Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Examination Of Preproduction Samples Of Uop Ionsiv ® Ie-910 And Ie-911

W. R. Wilmarth[a]; D. D. Walker[a]; F. F. Fondeur[a]; S. D. Fink[a]; M. Nyman[b]; J. Krumhansel[b]; J. T. Mills[a]; V. H. Dukes[a]; B. H. Croy[a]
[a] Westinghouse Savannah River Company, Aiken, South Carolina, USA [b] Sandia National Laboratory, Albuquerque, New Mexico, USA

To cite this Article Wilmarth, W. R. , Walker, D. D. , Fondeur, F. F. , Fink, S. D. , Nyman, M. , Krumhansel, J. , Mills, J. T. , Dukes, V. H. and Croy, B. H.(2003) 'Examination Of Preproduction Samples Of Uop Ionsiv ® Ie-910 And Ie-911', Separation Science and Technology, 38: 12, 3075 — 3091

To link to this Article: DOI: 10.1081/SS-120022587

URL: http://dx.doi.org/10.1081/SS-120022587

SEPARATION SCIENCE AND TECHNOLOGY
Vol. 38, Nos. 12 & 13, pp. 3075–3091, 2003

Examination of Preproduction Samples of UOP IONSIV® IE-910 and IE-911[#]

**W. R. Wilmarth,[1,*] D. D. Walker,[1] F. F. Fondeur,[1]
S. D. Fink,[1] M. Nyman,[2] J. Krumhansel,[2] J. T. Mills,[1]
V. H. Dukes,[1] and B. H. Croy[1]**

[1]Westinghouse Savannah River Company, Aiken, South Carolina, USA
[2]Sandia National Laboratory, Albuquerque, New Mexico, USA

ABSTRACT

Researchers from across the Department of Energy (DOE) complex performed experiments to assess the impact of manufacturing changes on

---

[#] This report was prepared for the United States Department of Energy under Contract No. DE-AC09-96SR18500 and is an account of work performed under that contract. Accordingly, the U.S. Government retains a non-exclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes. Reference herein to any specific commercial product, process, or does not necessarily constitute or imply endorsement, recommendation, or favoring of same by Westinghouse Savannah River Company or by the United States Government or any agency thereof. The views and opinions of the authors expressed herein do not necessarily state of reflect those of the United States Government or any agency thereof.

[*] Correspondence: W. R. Wilmarth, Westinghouse Savannah River Company, Aiken, SC 29808, USA; E-mail: bill.wilmarth@srs.gov.

DOI: 10.1081/SS-120022587 0149-6395 (Print); 1520-5754 (Online)
Published by Marcel Dekker, Inc. www.dekker.com

the use of IONSIV® IE-911, the engineered form of crystalline silicotitanate (CST), for the removal of cesium from Savannah River Site (SRS) high-level waste. Prompted by previously supplied data, UOP changed the manufacturing process to minimize the chemical instability of the inorganic sorbent that manifests itself as niobium and silicon leaching. This report includes results of the extensive examination of newly prepared laboratory-scale and preproduction samples of caustic-washed CST as compared to similar performance data for commercially available and baseline samples.

Testing indicates that the revised manufacturing process removed most of the niobium (Nb) that previously readily leached from the sorbent under test conditions. The revised manufacturing also reduced the amount of easily leached silicon (Si), but a significant fraction of this material remains. Microscopic analysis indicates the presence of amorphous Si. Cesium capacity (mg Cs/g CST) or distribution coefficient (K_d) of the preproduction sample compares favorably to the baseline sample and exceeds that observed for the laboratory-scale sample made using the revised manufacturing process. Column breakthrough experiment indicates that the manufacturing change did not affect the mass-transfer zone length. Lastly, pore analysis, particle size, thermal behavior, and packing density measurements indicate that the manufacturing process change does not affect these bulk properties for the engineered material.

Key Words: Salt waste processing facility; Cesium.

INTRODUCTION

The Savannah River Site (SRS) continues research into alternative cesium removal technologies to replace the sodium tetraphenylborate precipitation process used in the In-Tank Precipitation facility.[1] The alternatives considered include the use of inorganic ion-exchange materials. Crystalline silicotitanate in the engineered form (IONSIV IE-911 prepared by UOP, Inc., Des Plains, IL, hereafter UOP) serves as the preferred ion-exchange material.

During recent testing, observations by Savannah River Technology Center (SRTC)[2] and Oak Ridge National Laboratory (ORNL)[3] researchers led to questions regarding the presence and fate of excess materials of manufacturing and other impurity materials. These materials leach from the sorbent and can form precipitates in the caustic waste. Other observations substantiated by research results include lot-to-lot variability in sorbent performance. Specifically, experiments performed at ORNL and SRTC showed that elements added in excess above stoichiometric amounts during the production process at UOP leached from the IONSIV IE-911. These materials precipitated in both actual tank waste and simulated waste solutions. Additionally, in at least one instance, the material precipitated in sufficient quantity to plug an ion-exchange column.

Therefore, Westinghouse Savannah River Company (WSRC) and UOP entered into a contingent purchase agreement, whereby UOP will perform testing to evaluate options for removing the excess niobium and silicon of manufacture that readily leach in SRS waste solutions. UOP provided samples to WSRC for testing. This document describes the results of a battery of tests to determine if the manufacturing efforts to reduce the amount of materials that leach from the sorbent impact the properties of the supplied material.

EXPERIMENTAL METHODOLOGY

The samples of various crystalline silicotitanate sorbents used in testing are listed in Table 1. Table 2 lists the compositions of the waste simulants. These simulants included a Savannah River average waste and a simplified waste solution used for testing at UOP. Testing included cesium equilibrium distribution, K_d, measurements and cesium capacity measurements. These tests typically used a solids to liquid ratio of 0.1-g sorbent to 10 mL of waste simulant. The duration of the tests was 72 ± 4 hours (for UOP simulant) and 7 days (for SRS average simulant). The temperature was controlled to 35°C. Finally, the starting cesium concentrations were 100, 50, and 18 mg/L, spiked with a ^{137}Cs tracer. Column testing for cesium removal was conducted using a 1.5-cm I.D. glass tube loaded with the preproduction sample to a bed height of 10 cm. Average salt solution was passed through the bed at a superficial velocity of 4.1 cm/min. Cesium ion concentrations were measured by atomic absorption spectroscopy.

Table 1. Crystalline silicotitanate samples used in study.

Sample name	Vendor identification number
Baseline IE-911	9090-76
Commercially available IE-911	89991000009
Laboratory-scale IE-911	Lab 30950-49
Preproduction IE-911	Pre-prod 9098-9
IE-910[a]	30050-48

[a] IE-910 material used to prepare the laboratory-scale and preproduction IE-911.

Table 2. Composition of waste simulants used in studies.

	Concentration (molar)	
Component	Average	UOP simulant
Na^+	5.6	5.7
Cs^+	0.00014	0.0008
K^+	0.015	—
OH^-	1.91	0.6
$NO_3{}^-$	2.14	5.1
$NO_2{}^-$	0.52	—
$AlO_2{}^-$	0.31	—
$CO_3{}^{2-}$	0.16	—
$SO_4{}^{2-}$	0.15	—
Cl^-	0.025	0.0008
F^-	0.032	—
$PO_4{}^{3-}$	0.010	—
$C_2O_4{}^{2-}$	0.008	—
$SiO_3{}^{2-}$	0.004	—
$MoO_4{}^-$	0.0002	—

In the leach tests, a quantity of IONSIV IE-911 was placed into 100 mL of 3-M sodium hydroxide in Teflon bottles and then mounted the CST and caustic solutions in an orbital shaker at 150 rpm. The temperature was controlled 25°C. After 48 hours, the liquid phase was decanted. After filtering the caustic solution through 0.02-μm filters, we submitted samples for analysis. For the column tests, a quantity of IONSIV IE-911 is placed into a 1.5-cm I.D. ion-exchange column. The caustic solution, 3-M NaOH, passed through the packed bed of CST at a superficial velocity of 4.1 cm/min. A total of 1 L of caustic was passed through the bed, filtered in an aliquot through a 0.02-μm filter, and was submitted for analysis. Niobium, silicon, and titanium concentrations were measured using inductively coupled plasma emission spectroscopy.

Samples are prepared for TEM analysis by grinding a small quantity of the pellets in butanol and dispersing the slurry to dry on lacey carbon substrates on Cu support grids. TEM imaging, electron diffraction, and elemental analysis of phases in the samples are performed on a Philips CM30 TEM at 300 kV, equipped with an Oxford Instruments EDS spectrometer with a low-Z window to facilitate light element analysis.

Infrared spectra were obtained on a NICOLET 210 FT-IR spectrometer. About 2 mg of sample was mixed with 0.2 g of petroleum gel. The sample was mixed until a uniform color was achieved. The sample was squeezed between two potassium bromide plates until a film thickness of about 10 microns was achieved.

RESULTS AND DISCUSSION

Cesium Removal Performance

Cesium-sorption experiments on the various samples of sorbents included standardized distribution coefficient (K_d) measurements using methods such as described in previous related studies.[3] By agreement, these tests occurred at 35°C using a solution containing an initial cesium concentration of 100 mg/L. In addition to the standardized K_d measurement, the researchers also determined the capacity of the sorbent for cesium at these conditions.

Table 3 provides the results from the measurements of cesium capacity for the various samples. In all cases, the data represent the average and ranges for replicate measurements. As seen from the distribution coefficients in the table, the preproduction sample and the starting material, IONSIV IE-910, both gave satisfactory removal of cesium. The predictive model for the behavior, termed the ZAM model in deference to the developers,[4] indicate an expected value of 652 mL/g at these conditions. Only the first modified version of the sorbent failed to meet this target. The preproduction sample and the baseline material provide equivalent performance within the accuracy of the measurements.

It is noted that the capacity measurement, under the conditions applied in these tests, does not provide a reliable metric for relative performance. The measured capacity value depends strongly on the final cesium concentration of the solution. Unless measured at the same final concentration, the values can

Table 3. Cesium capacity measurements for sorbents (conditions: UOP simulant, 35°C, initial Cs = 100 mg/L).

	Kd (mL/g)	Capacity (mg/g)
Baseline IE-911	669 ± 15	10.36 ± 0.14
	694 ± 56	10.71 ± 0.19
Commercially available IE-911	773 ± 43	9.97 ± 0.16
	792 ± 24	10.41 ± 0.13
Laboratory-scale IE-911	569 ± 11	9.52 ± 0.16
Preproduction IE-911	683 ± 16	9.91 ± 0.10
IE-910	950 ± 30	9.91 ± 0.11
ZAM prediction	652	

prove misleading. For instance, compare the data for the IONSIV IE-910 sample to that for the preproduction sample. The IE-910, given the absence of the binder, provides a much higher distribution coefficient. However, the preproduction sample exhibits the same capacity as the IE-910 sample solely due to variance in the cesium concentration at the end of the experiment.

Figure 1 shows the time required for the samples to reach equilibrium with the simulated SRS average waste. The slurries required about 4 days to reach equilibrium. The kinetic behavior of the preproduction sample agreed very well with that demonstrated by samples from the baseline material and previous lots. Hence, the variation in the manufacturing process did not detract from sorption performance. In many cases, the data appear to show a slight decline in performance following 4 days, but the variance does not exceed the statistical accuracy of the experiment.

Figure 2 contains the cesium loading isotherm (25°C) for a number of samples. The data show little variance indicating the change in the manufacturing methods did not detract from performance. As expected, the IE-910 shows slightly higher sorption at comparable conditions, indicative of the lack of the binding material present in IE-911. A slight decrease in sorption occurred relative to earlier production samples. The data remain nearly linear

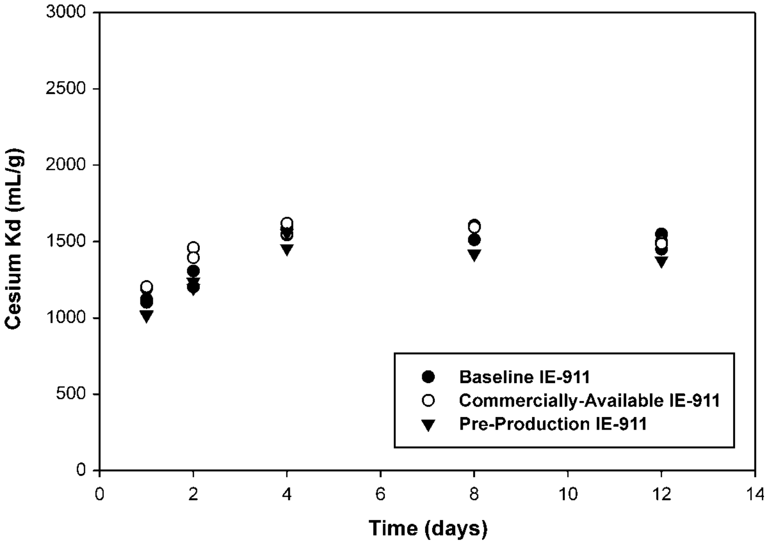


Figure 1. Time to reach equilibrium (second run).

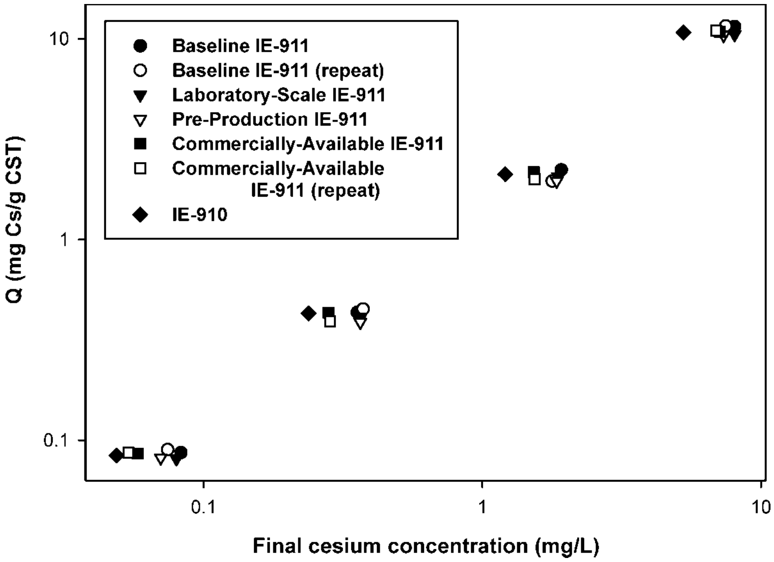


Figure 2. Cesium loading isotherms.

over the conditions studied indicating the validity of using a Langmuir formula to represent behavior.

The performance of the preproduction sample of IONSIV® IE-911 sample for cesium removal was also tested under column operation. In this column run, a 1.5-cm I.D. glass tube was loaded with the preproduction sample to a bed height of 10 cm. Average salt solution was passed through the bed at a superficial velocity of 4.1 cm/min. Figure 3 shows the cesium breakthrough curve for this run and the VERSE prediction of cesium breakthrough. The data agree with the model, and the column reached 95% breakthrough at approximately 1025 column volumes.

Leaching Performance

One main aspect of the chemical and thermal stability of IONSIV IE-911 involves the observed leaching of niobium and silicon. As mentioned previously, Taylor et al.[2] and Wilmarth et al.[1] measured leach rates at various temperatures. Wilmarth et al.[3] also showed that column operations would leach those components. Nyman and coworkers[6] identified a

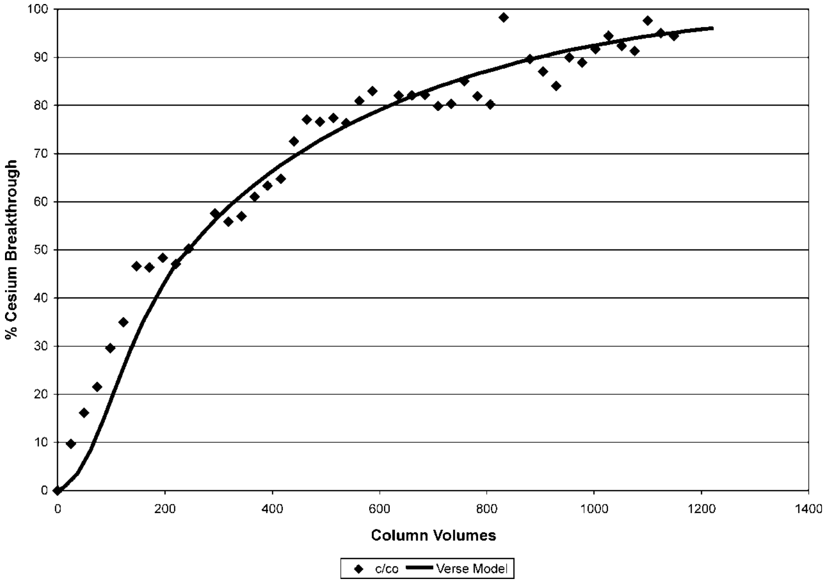


Figure 3. Cesium breakthrough curve using preproduction sample.

crystalline niobium phase and an amorphous silicon phase in the CST particles in previous production lots of IONSIV IE-911. Those investigators believe that these materials dissolve in caustic solution after acid treatment in the UOP production process previously discussed in this report.

Figure 4, for niobium, and Fig. 5, for silicon, show the results of the batch leach tests of the laboratory-scale sample and the preproduction sample produced using the new flowsheet. The data also include results from the commercially available IONSIV IE-911 and the baseline samples prepared at the UOP production facility in Mobile, AL. We performed batch leach tests on 5-, 10-, and 20-g samples for the preproduction sample and 5- and 10-g, samples for this laboratory-scale sample. The testing using baseline and commercially available sample testing used all three CST loadings.

The results for niobium leaching show that, at a 5-g CST/100 mL solid-to-liquid ratio, the solution concentration reached approximately 105 mg/L of niobium for the commercially available IE-911. The niobium concentration proved less for the other three samples of CST. The preproduction sample exhibits the lowest niobium concentration: 5.3 mg/L. This value represents a 20-fold reduction in niobium leaching. This behavior also occurred at higher solid-to-liquid ratios. At the highest ratio (20 g:100 mL), the commercially

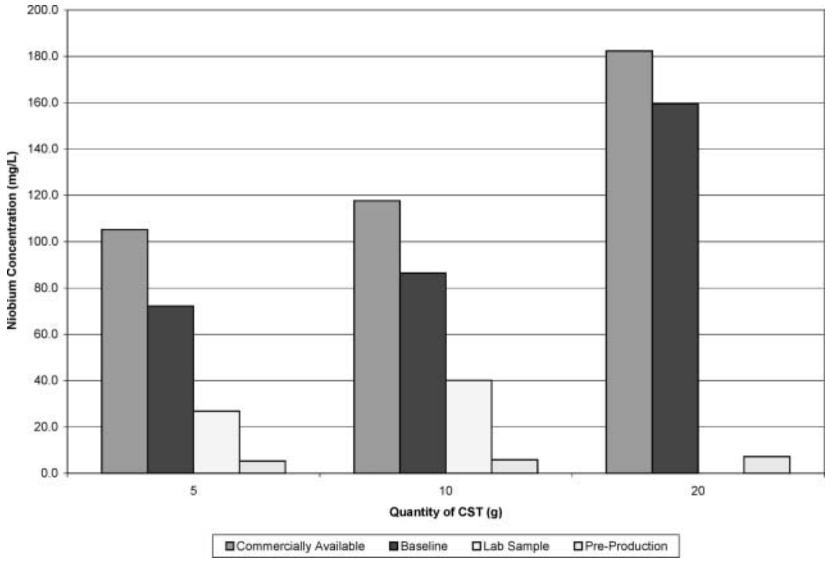


Figure 4. Niobium batch leachate test. There was insufficient sample to test the laboratory sample at 20-g loading.

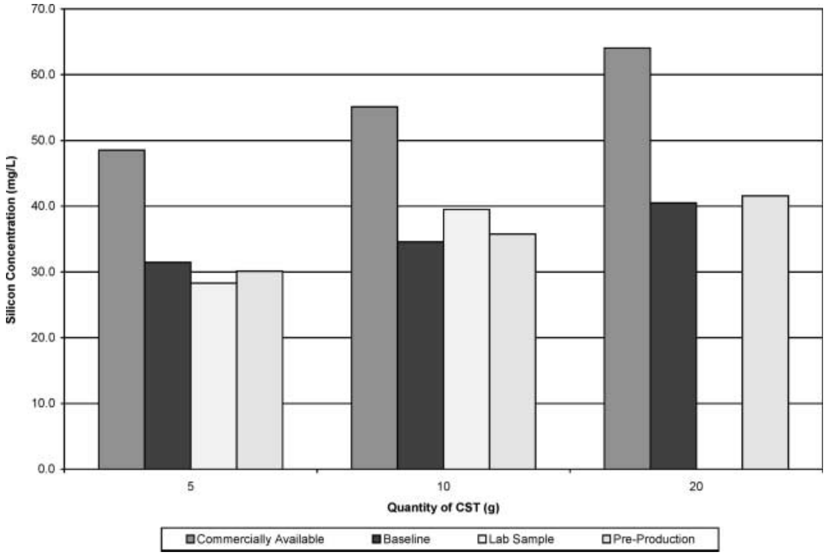


Figure 5. Silicon batch leachate test.

available sample leached greater than 150 mg/L compared to under 10 mg/L from the preproduction sample.

Less improvement resulted for the sample from the new manufacturing process relative to the behavior of silicon. Figure 5 shows the silicon concentration measured in the filtered caustic solution from the tests using various solid-to-liquid ratios. For example, at 5-g CST to 100 mL 3-sodium hydroxide, the silicon concentration in the test with the commercially available sample measured 48.5 mg/L, whereas the silicon concentration reached 30.1 mg/L in the preproduction sample test. This represents a 40% reduction in leached silicon at this solid-to-liquid ratio. At the higher solid-to-liquid ratio (20-g CST/100 mL 3-M NaOH), silicon concentrations reached 63 mg/L for the commercially available sample and 42 mg/L for the preproduction sample, or about a 20% reduction.

Personnel performed a comparable set of column leach tests using 1 L of 3-M sodium hydroxide. In these tests, researchers placed similar amounts of IE-911 in 1.5-cm I.D. columns and flowed sodium hydroxide through the bed at a superficial velocity of 4.1 cm/min. Figures 6 and 7 display the niobium and silicon concentrations measured in the column effluent after filtering using a 0.02-μm filter.

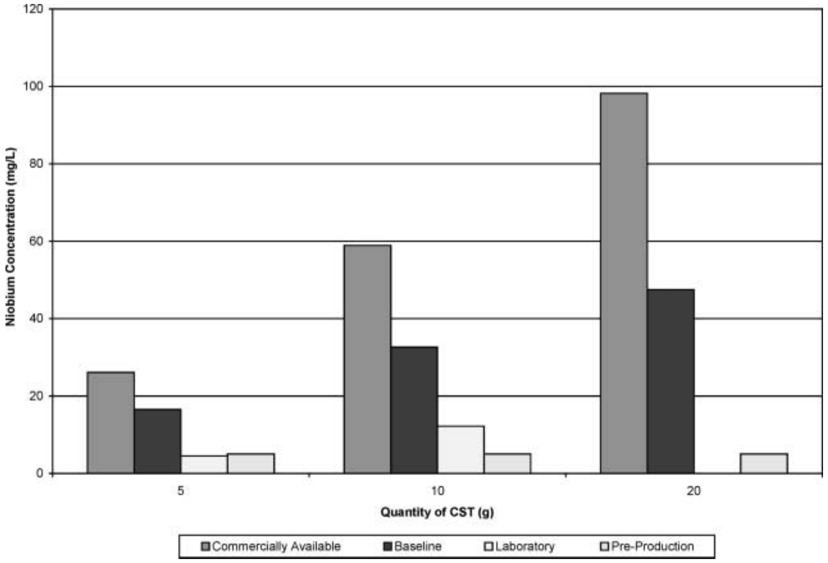


Figure 6. Niobium column leachate test.

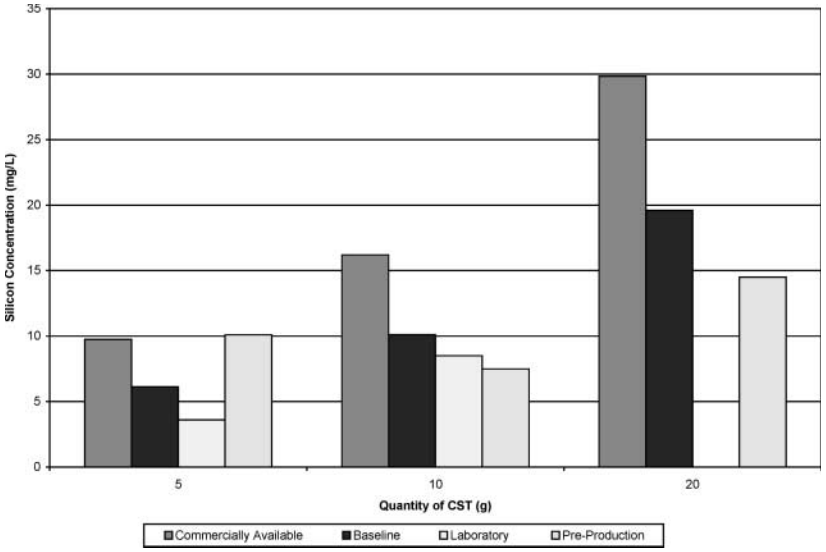


Figure 7. Silicon column leachate test.

As observed in the batch leach tests, the niobium leaching behavior decreased for the samples from the improved UOP flowsheet. In each of the three-column tests with increasing CST amounts, niobium remained below the detection limit of 5 mg/L. Personnel completed those tests, like the batch tests, in duplicate and sampled in duplicate. For comparison, the niobium concentration measured in the effluent from the column with the highest solid-to-liquid ratio (20-g CST/1 L 3-M NaOH) reached 98.2 mg/L for the commercially available CST. These data represent a 20-fold reduction in niobium leaching and agree well with batch test data.

The behavior of silicon in the column tests, like the batch tests, shows slight improvement for the preproduction sample compared to the commercially available CST and no improvement over the baseline sample. Figure 7 shows the silicon data from the column leach tests. At the low solid-to-liquid ratio (5-g CST/1 L 3-M NaOH), the silicon concentration from the commercially available CST and the preproduction sample measured ~ 10 mg/L. The amount of silicon leached from the baseline and laboratory-scale samples remained less than 7 mg/L in the low solid-to-liquid ratio tests. At the higher ratios, the amount of silicon leached proved lower for the preproduction samples.

The results of the batch and column leaching tests indicate significant (~ 20-fold) reduction in the amount of niobium that will leach into caustic solutions. The change in the UOP production manufacturing process, however, only reduced the amount of silicon that leaches under these conditions by a maximum of 50%. Additionally, the increased discipline in the original production method utilized in producing the baseline IE-911 material resulted in at least a 10 to 30% reduction in the amount of niobium and silicon that leaches under these conditions.

Physical and Molecular Characterization

We examined the various samples using Fourier transform infrared spectroscopy. Figure 8 shows that the infrared-active peak at 3550 cm^{-1} likely resulted from the OH stretch vibrations of Si—OH bonds. Note the absence of this peak in the spectrum of the samples of the IE-910 (CST hydrogen form), laboratory-scale IE-911 (sodium form), and the preproduction IE-911 samples (sodium form). This suggests removal of much of the excess silicon and probably niobium. Also, note the shorter width at half height of the broad peak near 3150 cm^{-1} in the preproduction batch. Again, this finding indicates less hydrogen bonded

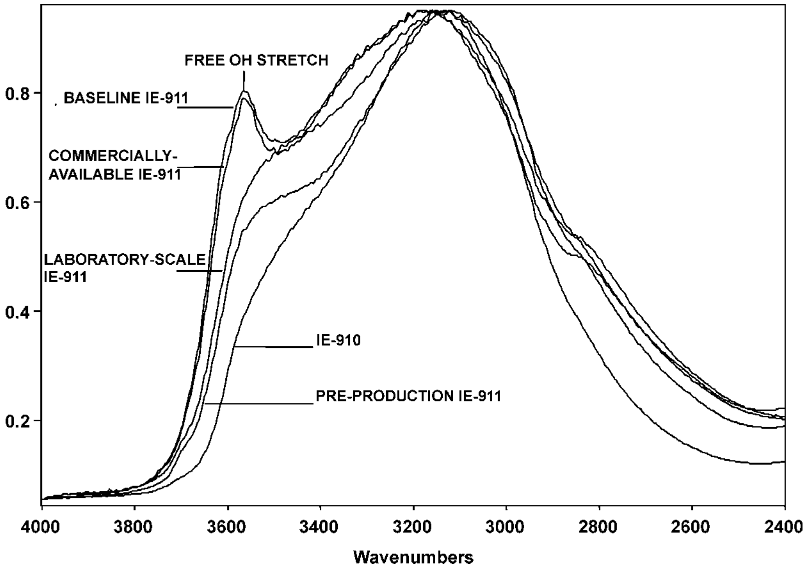


Figure 8. OH-stretch region of baseline, commercially available, laboratory-scale, preproduction IE-911, IE-910. Ordinate values given in Kubelka–Munk units.

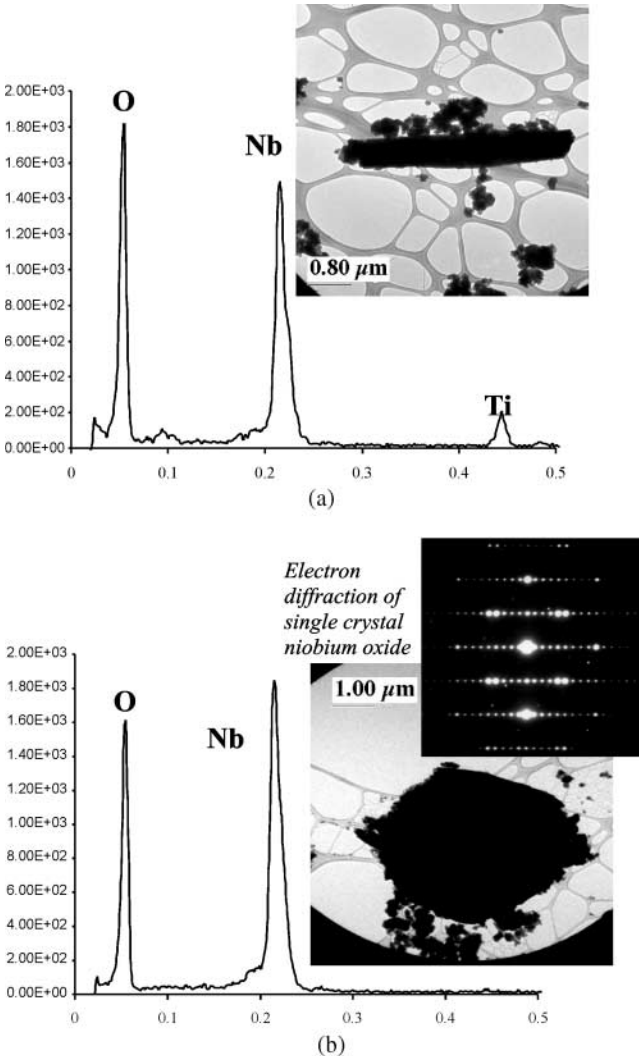
OH in the sample. Since researchers ground these samples to reduce the particle size for spectroscopy testing, one cannot ascertain if the lack of spectral features arises from the surface or the bulk of the samples.

The Sandia National Laboratory (SNL) co-authors used transmission electron microscopy, electron diffraction, and energy dispersive spectroscopy to analyze the commercially available, baseline, and preproduction samples. A significant decrease in the amount of Nb leached for the new acid forms of IE-911. Corresponding with this decrease, we observe about a 50% decrease in concentration of the impurity niobium phase (IPX) in the baseline IE-911, compared to commercial batch. The leached IE-911 shows essentially no Nb leaching, consistent with our observation of minimal IPX in this material. However, we do observe two additional Nb-containing phases.

We noticed a niobium titanate phase (Fig. 9a) observed primarily in the baseline material and a crystalline niobium oxide (Fig. 9b) abundant in both the baseline and preproduction materials. The niobium titanate material appears similar to IPX in that it is a hydrated phase (releases water and decomposes under the electron beam) removed (dissolved) by a caustic wash. This phase contains very large crystals, allowing us to observe it optically in the baseline IE-911. On the other hand, the second "new" niobium-based impurity, the niobium oxide phase, proves less soluble in NaOH, in that it remains present in the preproduction IE-911. The niobium oxide is identified as either Nb_2O_5 or $Nb_{12}O_{29}$ by electron diffraction. It is extremely crystalline, often single crystal. In fact, its low leaching may relate to its high crystallinity, since amorphous niobium oxide exhibits much higher solubility than crystalline niobium oxide. Therefore, at least with regard to the question of column conditioning, this Nb-based impurity should not create a column-plugging problem. However, how this impurity withstands dissolution in alkaline waste, especially with increased temperature or time of exposure, remains unknown.

The decrease in leached silicon from commercially available IE-911 to baseline IE-911 proves significant (reduction of 40%), yet not readily observable by TEM. The silicon impurities observed in the baseline and preproduction IE-911 prove quite similar to those observed in a sample from batch 98-7, described elsewhere.[7] We observe amorphous silica in the baseline material, often agglomerated with amorphous alumina. However, the crystalline aluminosilicate phase observed in the NaOH-treated batch 98-7 does not appear in the preproduction IE-911. Perhaps the caustic wash implemented by UOP to produce the leached material is not basic enough to result in this reaction. The photographs show two examples of silica (Fig. 10b) and silica plus alumina (Fig. 10a) impurities in the baseline IE-911.

In general, the form, composition, morphology, size, and other characteristics of silica impurities vary notably from one batch to the next.



(a)

(b)

Figure 9. (a) T-Nb-oxide impurity observed in Baseline IE-911: TEM image and EDS spectrum (left). (b) Crystalline Nb-oxide impurity abundant in both baseline and preproduction IE-911 samples: TEM image, electron diffraction, and EDS spectrum (right).

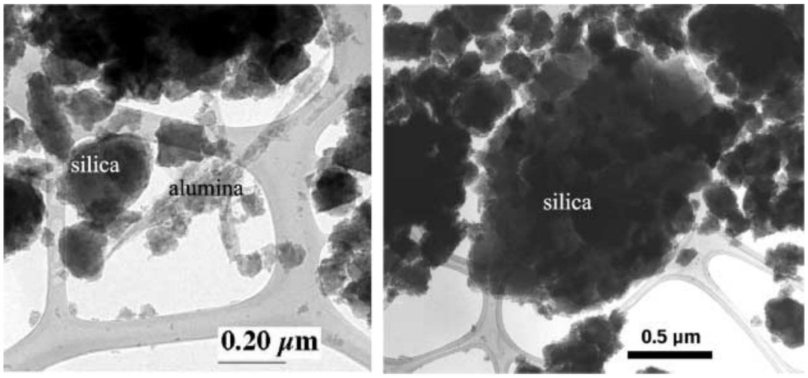


Figure 10.

These impurities may come from previous silicate and aluminosilicate syntheses at the UOP factory, which explains their inconsistencies.

We measured the porosity characteristics and surface area of the samples using a Micromeritrics pore sizer. Table 4 provides the nitrogen adsorption data and reveals no difference in the pore volume, surface area, or dimension between the different IE-911 batches. One data entry in Table 4 addresses the microporosity characteristics of the comercially available IE-911 sample.

Table 4. Pore surface area and volume.

Sample ID	Surface area (m^2/g)[a]	Pore volume (cm^3/g)[b]	Pore diameter (Å)[c]
IE-910 (CST)	23.0	0.16	35
Laboratory-scale IE-911 (Na-form)	32.0	0.11	38
Baseline IE-911 (H-form)	60.5	0.14	38
Commercially available IE-911	63.4	0.16	18
Commercially available IE-911 heated to 250°C for 2 hours	51.3	0.08	32
Commercially available IE-911[d]	84.9[d]	0.03[d]	4.4[d]
Preproduction IE-911	54.1	0.14	37

[a,b] BJH Desorption cumulative pore volume and surface area.
[c] Mode of the pore volume gradient and surface area gradient.
[d] Results from Micropore analysis.

The low pore volume indicates that the technique cannot successfully probe pores below 4 Å. Also, the table shows the effect of heating the commercially available IE-911 sample at 250°C. Both pore volume and surface area decreased, while the pore diameter increased with heating time.

CONCLUSION

The investigators authors examined the chemistry and performance of various samples from UOP. These samples, including materials obtained after modifications to the UOP manufacturing process used to prepare IONSIV IE-911, crystalline silicotitanate, ion-exchange material. The work examined programmatic elements of the CST performance as they relate to the CST flowsheet for removing cesium from SRS high-level waste.

Tests examined the cesium removal performance, chemical leaching of excess metal oxides, and solid-state characterization of vendor-supplied caustic-washed samples compared to commercially available samples of CST. Testing demonstrated that the material produced in the revised manufacturing process suffers less loss of niobium and silicon when contacted with simulated SRS waste and caustic at prototypical process conditions. Furthermore, the material removes cesium and strontium at least as well as previous samples of the ion exchange material.

ACKNOWLEDGMENTS

The contributors at the various DOE sites (SRS, ORNL, PNNL, and SNL) prove too numerous to list. Their efforts, though, behind the scenes enabled completion of this work. However, the contributions of four people who guided this testing deserve acknowledgement. They are Rich Braun and Nan Greenlay at UOP; Dennis Wester, who serves as the TFA System Lead for this technology; and Joe Carter from High Level Waste Engineering.

REFERENCES

1. National Academy of Sciences. *Alternatives for High Level Waste Salt Processing at the Savannah River Site*; National Academy Press: Washington, DC, 2000.
2. Wilmarth, W.R.; Walker, D.D. *Stability of UOP IONSIV$^{®}$ IE-911 in SRS Simulated Salt Solution at Elevated Temperature and Subjected to*

Radiation Exposure; WSRC-TR-99-00341; Westinghouse Savannah River Company: Aiken, SC, 1999.

3. Taylor, P.A.; Mattus, C.H. *Thermal and Chemical Stability of Crystalline Silicotitanate Sorbent*; ORNL/TM-1999/233; Oak Ridge National Laboratory: Oak Ridge, TN, 1999.
4. Zheng, Z.; Anthony, R.G.; Miller, J.E. Modeling multicomponent ion exchange equilibrium utilizing hydrous crystalline silicotitanates by a multiple interactive ion exchange site model. Ind. Eng. Chem. Res. **1997**, *36*, 2427.
5. Zheng, Z.; Anthony, R.G. Ind. Eng. Res. **1997**, *36*, 2427.
6. Nyman, M.; Headley, T.; Nenoff, T.M. Characterizations of As-received, Pre-treated, and Simulant-treated IE-911 (UOP batches 98-5, 99-7, and 99-9). Interim Report; Sandia National Laboratories, October 2000.
7. Nyman, M.; Headly, T.; Nenoff, T.M. Characterization of UP IONSIV® IE-911: Part 2. Final Report; April 2001.