This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U. S. Department of Energy.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available for sale to the public, in paper, from: U.S. Department of Commerce, National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161,
phone: (800) 553-6847,
fax: (703) 605-6900
email: orders@ntis.fedworld.gov
online ordering: http://www.ntis.gov/help/index.asp

Available electronically at http://www.osti.gov/bridge
Available for a processing fee to U.S. Department of Energy and its contractors, in paper, from: U.S. Department of Energy, Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831-0062,
phone: (865)576-8401,
fax: (865)576-5728
email: reports@adonis.osti.gov

WSRC-MS-2003-00792

COLUMN PERFORMANCE TESTING OF SUPERLIG® 639 RESIN WITH SIMULATED HANFORD WASTE SUPERNATES: IDENTIFICATION OF THE PRIMARY SORBING SPECIES AND DETAILED CHARACTERIZATION OF THEIR DESORPTION PROFILES

William D. King*
William A. Spencer
L. Larry Hamm
Sebastian Aleman
Cheryl E. Duffey

Savannah River Technology Center
Westinghouse Savannah River Co.
P. O. Box 616
Aiken, SC 29808

* To whom correspondence should be addressed
(email: william02.king@srs.gov)

Manuscript Submittal Date: November 10, 2003

ABSTRACT

Several bench-scale column tests (resin bed volume ≤75 mL) have been conducted with SuperLig® 639 resin and simulated Hanford waste supernates. Rhenium (surrogate for technetium in actual waste samples) breakthrough profiles were determined for three simulant compositions which are representative of the basic waste categories requiring treatment in the Hanford River Protection Project Waste Treatment Plant. Considerable loading performance variability was observed between the three waste types, although the resin is effective at rhenium removal from each solution. Careful and frequent analysis during elution studies conducted at the conclusion of the column loading tests confirmed that sodium nitrate and sodium perrhenate ion pairs are primary sorbing species on SuperLig® 639 resin. Furthermore, it was discovered that potassium nitrate and potassium perrhenate salts are significant competitors for sorption sites on the resin. Successive desorption profiles were identified for all four salt species during elution tests. Integration of the desorption profiles revealed that the resin is selective for removal of the potassium salts over the sodium salts.

BACKGROUND

The Hanford River Protection Project (RPP), funded by the United States Department of Energy, focuses on the design and construction of a Waste Treatment Plant (WTP) for the treatment of millions of gallons of radioactive waste. The waste, which is a legacy by-product of the production of nuclear weapons, is currently stored in tanks in Hanford, Washington. The tanks contain varying amounts and types of solids and millions of gallons of aqueous supernate. While all of the supernate is alkaline and primarily contains dissolved sodium salts, significant compositional variation is observed between tanks. The processing scheme for the Hanford waste therefore requires robust treatment technologies and extensive testing to validate performance under the range of feed solutions and potential operating conditions.

Technetium-99 ($t_{1/2} = 2 \times 10^6$ y) is one of several radioactive species initially targeted for removal from the supernate portion of the Hanford waste. The technetium primarily exists in solution as pertechnetate ion, TcO_4^-. The technology selected for technetium removal involves the use of SuperLig® 639 resin in a carousel (lead/lag) column configuration with off-line column regeneration. SuperLig® 639 is available in an engineered form that is suitable for use in column configuration and tests have confirmed acceptable technetium removal performance with this material. The resin contains a polystyrene substrate with an attached proprietary organic ligand which is highly selective for pertechnetate ion in alkaline sodium salt solutions. The technetium can be eluted from the resin with water, thus regenerating the material for reuse.

During the course of this work, technetium removal was cancelled from the Hanford waste treatment process. This decision was based on the fact that the need for technetium removal was marginal from a regulatory perspective. However, it is possible that technetium removal could return as part of the treatment process depending on the political environment. In addition, SuperLig® 639 resin is suitable for treatment of radioactive waste solutions at other locations (1). Regardless, it is certainly of interest to further understanding of a technology such as this which is so effective at removing a common radioactive component from legacy waste solutions.

INTRODUCTION

Much of the current testing with SuperLig® 639 resin focuses on thoroughly characterizing and optimizing performance. Extensive bench- and pilot-scale testing has been conducted over the past several years using both actual and simulated Hanford waste solutions. Besides validating resin performance under a variety of potential operating conditions, the tests provide input data for a scale-up model to predict and optimize performance in the full-scale facility. A set of tests was recently conducted to finalize the model input parameters and verify its predictive capabilities. The tests focused on three simulated waste compositions which are representative of the primary Hanford waste types to be treated in the initial operational phase of the Waste Treatment Plant. Two types of tests were conducted using the same pretreated batch of SuperLig® 639 resin and the same feed solutions: 1) sorption kinetics tests using a specially-designed test apparatus, and, 2) bench-scale column tests under prototypical plant processing conditions. The sorption kinetics tests were designed to determine fundamental mass transfer coefficients, which serve as primary model input. Specifically, film and pore diffusion coefficients were determined by manipulating the liquid flow rate in a small differential column apparatus (2). A separate report will describe the sorption kinetics test results and the modeling methodology and output. Results of the column testing are described in this report.

Column tests were conducted with simulants from the three general waste categories (designated as "envelopes"). In the simulant solutions, perrhenate ion is used as a surrogate for pertechnetate ion in the actual waste, since no non-radioactive isotopes of technetium are known. Significant variation was observed between the rhenium breakthrough profiles of the three waste compositions, although the column tests were conducted at constant temperature and volumetric flow rate. The primary factors influencing the breakthrough performance were believed to be the perrhenate concentration, the nitrate:perrhenate molar ratio, and the total solution ionic strength (3). Nitrate is considered to be the primary competitor for sorption sites on the resin and is present in the simulant solutions at concentrations that are orders of magnitude higher than perrhenate ion. The effective capacity of SuperLig® 639 resin has also been shown to increase with the total solution ionic strength. This is consistent with the fact that the resin can be eluted with water.

At the conclusion of each loading test, the feed was displaced from the columns with 0.1 M NaOH at a flow rate of 3 BV/hr. The columns were subsequently eluted with deionized water at 1 BV/hr and 65 °C. On-line (inductively couple plasma – emission spectroscopy) analysis of the feed displacement and eluate solutions provided detailed concentration profiles for numerous elements, revealing distinct desorption peaks for several species that were bound to the SuperLig® 639 resin during simulant contact. Examination of the on-line data and additional ion chromatography data from carefully collected samples provided the first direct evidence that sodium nitrate is a primary competitor for active sites on SuperLig® 639 resin. Furthermore, the potassium salts, KNO_3 and $KReO_4$, were identified as competitor species. Based on these observations, the mechanism of technetium removal would be described (in classical chromatography terms) as “reverse phase ion pair partioning” rather than ion exchange (4). Neutral ion pairs sorb to the active resin sites, although the salts exist predominately in the dissociated form in the mobile solution phase.

$$NaXO_4\text{—}L_{(s)} \bullet \quad Na^{+}_{(aq)} + XO_4{}^{-}_{(aq)} + L_{(s)}$$

L = active ligand site; X = Tc or Re

EXPERIMENTAL

A separate report describes the equipment, procedure, analysis, and results for the column testing in detail (5).

Simulant Preparation

Categorization of the waste was conducted in the initial stages of the plant conceptual design based on the anticipated treatment strategies required. Recipes were developed to prepare simulants of Hanford waste tanks 241-AN-105, 241-AZ-102, and 241-AN-107, which are representative of waste envelopes A, B, and C, respectively (6). 5 M sodium simulant solutions were prepared for testing, consistent with the plant feed target concentration. Each simulant solution was stirred overnight and filtered prior to use. Table 1 provides the chemical composition of each test simulant used for ion exchange testing based on the reagents added. Analysis data was generally consistent with the expected composition except for the aluminum concentration, which was lower than the target value. Measured density and viscosity data for each test simulant is also provided in Table 1. The Envelope C simulant was used for precipitation testing prior to ion exchange testing following the prototypical treatment strategy for this waste type (7). The AN-107 simulant was exposed to sodium hydroxide, sodium permanganate, and strontium nitrate reagent additions followed by filtration. The primary compositional changes resulting from these additions involved the sodium, nitrate, and free hydroxide concentrations (measured values: 5.74 M, 2.56 M, and 0.553 M, respectively.

Resin Handling

SuperLig® 639 resin (Manufacturer Lot #IR20327022045) was obtained from the vendor, IBC Advanced Technologies, American Fork, Utah. The sample contained 30-60 mesh, tan, spherical particles received under water. The mean particle diameter based on Lasentec chord length analysis was 481 μm (mean-squared chord). Prior to collection of a resin test sample, the 1 gallon bottle containing the resin was repeatedly tumbled end-over-end to promote mixing. A subsample was then collected by repeatedly dipping a 50 mL beaker into the bulk slurry sample to give a final volume of 150 mL. The 1 gallon bottle was also tumbled intermittently between dips with the beaker. Prior to use, the bulk of the shipping liquid was decanted from the resin subsample and the resin was washed several times with equal volumes of deionized water. The resin was then heated overnight at 65 °C in a 10-fold volume excess of water. The bulk of the water was decanted away prior to sample cooling. The sample was then washed several times and stored in water.

Resin samples used for testing were never fully dried prior to use. The entire pretreated resin sample was transferred to a disposable Nalgene Nylon filter unit and the free-flowing liquid was removed from the sample by vacuum filtration. The resin subsample to be used for testing was then quickly collected from the damp material in the filter along with two small (0.1 g) samples for water content determination. Water content was determined by drying these small samples at 50 °C under vacuum (-20 in. Hg). The resin test sample was then soaked in 0.25 M NaOH solution (10:1 liquid:solid by volume) overnight prior to being transferred to the column for testing.

Apparatus and Procedure

Jacketed columns were prepared from medium-wall Pyrex glass tubes with inside diameters of 1.5 and 2.54 cm. The basic column design and equipment setup were as reported previously (1). All processing solutions were pumped down-flow through the columns using positive displacement pumps. The column temperature was controlled at 25 ± 1 °C using a water recirculator. A 1.5 cm ID column containing 10.1 mL (6.3285 g) of resin was used for testing the Envelope A simulant. A 2.54 cm ID column containing 74.6 mL (46.2471 g) of resin was used for testing the Envelope B and C simulants.

The test columns were assembled and filled with 0.25 M NaOH solution. The pretreated resin/NaOH slurries were transferred to the columns in portions with intermittent mixing of the bottle containing the slurry. A packed resin bed was formed by free-fall of the beads through the solution. The resin beds were then restrained with quartz wool and glass beads. The beds were preconditioned by passing 6 bed volumes (BV) of 0.25 M sodium hydroxide solution through the columns over a 6 hour period. One bed volume was defined as the solution volume equivalent to the volume of the wetted and packed resin bed.

The feed simulant solutions were pumped at a flow rate of 3 BV/hr through the column. The effluent was continually monitored in real time by inductively coupled plasma – emission spectroscopy (ICP-ES). The on-line monitor utilized an automated sampling system developed for potential use in the full-scale waste treatment plant (8). Grab samples of the effluent were also collected for anion chromotography analysis. The loading cycle was terminated when the available feed was consumed. The simulant was displaced from the columns with 0.1 M sodium hydroxide solution at a flow rate of 3 BV/hr. The columns were then eluted with deionized water at 65 °C using a flow rate of 1 BV/hr. The packed column utilized for testing the Envelope B simulant was reconditioned after elution with 0.25 M NaOH solution, as described above, and was used for Envelope C simulant testing.

RESULTS AND DISCUSSION

Rhenium column breakthrough profiles obtained for Envelope A, B, and C waste simulants are provided in Figure 1. SuperLig® 639 resin is effective at removing perrhenate from all three waste types, although the breakthrough profiles vary dramatically. The poorest performance was observed with the Envelope C simulant, for which 50% rhenium breakthrough was observed after processing ~80 BV of solution. In contrast, only 30% rhenium breakthrough was observed after processing 210 BV of Envelope B simulant. Intermediate performance was observed with the Envelope A simulant. The trends in performance are consistent with the nitrate:perrhenate mole ratios for these waste types (NO_3^-/ReO_4^-: Env. C = 8.4 E4 > Env. A = 2.0 E4 > Env. B = 2.5 E3) with lower values corresponding to improved performance.

Careful inspection of the concentration profiles for numerous species obtained by on-line analysis at the beginning of column loading with Env. B simulant revealed a delay in the potassium wavefront exiting the column. The 50% potassium breakthrough point was observed approximately 1 BV after breakthrough of all other species analyzed (expect for rhenium). A less pronounced delay in potassium breakthrough was observed with the Envelope A and C simulants. This was the first indication of potassium uptake by the resin. The Envelope B simulant contained the highest rhenium concentration of the three simulants tested. The delay in the potassium breakthrough could be explained by sorption of potassium perrhenate salt with this simulant.

At the conclusion of the loading experiments, the simulant was displaced from the columns with 0.1 M NaOH and the columns were eluted with water at 65 °C. ICP-ES and anion chromatography analysis data collected during the transitional period between column loading and elution revealed that the concentration profiles of certain species did not decrease at the same rate as the majority of the species analyzed. It was apparent after further inspection that several species were desorbing from the resin during feed displacement and during the onset of the elution cycle. Background subtraction of simulant matrix contributions to the concentration profiles based on the trends observed for non-interacting species revealed successive, partially-resolved desorption peaks for four species: $NaNO_3$, KNO_3, $NaReO_4$, and $KreO_4$. The background-corrected desorption profiles for sodium, potassium, rhenium, and nitrate are provided in Figure 2. The sodium concentration profile depicts the matrix compositional changes from 5 M Na^+ simulant, to 0.1 M Na^+ feed displacement solution, and finally to water. Matrix contributions from the 0.1 M NaOH feed displacement solution were not subtracted from the sodium profile.

Although the composition, flow rate, and temperature of the mobile phase are changing during the transition from simulant to eluate, it is useful to view the desorption profiles in classical chromatography terms. In this simplified view, the sequence of desorption profiles is representative of the distribution coefficients (K_d) for the various species, with earlier elution corresponding to lower K_d values. Based on the order of elution the distribution coefficients should follow the sequence: $NaNO_3 < KNO_3 < NaReO_4 < KReO_4$. Loading levels determined for each species on the resin by integration of the desorption profiles indicate that in the solid phase the nitrate and the perrhenate salts are each enriched in potassium (lower Na:K mole ratio) relative to the feed. The eluate is also enriched in perrhenate ion relative to nitrate ion. These observations are consistent with the assigned ordering of the K_d values above.

Another feature of the desorption data is the apparent broadening of the concentration profiles for the potassium salts relative to those observed for the sodium salts. This feature is most notable for the profile associated with potassium perrhenate. A classical explanation for peak broadening is slow sorption/desorption kinetics (9). Alternatively, since the column used with the Envelope B solution was not loaded to rhenium saturation, the relative broadening of the $KReO_4$ band may be due to differences in the distributions of the sodium and potassium perrhenate salts on the column during loading. In this case the two species would experience differing levels of axial dispersion during elution. This would not be the case for the potassium nitrate salt, since the on-line data indicated saturation with this species after processing <5 BV of effluent during column loading. It appears from the data in Figure 2 that the desorption profile for KNO_3 is also broadened relative to that for the sodium salt, which indicates that slower kinetics for the potassium salts is the reason for the broadening.

Rough estimates of selectivity coefficients between the sodium and potassium salts were obtained from the calculated loading levels for each species on the resin. The selectivity coefficient for KNO_3 over $NaNO_3$ was determined to be ~16 The selectivity coefficient for $KReO_4$ over $NaReO_4$ was determined to be ~25. Based on this information, one would expect improved perrhenate (or pertechnetate) removal performance for SuperLig® 639 with higher potassium feeds. Soon after the discovery of the potassium selectivity, enhanced performance was observed for an actual waste sample from Hanford tank 241-

AP-101 containing 0.75 M K^+ (10). Details and discussion of the degree of performance enhancement with this sample will be provided in a separate report.

CONCLUSIONS

The performance of SuperLig® 639 resin with regard to perrhenate removal from Hanford waste simulants is considered adequate for use of this material in the River Protection Project Waste Treatment Plant. Observed variabilities in loading performance are fairy well understood, considering that the resin composition was not provided by the vendor. Resin performance varies with the solution NO_3^-:ReO_4^- mole ratio, due to the fact that nitrate is the primary competitor for resin sorption sites. Careful and frequent analysis during feed displacement and elution of the SuperLig® 639 columns confirmed that sodium nitrate and sodium perrhenate salts sorb to the resin during loading with high sodium simulants. Surprisingly, it was also discovered that significant amounts of potassium nitrate and potassium perrhenate sorb to the resin as well. Comparison of the relative amounts of each sorbed species to their concentrations in the feed solutions revealed that SuperLig® 639 resin is selective for the removal of the potassium salts. Discovery of the potassium selectivity significantly improved understanding of the factors influencing the performance of SuperLig® 639 resin. Furthermore, observation of nitrate desorption peaks validated the existing conceptual model for this material. These discoveries speak to the value of frequent and careful analysis of column effluent and eluate solutions.

REFERENCES

1. King, W. D.; Hassan, N. M.; McCabe, D. J.; Hamm, L. L. *Separation Science and Technology,* **2003**, 38 (12-13), 3115.
2. Duffey, C. E.; Hamm, L. L.; King, W. D. *Westinghouse Savannah River Company Report*, WSRC-TR-2002-00548, Rev. 0, **2002**.
3. Hamm, L. L.; Smith, F. G.; McCabe, D. J. *Westinghouse Savannah River Company Report*, WSRC-TR-2000-00305, Rev. 0, August **2000**.
4. Pryde, A.; Gilbert, M. T. Applications of High Performance Liquid Chromotography Chapman and Hall, London, 1979. pp. 48-49.
5. King, W. D.; Spencer, W. A.; Bussey, M. P. *Westinghouse Savannah River Company Report*, WSRC-TR-2002-00580, Rev. 0, May **2003**.
6. Eibling, R. E; Nash, C. A. *Westinghouse Savannah River Company Report*, WSRC-TR-2000-00338, Rev. 0, February **2001**.
7. Duignan, M. R. *Westinghouse Savannah River Company Report*, BNF-003-98-0226, Rev. 0, March **2000**.
8. Spencer, W. A.; King, W. D.; Pennebaker, F. M. *Westinghouse Savannah River Company Report*, WSRC-TR-2002-00447, Rev. 0, January **2003**.
9. Hamilton, R. J.; Sewell, P. A. Introduction to High Performance Liquid Chromotography Chapman and Hall, London, 1977. pp. 16-19.
10. Burgeson, I. E.; Blanchard, D. L.; Deschane, J. R. *Batelle Company Report*, WTP-RPT-030, Rev. 0, December **2002**.

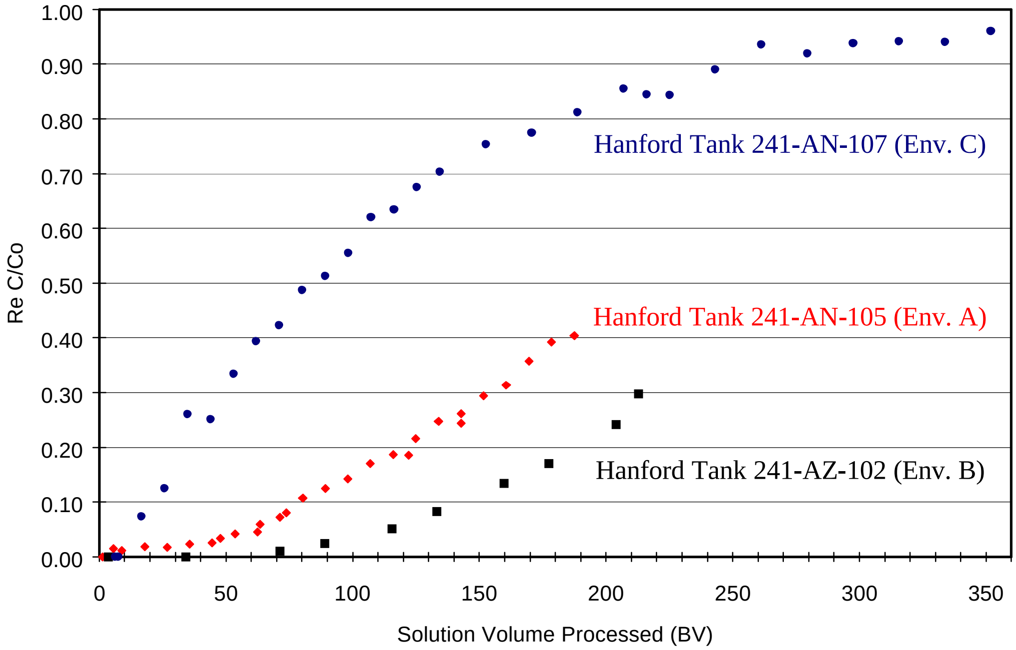

Figure 1. Rhenium Breakthrough Profiles During Column Loading with Envelope A, B, and C Simulants.

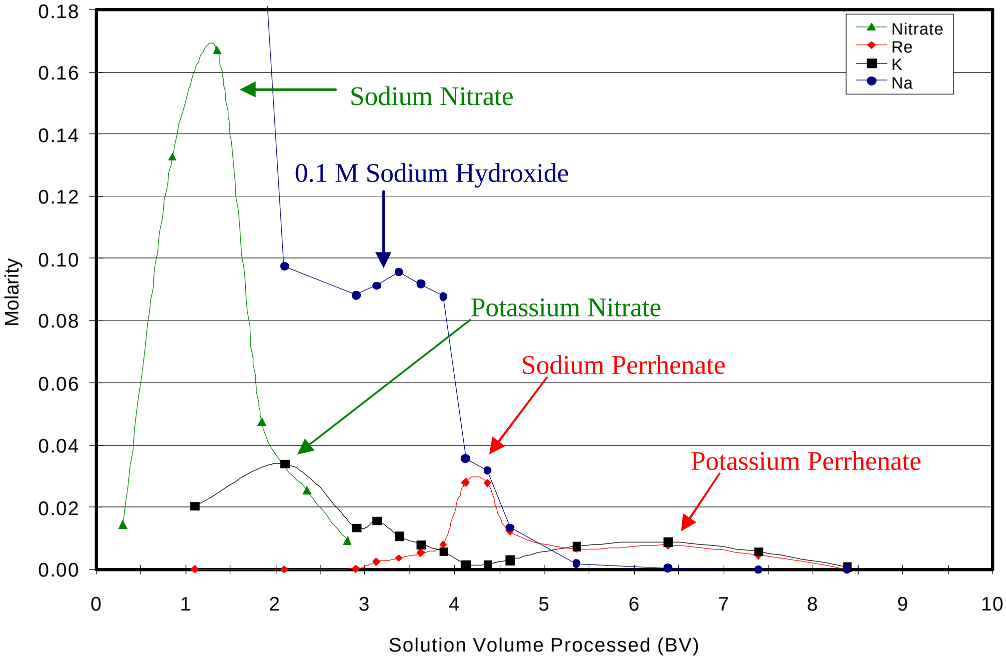

Figure 2. Concentration Profiles for Selected Species During 0.1 M NaOH Feed Displacement (25 °C, 3 BV/hr) and Water Elution (65 °C, 1 BV/hr) After Column Loading with Envelope B Simulant (25 °C, 3 BV/hr).

Table 1. Chemical Composition (Based on Reagents Added) and Measured Physical Property Data for Hanford Simulants.

	Env. A AN-105 [M]	**Env. B AZ-102 [M]**	**Env. C AN-107[a] [M]**
Na	5.000	5.000	5.000
K	0.090	0.153	0.027
Al	0.687	0.053	0.008
S	0.004	0.325	0.051
P	0.003	0.009	0.007
Cr	0.012	0.037	0.0E 00
Mg	1.04E-04	6.94E-05	6.07E-04
Ca	4.66E-04	5.08E-03	1.59E-03
Sr	0.0E 00	4.34E-06	4.46E-05
Ba	0.0E 00	1.08E-05	3.20E-05
Cd	1.37E-05	3.26E-05	0.0E 00
B	2.21E-03	1.08E-05	1.91E-03
Si	3.51E-03	3.75E-02	0.0E 00
Mn	0.0E 00	6.94E-05	6.01E-03
Fe	0.0E 00	3.79E-04	1.79E-02
Ni	0.0E 00	6.94E-05	5.32E-03
Mo	4.00E-04	1.14E-03	2.20E-04
Pb	1.20E-04	5.43E-05	0.0E 00
Re[b]	6.27E-05	2.07E-04	3.06E-05
Nitrate	1.243	0.515	2.188
Nitrite	1.126	1.243	0.784
Sulfate	0.004	0.325	0.051
Phosphate	0.003	0.009	0.007
Chloride	0.120	0.013	0.030
Fluoride	0.005	0.101	0.004
Oxalate	3.24E-03	0.061	0.006
Formate	2.99E-02	0.0E 00	0.136
Added Hydroxide	1.60	0.206	0.012
Carbonate	0.098	0.964	0.825
TIC	0.098	0.964	0.825
TOC	0.140	0.949	1.981
Physical Property Data			
Density (g/mL)	1.234	1.232	1.255
Viscosity (cP)[c]	2.98	3.05	3.37

[a] The AN-107 simulant solution was significantly altered from the original composition during strontium/transuranics precipitation testing. See comments in Experimental Section.

[b] Measured [Re]; assumed to be equivalent to $[ReO_4^-]$.

[c] Viscosity measured at ambient temperature using a Cannon-Fenske viscometer.