone char treatment, activity concentrations were about 2600 dis/min/ml. This solution was then passed through a PM-5 hollow fiber U.F. module where the activity was further reduced to about 560 dis/min/ml.

An experiment was also conducted using influent to the Mound Laboratory Waste Disposal Facility as the feed. The activity of the raw influent (1890 dis/min/ml), after passing through a PM-5 module, was lowered to 7.3 dis/min/ml. The addition of 250 ppm $\text{Al}_2(\text{SO}_4)_3$ further reduced the activity to 2.1 dis/min/ml; however, the resultant precipitate plugged the pores in the membrane surface.

Addition of a polyelectrolyte, after addition of $\text{Al}_2(\text{SO}_4)_3$, only added to the plugging problem.

Test runs were made on incinerator scrubber solution using an AM-2 hollow fiber U.F. membrane. The initial feed contained 14 dis/min/ml of gross alpha, and the U.F. membrane was not effective in reducing this appreciably. However, when scrubber solution containing 25.8 dis/min/ml gross alpha was passed through a small bone char column, this activity count was reduced to 1.0 dis/min/ml. The color of the product was much lighter than the color of the feed, indicating removal of some organics. The results of these preliminary tests would indicate that bone char has more promise for the decontamination of incinerator scrubber solutions.

During the past three months, regular analyses have been conducted on the incinerator scrubber solution to keep abreast of changes in activity levels, suspended

solids, dissolved solids, carbonate, pH, and conductivity. During this period, gross alpha concentration has gone from near zero to a peak of 75 dis/min/ml and then fluctuated daily between about 3 to 50 dis/min/ml. Suspended solids have remained less than 10 ppm throughout this period. Dissolved solids have increased steadily from ~30 g/l on January 6, 1977, to nearly 200 g/l on March 31, 1977. Conductivity has also increased steadily from about 30 millimhos on January 6, 1977, to the upper limit of our detector (100 millimhos) by mid-February.

The pH is adjusted, when needed, by addition of sodium carbonate and is generally kept in the range of 8 to 9, while the carbonate concentration is generally kept between 5 and 15 g/l.

Membrane radiation tests are being conducted by Walden Research on membranes evaluated at Mound using the MITR-II, 5-MW research reactor at M.I.T. The test solute for characterizing membrane rejection consists of Carbowax 6000, a polyethylene glycol manufactured by Union Carbide. This carbowax has an average molecular weight of 6000. The flux and rejection of Abcor type HFD and HFM membranes is being measured on a 10% solution of Carbowax 6000. The membrane samples (less control samples) are then exposed to varying levels of β and γ radiation at the M.I.T. research reactor. After irradiation, the membranes are retested to measure any apparent degradation in membrane flux or rejection. Also, degradation of membrane mechanical properties is being assessed by measuring changes, if any, in membrane tensile strength and elongation characteristics. This task is expected to be completed by the end of the third quarter.

One sample membrane disc has been taken through the normal pre-irradiation test procedures and has been left at M.I.T. for irradiation. This preliminary radiation experiment will determine whether any constituents, introduced during handling or present in the test solute, have long half-lives which could delay subsequent membrane handling. There are no elements in the membranes themselves which should prove troublesome in this regard.

A project review meeting was held at Abcor on February 15, 1977. The final equipment and flowsheet drawings of the U.F. pilot system were presented and the physical dimensions, modes of operation, and major components of the system were discussed and approved. Blueprints of

the electrical circuits were tentatively approved at this meeting and formally approved on February 22. The anticipated shipping date of the pilot plant remains April 18. However, up to a one-week delay in system shipment may occur if any unforeseen difficulties in system assembly should develop. All system components have been purchased and received. The system frame has been assembled and piping and electrical work are in progress. (See Figure 1 for photographs of the U.F. system.

Small laboratory columns (0.7 cm I.D.) containing approximately 6 cm of resin (Figure 2) were tested with solutions containing uranium-233(VI), plutonium-238(IV) and plutonium-238(VI). The three resins (XN1010, 200, and MSC) chosen for these tests were based on Kd values obtained in batch tests at pH's of 4, 7, and 10. Breakthrough and loading rates for the resins were determined for the uranium and plutonium isotopes. At pH 7, the three resins have adsorbed 4.5×10^8 dis/min/g of uranium-233, to date. For plutonium-238(IV) and for plutonium-238(VI), the resins have adsorbed 1.7×10^8 dis/min/g, to date. The feed for both uranium-238 and plutonium-238(IV) and (VI) was held at 20,000 dis/min/ml and a feed rate of 2 ml/min. The velocities for the uranium and plutonium tests were kept the same; however, the residence times varied by a factor of 2 (uranium had the larger residence time). The latest decontamination factors (DF) to date, for adsorbents MSC and XN1010 are 200 for uranium-233. Using the resin Amberlite 200, the latest DF was 108. With plutonium-238(IV), the DF was 50, and with plutonium-238(VI), the DF was 100.

A similar system of small columns was set up at the Waste Disposal Facility to test adsorbents with an actual waste stream (see Figure 3). Waste solution was taken from the incoming liquid waste storage tank prior to any chemical treatment. This was filtered through a 1 μ m filter. This solution from different areas of Mound Laboratory contains plutonium-238 with small amounts of uranium and thorium. The gross alpha concentration for the waste stream averaged 800 dis/min/ml. Plutonium-238(IV) is being added to this waste stream to increase the alpha activity to 20,000 dis/min/ml.

Batch tests were started on three inorganic adsorbents: ammonium molybdophosphate, zirconium phosphate, and titanium phosphate (see Figure 4). These tests are not complete at this time; however titanium phosphate appears to be the most promising

of the three adsorbents over the whole pH range. The equilibrium distribution coefficient (Kd) for titanium phosphate is approximately 700, using plutonium-238

(VI), 10^3 for uranium-233, and 20 for polymeric plutonium-238(IV). Isotherms will be completed on all three adsorbents by next quarter.

Conclusions

Bench scale tests using hollow fiber ultrafiltration modules were continued. Caustic waste containing high concentrations of plutonium were processed following a treatment with an adsorbent column.

The large-scale pilot plant is scheduled to be shipped April 18, 1977. Delivery is expected one week later. Final installation at Mound Laboratory is expected to be completed May 8, 1977.

Membrane radiation tests were started using the MITR-II, 5-MW research reactor at M.I.T. Membrane samples are exposed to varying levels of β and γ radiation. One sample membrane disc has been taken through the pre-irradiation test procedures and has been left at M.I.T. for irradiation. This preliminary radiation experiment will determine whether any constituents introduced during handling

or present in the test solute have long half-lives which could delay subsequent membrane handling. There are no elements in the membranes themselves which should prove troublesome in this regard.

The small laboratory adsorbent column tests were continued in order to complete breakthrough and loading rates for uranium-233, plutonium-238(IV), and plutonium(VI). To date, 4.5×10^8 dis/min/g of uranium and 1.7×10^8 dis/min/g plutonium-238(IV) and (VI) have been adsorbed by the columns. A similar system was set up at the Waste Disposal Facility to test adsorbents with an actual complicated waste stream containing plutonium-238, calcium, iron, sodium, and other constituents. The data generated in these tests will aid in design of the engineering test facility.

Reference

1. Development of Ultrafiltration and Inorganic Adsorbents for Reducing Volumes of Low-Level and Intermediate-Level Liquid Waste - Quarterly Report: October, November, December 1976, MLM-MU-77-62-0005, 5 pp.

FIGURE 1 - Partially assembled U.F. Pilot Plant.

FIGURE 2 - Continuous column tests for uranium-233(VI), plutonium-238(IV), and plutonium-238(VI).

FIGURE 3 - Continuous column tests on actual waste at the Waste Disposal Facility.

FIGURE 4 - Shaker apparatus for completing adsorption isotherms.

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