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Remediation Flowsheet*

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MASTER

SCALE-UP OF THE SY-102 REMEDIATION FLOWSHEET

by

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ABSTRACT

An anion exchange unit operation for the removal of actinides from a high-nitrate, low-acid solution was successfully scaled up more than one order of magnitude. The behavior of the scaled-up system was similar in many ways to the previous small-scale experiments. It was characterized by a slow approach to equilibrium, displacement of americium by the other actinides, and improved column performance with increasing column length. With reasonable accuracy, we predicted for the larger system the breakthrough of americium, the most weakly sorbed actinide of those present.

I. INTRODUCTION

As part of the Tank Waste Remediation System (TWRS) at the Hanford Site, personnel at Los Alamos National Laboratory (LANL) developed and demonstrated a flowsheet to remediate the high-level radioactive contents of tank SY-102. The results of this work are detailed in a previous LANL report (Yarbro et al. 1994).

In bench-scale experiments with a simulated but radioactive waste, we demonstrated that the tank contents could be processed by using ion exchange to isolate the actinide fraction in a relatively small volume. The remainder of the material could then be handled as low-level radioactive waste. The key unit operation of this flowsheet is anion exchange of the dissolved sludge in a low-acid, high-nitrate solution that selectively retains the actinides. To further demonstrate the viability of the anion exchange step, we scaled up the process and successfully predicted its performance. This report documents the results of an intermediate-scale anion exchange experiment at the Los Alamos Plutonium Facility.

II. EXPERIMENTAL

The previous bench-scale studies used a series of five ion exchange columns, each 1 cm by 15 cm with a bed volume of ~12 ml. We performed the intermediate-scale experiment with a total column volume approximately 16 times that of the bench-scale experiments. We chose this value for several reasons. The scaling factor at greater than one order of magnitude represented a significant increase over the bench-scale size, and the amount of simulant solution at ~15 L processed represented a significant volume increase over the bench-scale volumes of 600 mL to 700 mL. This volume of simulant represented a reasonable compromise between the intermediate-scale demonstration and excessive waste generation. Commercial ion exchange columns were also readily available in this size range. Finally, to achieve a full- or production-scale operation would require a similar order of magnitude increase in the equipment and flow rates from this intermediate scale.

Figure 1 shows the experimental setup. The ion exchange bed consisted of two columns, each 2.5 cm in diameter by 100 cm long, connected in series. One

Fig. 1. The intermediate-scale experimental apparatus for removal of actinides from dissolved tank sludge simulant.

sample collection valve was located between the columns, and another valve was located at the outlet of the second column. An in-line x-ray fluorescence (XRF) cell, located after the second valve, provided additional near-real-time analytical data for several cations including americium.

Reillex HPQ, a macroporous polyvinylpyridine strong-base anion exchange resin developed jointly by LANL and Reilly Industries, Inc., was used in this study as in all previous bench-scale flow experiments. Originally developed for the recovery of plutonium from aqueous nitrate process streams, Reillex HPQ is strongly resistant to chemical attack and radiolytic degradation (Marsh 1989, and Marsh 1990). We converted the resin, 40 to 70 mesh, from its "as-received" chloride form to the nitrate form before use. The metering pump used in the setup was a Lab Pump Jr., model RHSY, manufactured by Fluid Metering, Inc. The gamma spectrometer was a germanium-based detector system manufactured by EG&G Ortec. The resin, metering pump, and gamma spectrometer were the same as those used in the bench-scale experiments.

We prepared 25 L of simulant with the composition given in Table 1. This is same composition as that used in the latter bench-scale experiments, except that the chromium was replaced with an equivalent amount of Fe(III) in order to minimize the generation of mixed hazardous waste. We pumped the feed through a nominal 2 μ m filter with a diaphragm pump to remove any particulates. A transfer flask placed between the filter and the metering pump maintained a constant inlet pressure to the pump, thereby ensuring a uniform flow rate to the columns. The flow rate was set to a nominal 25 mL/min and was measured with a stop watch and graduated cylinder at 26.5 mL/min. Samples of 5 mL each were collected from both sample valves every 20 min, corresponding to an additional ~500 mL of processed feed. We submitted these samples for gamma spectrometry analysis, which determined the americium concentration and corroborated the XRF analysis.

Table 1. Simulant Feed Composition

Component	mol/L	Component	mol/L
Al ³⁺	1.286	Pu ⁴⁺	3.59E-04
Ca ²⁺	0.125	Th ⁴⁺	0.0156
Fe ³⁺	0.698	U ⁴⁺	0.0156
Na ⁺	0.047	H ⁺	0.05
Mn ²⁺	0.129	NO ₃ ⁻	7.67
Sr ²⁺	7.79E-04	F ⁻	0.075
Am ³⁺	12.4 ppm	SO ₄ ²⁻	0.01

III. RESULTS AND DISCUSSION

As described in the conceptual design report (Yarbro et al. 1994), the actinides associate with nitrate when the concentration of nitrate is high enough (several moles per liter). It is the resulting anionic actinide nitrate complexes that undergo exchange on the resin. In this study we used the breakthrough of americium to track column performance because the Am(III) nitrate complex is the most weakly sorbed actinide complex of those present.

Figure 2 shows the americium effluent concentration profiles as measured with gamma spectrometry. The first profile, H = 0.5, is a plot of the relative americium concentration in effluent taken from the first sample valve. This represented the americium concentration in the liquid at the mid point of the total column length. The profile H = 1 is a plot of the relative americium concentration in effluent taken from the second sample valve at the outlet of the second column.

In both profiles the effluent was first observed to contain no measurable amount of americium. After many column volumes were eluted, americium began to appear in the effluent. In both profiles the americium concentration rose sharply, overshooting the feed americium concentration [$(Am)/(Am)_f > 1$]. This rise was followed by a decrease in the americium concentration to that of the feed. These features are typical of those observed in the bench-scale studies.

Fig. 2. Effluent concentration profile: $(Am)_f = 12.4$ ppm; average flow rate = 26.5 mL/min; column length = H; column volume = 982 mL; $(Am)/(Am)_f = 1\%$ at 9.65 column volumes (9.5 L).

The general profile shape was a result of the americium first loading on the resin, followed by displacement of the americium by the other actinides. In effect, the americium "piled up" in a front that traveled down the column, resulting in the overshoot. As the americium was pushed off the column, the concentration of americium in the effluent returned to that of the feed. As expected, americium breakthrough at $H = 1$ occurred after breakthrough at $H = 0.5$ simply because of the increased column length. Breakthrough was defined as that point when the concentration of americium in the effluent reaches 1% of that of the feed. The larger overshoot for the $H = 1$ profile was a result of more americium concentrating in the front as it traveled farther down the column.

Figure 3 plots the same profiles shown in Fig. 2, along with the XRF profile for americium at $H = 1$. Although the XRF consistently indicated higher americium concentrations than the gamma spectrometry analyses, the profiles were essentially identical in shape. This profile duplication indicated that the XRF can be used to track on-line species concentration data with reasonable accuracy.

Another important feature of the profiles in Figs. 2 and 3 is the "spike" in the overshoot for the $H = 1$ profile at ~16 column volumes eluted. An explanation for this observation is that local equilibrium between the various

actinide nitrate complexes and the resin was not attained rapidly. After ~15 column volumes of simulant were processed, the system was shut down; that is, the pump was turned off for the day. During this down period, local exchange continued between the americium complex and the other actinide complexes with the result that additional americium was displaced from the resin. When the pump was restarted the next day (after ~16 hours of down time), a surge of americium came off the column, resulting in the second peak, or spike, on the curve.

Figure 4 shows the XRF concentration profiles for americium, thorium, and uranium. The XRF profile for plutonium was not plotted because its signal was always at or below background levels. These profiles show that the thorium and uranium reached breakthrough when ~15 column volumes were eluted. As noted previously, it was after ~15 column volumes had been eluted that the run was stopped for the day. The next data point, corresponding to starting the pump the next day, clearly shows the second americium overshoot. The corresponding thorium and uranium concentrations dropped back to zero, further supporting the speculation that equilibrium is only slowly achieved, and thorium and uranium continued to displace the americium during the time that the pump was turned off. Succeeding data points show the continued rise of the thorium and uranium concentrations and the decline of the americium concentration.

Fig. 3. Comparison of gamma/XRF effluent concentration profiles: $(Am)_f = 12.4$ ppm; average flow rate = 26.5 mL/min; column length = H ; column volume = 982 mL; $(Am)/(Am)_f = 1\%$ at 9.65 column volumes (9.5 L).

Fig. 4. Effluent concentration profile (XRF): $(Am)_f = 12.4$ ppm; $(Th)_f = 0.0156$ mol/L; $(U)_f = 0.0156$ mol/L; column length = 200 cm; column volume = 982 mL.

Because of the results of the previous bench-scale runs, we were able to predict the behavior of the intermediate-scale system. In particular, it was desirable to know when the americium would reach breakthrough. It is well known that ion exchange data taken in small-scale columns can be directly scaled up to columns of any diameter as long as the column bed height and the linear flow rate remain the same (Schweitzer 1979). In addition, the feed must flow uniformly over the top of the resin bed and be collected uniformly from the bottom of the bed (i.e., no channeling). We know from our previous bench-scale experiments that column performance improves as the length of the column increases, if all other variables remain the same. In addition, we observed that reducing the volumetric flow rate in identical columns also improves column performance. Here, column performance is defined as the number of column volumes of solution processed before americium breakthrough occurs.

We performed the intermediate-scale run at a linear volumetric flow rate of $5.40 \text{ cm}^3/\text{min-cm}^2$, 4.3 times that of the bench-scale run. Although the direction is toward decreasing column performance, the effect is offset to some degree by the longer column (200 cm), 2.7 times that of the bench-scale run. Although the two differences are not linearly related, we predicted roughly that the intermediate-scale run would not perform quite as well as the bench-scale run. In fact, the bench-scale run

experienced americium breakthrough at ~ 11 column volumes, whereas the intermediate-scale run experienced breakthrough at ~ 9.6 column volumes.

The final series of bench-scale experiments, as detailed in the conceptual design report (Yarbro et al. 1994) were conducted to optimize the liquid flow rate so that an effective separation could be achieved with a minimum amount of resin. The americium concentration profiles for runs made at different volume velocities are shown in Fig. 5 (Fig. 21 in the previous report). A plot of the on-line resin volume as a function of volume velocity is shown in Fig. 6 (Fig. 22 in the previous report). The resulting optimal flow rate of 7.5 bed volumes/hour was determined from Fig. 6.

Although the column arrangement in the intermediate-scale run was not optimized with respect to column length, it was possible to use the data obtained in the bench-scale optimization experiments (Fig. 5) to predict when the americium should break through the second column in the intermediate-scale run. The volume velocity in the intermediate-scale experiment was 1.62 L of solution per liter of resin-hour. Interpolation of the data in Fig. 5 suggests that the americium should break through at approximately nine column volumes. As stated before, breakthrough was actually observed at ~ 9.6 column volumes.

Fig. 5. Column capacity for americium vs. feed volume velocities.

Fig. 6. Resin volume vs. feed volume velocities.

IV. FUTURE WORK

Although the results of this study provide a means of predicting americium breakthrough for a scaled-up system, it would also be useful to know the distribution of actinides on the ion exchange column at any given time. Such a predictive capability could be used to tailor the ion exchange unit operation depending on the desired separation (e.g., if uranium is to be separated from thorium). A mathematical model of the process can also be used to optimize the actinide separations and the overall flow sheet.

Planned future work includes the development of a mathematical model with this predictive capability. One early model to describe ion exchange was developed (Thomas 1944) and later simplified and expanded (Hiester and Vermeulen 1952, Vermeulen and Hiester 1954). This model has an analytical solution, important for the era in which it was developed, since routine access to computers for numerical codes was not yet possible. Although the model adequately describes systems such as sodium exchange on a cationic resin, it is not adequate for the more complex actinide-nitrate system described in this study. Future work will focus on modifying Vermeulen's model so that it can be applied to these systems. A model that adequately describes actinide anion exchange could be applied to many other ion exchange systems in which complexation reactions occur.

V. SUMMARY AND CONCLUSIONS

The same type of ion exchange behavior was observed in both the bench-scale and intermediate-scale runs. This behavior was characterized by a slow approach to equilibrium, displacement of americium by the other actinides, and improved column performance with increasing column length. The results of this study demonstrated that the bench-scale anion exchange process for the removal of actinides can be successfully scaled up. In addition, the point of actinide breakthrough of the scaled-up system can be predicted with reasonable accuracy.

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