SuperLig® Ion Exchange Resin Swelling and Buoyancy Study

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DOE Contract No. **DE-AC09-96SR18500**

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March 25, 1999

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SUMMARY

Characteristic volume changes of the SuperLig[®] ion exchange resins were studied in column tests. The sensitivity of these resins to pH and ionic strength changes and the density of salt solutions that leads to resin floating were determined to establish a limit for operation. The volume changes of SuperLig[®] 644 were significant when solutions of varying pH and ionic strength were used for loading, washing, and elution. In contrast, the SuperLig[®] 632 and 639 resins can withstand changes of ionic strength and pH without appreciable swelling and shrinking. The latter resins, however, float in salt solutions with sodium concentrations of 6 M, which corresponds to a specific gravity greater than 1.25 g/mL. The SuperLig[®] 639 exhibits batch-to-batch variability and a range of densities, with a significant portion of the resin floating at 1.22 g/mL. Inconsistencies in floating behavior may be attributable to the history of the resin, indicating that once beds are packed, dense solutions do not always cause floating. Recently received batches of SuperLig[®] 632 exhibit ~25% volume increase during the first caustic treatment and remain stable to subsequent treatments.

SuperLig[®] resin beds were coherent and intact showing no strenuous effects such as deformation, cracks, or bubble formation during column operations. However, small fines of some of the SuperLig[®] resins are generated due to stresses caused by osmotic shock when the resin particles are contacted with solutions of different pH and ionic strength. Continuous bleeding of dark, brown-colored solution from the SuperLig[®] 644 resin bed was observed when the bed was left in de-mineralized water and also after the liquid passing through the resin bed had changed from acid to base. This suggests a slow decomposition of the organic resin.

INTRODUCTION

The conceptualized process for pretreatment of Hanford High Level Waste decontaminates radioactive solutions by ion exchange removal of Cs¹³⁷ with SuperLig[®] 644 or 632 resins, Tc⁹⁹ removal with SuperLig[®] 639, and sulfate ion removal with SuperLig[®] 655. SuperLig[®] resins, like several other organic resins, exhibit changes in volume as a result of changes in pH and ionic strength of the solution.¹ SuperLig[®] 644 resin beds, in particular, have been observed to shrink and swell, both horizontally and vertically, depending on the Hanford Tank Waste sample being processed.² Thus, the resin is pretreated to avoid rapid breakthrough and subsequent loss of column performance due to channeling. A key requirement for successful pretreatment of new "as received" SuperLig[®] 644 resin is an acid/caustic pretreatment that must yield similar swelling characteristics to the solution being processed.³

The objective of this study was to achieve a fundamental understanding of SuperLig[®] resin swelling and shrinking characteristics, which lead to channeling and early breakthrough during loading cycles. The density of salt solution that causes resin floating was also determined to establish a limit for operation. Specific tests performed

include (a) pH dependence, (b) ionic strength dependence and (c) buoyancy effect vs. simulant composition.

EXPERIMENTAL

Materials: The ion exchange materials used in the swelling and shrinking experiments were SuperLig[®] 644 (batches # 644BZ and 981020MB48-563), SuperLig[®] 632 (batches #980715046SMC and 981015SMC-11-80), and SuperLig[®] 639 (batch # 980624001DC). These resins were obtained from IBC Advanced Technologies, Fork, Utah. The measured particle density of new, hydrated resin and the particle size analysis of the resins are listed in Tables 1 and 2. The "Physical Characteristics" section discusses measurement of these material properties. Nitric acid, sodium hydroxide, and simulant solutions were prepared from ACS certified, high-purity reagents from Fisher Scientific, Inc. The concentrations of chemical species in the preparation of simulant solutions are listed in Table 3.

Table 1. Physical characteristics of "as received" SuperLig[®] resin

Resin	Batch #	Particle density (g/mL)	Bulk dry density (g/mL)	water content original (%)	Particle size range (μm)
SuperLig 644	644BZ	1.611	0.793	10	212-600
SuperLig 644	981020MB48-563	1.549	0.758	9.6	62-600
SuperLig 632	980715046SMC	na	0.502	na	62-600
SuperLig 632	981015SMC-11-80	1.221	0.538	10.3	212-600
SuperLig 639	980624001DC	1.219	0.489	1.4	-
SuperLig 639	981015DHC720011	1.147	0.468	1.3	-

Table 2. Particle size distribution of "as received" resins

	wt% greater than (μm)			
	600	425	212	62
SL632 (980715046SMC)	0	40	48	12
SL632 (981015SMC-11-80)*	61	24	15	1
SL644 (644BZ)	14	44	40	0
SL644 (981020MB48-563)*	51	22	24	3

* 2-L batch

Table 3. Composition of simulant solutions

0.75 M Hydroxide		2.00 M Hydroxide	
Chemical	Concentration (M)	Chemical	Concentration (M)
NaAlO ₂	0.759	NaAlO ₂	0.759
NaCl	0.163	NaCl	0.163
Na ₂ SO ₄	0.029	Na ₂ SO ₄	0.029
Na ₂ CO ₃	0.306	Na ₂ CO ₃	0.306
NaNO ₂	1.282	NaNO ₂	1.282
NaNO ₃	1.376, 2.376, 3.376, 5.376*	NaNO ₃	1.376, 2.376, 3.376, 5.376*
Total Na ⁺	5, 6, 7, 9	Total Na ⁺	5, 6, 7, 9

* Note: Solutions were prepared at each NaOH concentration with different amounts of NaNO₃ to give a range of total sodium concentrations.

Equipment and Procedure:

Two identical ion exchange columns were assembled. The columns were made of Pyrex glass and had an inside diameter of 2.5 cm and a total length of 30 cm. The resin bed was retained in place by a stainless steel mesh screen, but the top of the bed was unobstructed and free to accommodate resin volume changes. A ruler affixed to the column walls was used to measure resin height changes. Solutions were introduced at the top of the columns and allowed to drain downward by gravity at nearly constant flow rate (i.e. specified number of column volumes per hour). If the top surface of the resin bed was disturbed by the introduction of liquid, it was re-leveled by gentle stirring and the exterior of the column was tapped to promote re-settling. The liquid in the column headspace was minimized between solution cycles to reduce mixing.

The essential steps for resin pretreatment are summarized as follows:

- (1) In a bottle, soak resin with de-mineralized water overnight and decant dust and other floating particulate matter
- (2) Transfer resin into column with de-mineralized water while tapping column sides with a rubber stopper to ensure uniform packing.
- (3) Gravity flow aqueous base (0.25 M sodium hydroxide) followed by de-mineralized water rinse, dilute nitric acid (0.5 M) elution, de-mineralized water rinse, and aqueous base regeneration, all at approximately three column volumes per hour.
- (4) Measure swollen resin bed height and calculate resin bed volume. Record observations as related to resin floating, bubble formation, cracks, and effluent color changes.

Details of the procedures used to determine resin swelling and buoyancy characteristics with changing solution pH, ionic strength, and simulant composition are given below:

pH dependence column test:

Freshly pretreated resin beds in duplicate, 2.5-cm diameter columns were contacted with aqueous base of varying concentrations (0.5 M to 10 M) by carefully adding solution to the top of the columns. Gravity flow of solutions through the resin bed was adjusted to approximately three column volumes per hour using metering valves at the bottom of each column. The height of the resin bed was measured after every half-hour using the ruler fixed to the column wall. The resin bed volume changes (swelling and shrinking) were calculated from the cross-sectional area of the columns and the height of the resin bed before and after 1.5 column volumes of effluent was collected. Addition of more aqueous solution of the same concentration was continued until two consecutive resin bed volume measurements were identical. If present, observations related to resin bed deformation, cracks, bubble formation, and effluent solution color changes were recorded.

The pH dependence test was terminated after a portion or all of the resin bed floated over the full length of the liquid headspace and remained suspended for more than 30 minutes. The resin bed was then rinsed with de-mineralized water, followed by 0.5 M nitric acid elution, de-mineralized water rinse, and an aqueous base (0.25 M sodium hydroxide) regeneration. All rinse, elution, and regeneration solutions were passed through the column at three column volumes per hour or until two consecutive measurements of the resin height were identical. The resin bed was stored in dilute aqueous base or in de-mineralized water for storage periods of more than three days.

Ionic strength dependence column test:

After completion of the pH dependence test, the regenerated resin bed was contacted with salt solutions containing various concentrations of sodium nitrate in 0.25 M sodium hydroxide solution. Sodium nitrate salt solutions were carefully added to the top of the resin bed and allowed to flow by gravity usually at three column volumes per hour, but occasionally performed at two column volumes per hour. The height of the resin bed was measured at half-hour intervals or when approximately one and one-half column volumes of effluent were collected. At the completion of the sodium nitrate solution addition cycle or when the resin bed floated, the column was contacted with 0.25 M sodium hydroxide to remove residual nitrate solutions. The bed was then contacted with salt solution containing sodium sulfate in 0.25 M sodium hydroxide at three column volumes per hour or until two consecutive resin bed volume measurements were identical. If applicable, observations of bed deformation, cracks, bubble formation, and effluent color changes were recorded.

At the conclusion of the ionic strength test, the bed was rinsed with de-mineralized water, followed by 0.5 M nitric acid elution, de-mineralized water rinse, and aqueous base (0.25 M sodium hydroxide) regeneration. The resin bed was stored in dilute aqueous base or in de-mineralized water for storage periods of more than three days.

Buoyancy vs. simulant composition test:

Upon completion of the ionic strength test, the buoyancy effect vs. simulant composition test was conducted with the regenerated resin bed. A simulant containing a constant 0.75 M free hydroxide (OH⁻) ion concentration along with 5, 6, 7, or 9 M sodium ion was carefully added to the top of resin bed. The balance of non-hydroxide anions was a mixture of nitrite, nitrate, aluminate, chloride, sulfate, and carbonate ions as shown in Table 3. The column effluent was collected at 1.5 column volumes in half-hour intervals. At the end of each interval, the resin bed height was measured with the ruler affixed to the column wall and the resin bed volume was calculated as described previously. Observations related to resin flotation, bed deformation, cracks, bubble formation, and effluent color changes were recorded. At the conclusion of the 0.75 M free hydroxide (OH⁻) ion simulant contacts, the liquid in the column headspace was drained to approximately 0.5 cm above the resin bed surface and resettled by tapping the exterior of the columns with a rubber stopper. The bed was then contacted with simulant containing 2.0 M free hydroxide (OH⁻) ion along with 5, 6, 7, or 9 M sodium ion in the same manner as described above. The buoyancy vs. simulant composition test was terminated when the resin bed floated in any one of the solutions mentioned above. Upon termination, the bed was rinsed with de-mineralized water, followed by a 0.5 M nitric acid elution, a de-mineralized water rinse, and an aqueous base regeneration, all at three column volumes per hour or until two consecutive resin bed height measurements were identical. The buoyancy of the second batch (981015DHC720011) of SuperLig[®] 639 was measured by placing the "as received" resin in centrifuge tubes containing 5.0 M Na⁺ Envelope A simulant (specific gravity 1.22 g/mL).

Physical Measurements

The physical characteristics of the "as received" resins were measured without prior treatment. The specific gravity of the resins was measured using a pycnometer filled with de-mineralized water. The water content of the "as received" resins was determined by weight difference between the received resins and resins dried at 95 °C for 24 hours. The resin particle size distributions were determined by a standard sieve analysis.

RESULTS AND DISCUSSION

The resin swelling characteristic of SuperLig[®] resin was studied in small column tests using solutions with varying pH and ionic strength. The swelling and shrinking measurements were performed on several IBC SuperLig[®] resins, namely: SuperLig[®] 644, 632 and 639, although the bulk of the testing was with SuperLig[®] 644, since this resin was known to swell more than the other resins. The "as received" resins were pretreated with an acid/caustic cycle with a de-mineralized water rinse between cycle sequences. This pretreatment procedure was repeated at the conclusion of each test segment. A dark, brown-colored effluent solution was observed during the acid/caustic pretreatment cycles of SuperLig[®] 644 resin, and when the resin was left standing in de-mineralized water over a short period of time. The brown color of the effluent becomes light yellow during the column rinsing and it completely disappears within the first 2-3 column volumes. The density and color of the SuperLig[®] 644 effluent solutions are shown in Table 4. The

SuperLig® 632 and 639 effluents were yellow during the initial resin pretreatment, but were colorless during all other experiments except when the SuperLig® 632 decomposed (see below).

Table 4. Density and color of effluent solutions from SuperLig® 644 - pH dependence

Effluent solution after contact w/	Density- column # 1 (g/mL)	Description
0.25 M NaOH	0.989	Dark brown
0.5 M NaOH	0.993	Brown tint
1.0 M NaOH	1.081	Light brown
3.0 M NaOH	1.011	Yellow tint
5.0 M NaOH	1.117	Yellow tint
7.0 M NaOH	1.193	Light tint
8.0 M NaOH	1.221	Light tint
9.0 M NaOH	1.248	Almost clear
10.0 M NaOH	1.279	Clear
11.0 M NaOH	1.307	Clear
Di-H ₂ O post	1.069	Brown tint
0.5 M HNO ₃	1.005	Light yellow tint
Di-H ₂ O post	0.993	Almost clear

The results for the acid/caustic pretreatment of the "as received" SuperLig® 644 and 639 resins are presented in Figures 1(a,b) and 2. The abscissa of the two figures shows the volume of effluent collected and the ordinate shows the resin volume changes per unit mass. It can be seen that the SuperLig® 639 resin bed (Figure 2) did not change during the acid/caustic cycle. In contrast, the SuperLig® 644 resin bed volume increased from 1.5 mL/g in de-mineralized water to 2.70 mL/g, or an increase of more than 80%, after contact with three column volumes of an aqueous base (0.25 M sodium hydroxide). Replacement of the aqueous base with nitric acid solution results in a decrease in the resin bed volume to about 1.8 mL/g, which is slightly higher than its initial swollen volume in de-mineralized water. The maximum swollen bed volume of 3 mL/g was observed at the end of the acid/caustic cycle and that corresponds to a net resin volume increase of 100% or 2x the initial bed volume of the fresh resin in de-mineralized water.

This observation of resin bed volume expansion points to the safety consideration that the resin must be swelled in sodium hydroxide solution prior to charging large columns. Swelling the resin after charging the columns with SuperLig[®] 644 may result in shattering brittle columns (glass or plastic) or severe compression of the resin leading to reduced flow rates in rigid columns (metal). Using an upflow of sodium hydroxide solution to suspend the resin while swelling it may avoid this problem, although it has not been shown that this method will yield a well-packed column. The difference in the resin bed volume between the first and second caustic treatments (i.e., 2.70 mL/g vs. 3.0 mL/g) may be attributed to hindered expansion from charging the column with unswollen resin.⁴ As the resin expanded during the first caustic cycle, it may have been compressed against the side of the column wall and unable to migrate upward to fully expand. Alternatively, the acid elution step may have altered the chemical or physical form of the resin, increasing its capacity for sodium ion and thereby causing more swelling.

The variation in resin bed height is also associated with a similar variation in the flow rate as the liquid is drained from the bottom. During the acid cycle when resin shrinking was occurring, the resin released water into the surrounding acid solution and the effluent volume was higher than expected. Likewise, when swelling was occurring during caustic resin hydration, a net shift of water into the resin phase took place and the influent liquid volume was increased to maintain a near constant effluent volume. These observations were recorded for various SuperLig[®] 644 pretreatment column runs and are deemed necessary to consider in large-scale operation. As the resin shrinks during the elution, more water is in the aqueous phase than in the solid phase (absorbed in the resin). This corresponds to one-half of the (swelled) resin volume. This will cause increased mixing in the column headspace of the subsequent water washes and caustic regenerate, i.e., the resin volume in the full-scale system is only ~25% of the total column volume, not 50% as during operation.

For some experiments, the flow rate of liquid through the column was two column volumes per hour instead of three column volumes per hour. This was due to setting the effluent metering valve during initial water washes and not adjusting it with different solutions. As the resin swelled during caustic solution treatment, the resistance to flow increased and the gravity flow rate decreased. Although only two column volumes of solution passed through the resin in these cases, the resin bed height remained unchanged between readings, indicating that the resin had reached equilibrium.

The first nitric acid (0.5 M) treatment of SuperLig[®] 632, batch # 980715046smc, resulted in significant formation of gas bubbles within the resin bed, although subsequent treatments of this batch with nitric acid did not result in gas formation. In addition, when this batch of SuperLig[®] 632 resin was left standing in aqueous base (5 M sodium hydroxide), the resin partially disintegrated to fine beige particles and the flow rate through the resin bed was severely restricted. Closer inspection revealed that the resin bed was no longer composed of discrete particles, but was compacted into a viscous solid mass, which could only be removed from the column by breaking up the solid with a glass rod. Subsequent washing of the bed resulted in the loss of 50% of the total resin volume as fine particles suspended in the wash solution. The color of the liquid in the

column headspace was yellow and turbid. The problems, such as gas bubble formation with nitric acid, partial resin disintegration, and flow rate restrictions, that were encountered with SuperLig[®] 632 resin (batch # 980715046smc) were not observed with the latter batch # 9801015smc-11-80. This latter batch was washed repeatedly with de-mineralized water to remove fine particulate matter, which amounted to as much as 2% of the total resin weight. The acid/caustic cycle was then conducted batchwise in polyethylene bottles. When the resin was contacted with concentrated base (10 M sodium hydroxide), some fines became suspended at this concentration perhaps due to the effect of osmotic shock, which could result from prior acid/caustic cycles and concentrated base solution contacts.

Figures 3 and 4 show the swelling and shrinking behavior of SuperLig[®] 632 and 644, respectively, due to varying concentrations of base, followed by de-mineralized water rinse, dilute acid elution, and caustic regeneration. The portion of the data from Figure 4 that illustrates the effects of increased concentration of base on SuperLig[®] 644 resin swelling and shrinking characteristic is re-plotted in Figure 5. Since SuperLig[®] 639 resin was not expected to swell or shrink with changing base concentration, the pH dependence tests were not performed for this resin. As shown in Figure 3 the external solution pH has little or no effect on swelling of SuperLig[®] 632. However, it is noted in Figures 4 and 5 that SuperLig[®] 644 swells over a narrow range of concentrations of base where the resin is being hydrated. A further increase in the concentration of base dehydrates the resin, which results in resin bed shrinkage. Thus, the swollen resin volume decreased from 2.90 to 2.35 mL/g as the concentration of base was increased from 0.5 to 10 M sodium hydroxide (sections 1-8, Fig. 4 and Fig. 5). At 10 M sodium hydroxide, a portion of the resin particles was suspended over the full length of the liquid headspace, but gradually settled within 20 minutes. A stable suspension of the SuperLig[®] 644 resin bed was not observed over the range of concentrations examined.

Decomposition of the first batch of the SuperLig[®] 632 (batch #981015smc) occurred at high sodium hydroxide concentration (5 M). While this concentration is not expected in the Hanford tank waste, this behavior suggests that long-term exposure at sodium hydroxide concentrations lower than 5 M should be examined. The second batch of this resin (#98715046smc-11-80) was stable up to 10 M sodium hydroxide. The vendor's treatment of this latter batch of the SuperLig[®] 632 resin appears to have significantly improved the stability of the resin as compared to the first batch.⁴ Additional stability tests under realistic conditions will be performed with the selected resin as part of upcoming pilot-scale tests. In addition, the vendor claims that a slight change in the resin manufacturing process⁴ avoided the gas bubbles generated in the first batch (#98715046smc) of SuperLig[®] 632, and this problem is not expected to recur with the latter batch (# 981015smc-11-80).

The addition of de-mineralized water into dehydrated SuperLig[®] 644 resin following the base treatment caused an osmotic shock that abruptly increased the resin volume beyond the initial hydrated swollen volume. This was followed by a gradual decrease in resin bed volume after the resin was contacted with de-mineralized water to rinse the bed (section 9, Fig. 4). The introduction of nitric acid and the de-mineralized

water rinse that follow caused a net bed volume decrease to 1.4 mL/g resin (sections 9 and 10, Fig. 4), or a bed volume shrinkage of 80%. Caustic regeneration caused the resin bed to recover slightly above its initial swollen volume.

The effects of increased ionic strength (i.e. increasing sodium nitrate and sodium sulfate concentrations) of an aqueous sodium hydroxide solution on the swelling and shrinking behavior of SuperLig[®] 644 and 632 resins are shown in Figures 6 and 7, respectively. The data represented in Figures 6 and 7 also include the resin bed volume changes with de-mineralized water rinse, acid elution, and base regeneration. As shown in Figure 7, an increase in ionic strength of the external solution had limited effect on SuperLig[®] 632 swelling and shrinking behavior. However, approximately 20% of the resin bed floated in aqueous base containing 5 M sodium nitrate salt solution, with very slow settling. With 7 M sodium nitrate/hydroxide solution, the majority of the SuperLig[®] 632 resin bed floated and did not settle. The small resin fines in suspension may have been generated due to repeated osmotic shock during loading and elution cycles, or may have been present in the "as-received" resin. Although the resin had not floated in 10 M sodium hydroxide solution, but floated in 7 M sodium nitrate solution, the solutions are roughly equal in density and only slight differences in disturbance of the resin may account for the behavior. Figures 6 and 8 show that SuperLig[®] 644 had swollen over a narrow range of increased ionic strength where the resin bed is being hydrated and then, as expected, a further increase in the ionic strength dehydrates the resin, resulting in reduced volume. In 5 M sodium nitrate/hydroxide salt solution, a small portion of the SuperLig[®] 644 resin bed was suspended over the full length of the liquid headspace, but gradually re-settled. No deleterious effects on resin bed packing conditions, such as cracks or gas bubbles were observed.

The buoyancy effects of simulant solutions containing varying concentrations of sodium ions and free hydroxide ions on SuperLig[®] 644 resin are shown in Figure 9 (sections 1-7). The data from the buoyancy effect vs. simulant test on SuperLig[®] 644 are re-plotted in Figure 10. These results indicate that the resin shrinks gradually as the concentration of sodium ion in solution is increased at constant free hydroxide ion. While a small portion of the resin bed was suspended when disturbed by pouring liquid into the column, the resin immediately re-settled at the lower end of the concentration range (5-6 M Na⁺). At the higher end of the range (7-9 M Na⁺), a fraction of the resin particles on the top of the bed became suspended over the full length of the column headspace and remained suspended in solution for more than 20 minutes. The entirety of the SuperLig[®] 644 resin bed did not float over the range of concentrations examined. No deleterious effects on resin bed packing conditions, such as cracks or gas bubbles were observed.

The swelling effects of the simulant on SuperLig[®] 632 and 639 resins were minimal after contact with simulant containing 6.0 M Na⁺ and either 0.75 or 2.0 M free hydroxide ions. However, the resin beds of both ion exchange materials floated in simulants containing 6.0 M Na⁺ and either 0.75 or 2.0 M free hydroxide ions. A significant portion (~40%) of the second batch (981015DHC720011) of SuperLig[®] 639 floated in the 5.0 M Envelope A simulant which had a specific gravity of 1.22 g/mL. This is consistent with the measured average particle density of 1.147 g/mL (Table 1).

Smaller portions of the resin floated in 2.0 M simulant, indicating a wide range of particle densities. Vacuum and pressure were applied to the resin and liquid to ensure that air was not entrained in the beads, but no change was observed. Heating the samples increased the portion of resin that floated. A possible explanation for inconsistencies observed in SuperLig[®] 632 floating tests is that the behavior appears dependent on both solution density and resin history. If the resins are settled into a single bed using dilute solution (0.5 M NaOH), subsequent treatment with a high density solution (10 M NaOH) does not appear to break up the bed. However, if the dry resins are introduced directly into a high density solution, they separate into floating and sinking fractions, which do not easily form a contiguous bed. The SuperLig[®] 639 behavior appeared to be less dependent on resin bed history. It is not known if this effect will be observed on large diameter columns, where wall effects are less significant. Samples of SuperLig[®] 632 received after these tests were complete indicated that treatment with 1 M NaOH swelled the resin by approximately 25%. However, the resin volume did not change further with either acid or caustic treatments.

In the period between the ionic strength effect test (Figure 6) and the simulant composition tests (Figure 9), the SuperLig[®] 644 resin shrank. This was apparently due to gravity settling over the four days of quiescent storage in 0.25 M sodium hydroxide solution. Addition of liquid to the top of the column caused disturbance of the surface of the resin bed. This is an artifact of the experimental method throughout these tests, but likely has no impact upon the results due to the slow settling rate of the resin. The settling that occurred over a single night was minimal.

The particle size distributions of the resins vary considerably between batches (Table 2). Variability in particle sizes can affect the ion exchange kinetics, and thereby impact the breakthrough profile. It is not known if the variances observed here are adequate to measurably impact performance of a large-scale column. Further testing would be needed to determine if this is significant.

PRETREATMENT IMPACT

During "Part A" testing of SuperLig[®] 644 resin, radioactive cesium frequently broke through ($C/C_0 > 0.10$) the column within 10 column volumes of operation. The key pretreatment steps for new resin included charging the column with swollen resin, "activating" the resin by performing a 0.5 M nitric acid elution, and pre-swelling the resin with varying concentrations of sodium hydroxide solution³.

Hanford Waste Envelope characteristics and the concentration of sodium hydroxide used for pre-swelling are shown below (all units in Molarity).

Envelope	[Na ⁺]	free [OH ⁻]	[NaOH] used for swelling
A	5.07	2.33	1.0
B	5.7	2.25	0.25
C	5.7	0.3*	0.25

*Sodium hydroxide solution was added to Envelope C to increase the free hydroxide concentration by 0.3 M. Initial analysis of free hydroxide was complicated by the presence of organic bases yielding 0.394 M free hydroxide.

The swelling data presented above for high ionic strength solutions (5-7 M Na⁺) appear to be relatively small changes in the volume of SuperLig[®] 644 resin. These changes are thought to be too small to account for the large differences in the behavior of the resin with each envelope. Based on the above characterization of Envelope A, B, and C, it would appear that all three envelopes should be pretreated in the same way. However, this was not the case in "Part A" testing, where Envelope B and C were successfully pretreated differently from Envelope A. Although the impact of ionic organic compounds in "C" has not been established, the present study suggests that the difference in hydroxide concentration used for swelling was not important, as the difference between 0.25 M NaOH and 1 M NaOH was minimal.

A review of "Part A" data suggests that resin pretreatment with nitric acid shortly before initiating column runs was vital to successful column performance. In the case of Envelope A, the resin was new and the acid cycling occurred just prior to initiating the column run. For Envelope C (next in chronological order), the resin sat idle for 11 days in 0.25 M sodium hydroxide solution prior to commencement of the successful run. Earlier treatments with 1.0 M sodium hydroxide were unsuccessful, so the resin was eluted and pretreated with 0.25 M sodium hydroxide. Although it was not eluted immediately before the column run, flushes with de-mineralized water occurred in the eleven day storage period prior to the column run. The column was again flushed with six column volumes of dilute caustic (0.25 M sodium hydroxide) immediately before the run. Likewise, resin used for Envelope B was unsuccessfully pretreated with 1 M sodium hydroxide and was later eluted and pretreated with six column volumes of dilute caustic (0.25 M sodium hydroxide) just prior to initiating the successful test.

These observations, coupled with the observations of colored effluent from thoroughly washed resin and high eluant Total Organic Carbon measurements observed during Part A tests, suggest that the resin is losing organic material from its polymer matrix during the nitric acid elution. This soluble organic material may, therefore, be interfering in the cesium exchange by complexing it in solution. This explanation for the observed early breakthrough of cesium from SuperLig[®] 644 was first postulated by the vendor.⁴ Alternatively, perhaps the organic material blocks resin pores or surfaces and obstructs cesium diffusion. It may also simply be that a 1.0 M sodium hydroxide pretreated SuperLig[®] 644 resin with only three column volumes was strained and became susceptible to osmotic shock when contacted with Envelopes C and B. When the pretreatment was done with six column volumes of 0.25 M sodium hydroxide, an orderly

swelling of the resin may have eliminated the osmotic shock. To verify if any postulated explanation is correct, longer-term storage and elution tests are needed. These tests are also important to operation of the resin beds, as processing delays may cause loss of organic material from the resin. If the cesium also releases and is complexed by the organic, it may not be removed by a guard column or by recycling. Likewise, significant care must be taken to prevent mixing the pretreatment or rinse solutions with the feed, as the presence of complexing organic may prohibit subsequent removal of cesium. While this scenario has not yet been proven, research is needed to verify if this is a valid explanation for the observations.

CONCLUSIONS

The swelling and shrinking characteristics of SuperLig[®] resins from IBC Advanced Technologies were examined. The "as received" SuperLig[®] resins were pretreated with an acid/caustic cycle before testing the effects of ionic strength and concentration of base (pH dependence). The buoyancy effect of simulant on resin was also examined.

Swelling and shrinking of SuperLig[®] 639 resins was not significant during any acid/caustic pretreatment cycle. Swelling and shrinking of SuperLig[®] 632 resins was not observed with the second batch discussed above. Subsequent samples have shown ~25% swelling during the first caustic treatment, but subsequent acid or caustic cycles do not change the resin volume. The change in pH and ionic strength of the external solution had no obvious swelling and shrinking effects on the second batch of SuperLig[®] 632 resin. However, a portion of this resin, which consist of small fines, floated in aqueous solution containing 5 M sodium nitrate/hydroxide salt. The fine particles are presumably generated due to the effect of osmotic shock during loading and eluting cycles. Complete suspension of both SuperLig[®] 632 and 639 occurred in simulant solutions containing 6 M sodium ion with either 0.75 or 2 M free hydroxide ions. Partial suspension of the second batch of SuperLig[®] 639 occurred in 5 M sodium ion simulant (specific gravity = 1.22 g/mL). It is recommended that the specific gravity of the ion exchange influent not exceed 1.22 g/mL with the current resin formulations. The resin should be placed into a solution with a specific gravity of 1.22 g/mL and the floating portion discarded prior to packing a column. If other studies indicate that the resin columns may heat up during process upsets and external cooling is required, the external cooling of the full-scale columns should extend for the entire height of the ion exchange column. Otherwise, if the specific gravity of the beads and solution are nearly identical, heating the resin may cause the bed to float. If the cooling system were only on the lower half of the columns, it would not be effective on a floating bed.

SuperLig[®] 644 resin swelling and shrinking was significant during the acid/caustic pretreatment. Appreciable resin swelling was observed when the bed was in contact with an aqueous base. Likewise, the resin bed was observed to shrink when in contact with a dilute nitric acid solution. The percent volume change of SuperLig[®] 644

resin between an acid and a caustic cycle is more than 82%. This behavior must be considered when designing facilities and procedures for handling this material to prevent column breakage or resin compression. Likewise, the resin volume reduction during acid elution will increase the amount of mixing of solutions in the column headspace, increasing the potential for undesirable chemical reactions.

SuperLig® 644 swells moderately over a narrow range of increased ionic strength and base concentrations (pH) where the resin is being hydrated. The resin bed shrinks gradually as the concentration of base increases further. Likewise an increase in the ionic strength further shrinks the resin due to resin dehydration caused by osmotic effect. The resin bed did not float over the range of solution concentrations examined. However, portions of the resin particles were suspended at sodium concentrations $> 6 \text{ M}$. This was due to disturbance of the resin bed surface during liquid addition and to the near identical particle and liquid specific gravity.

Despite the swelling and shrinking of SuperLig® 644 resin bed with varying ionic strength and solution pH, the resin beds remained coherent and showed no strenuous effects such as deformation, cracks, and bubble formation. However, the SuperLig® 644 resin is prone to continuous leaching of brown color when in contact with a dilute aqueous base.

Performance of the second batch of the SuperLig® 632 resin corroborates the vendor's (IBC Advanced Technologies, Inc.) claims of improved chemical stability for SuperLig® 632. Further refinements in the manufacturing methods for SuperLig® 632 are expected to improve this resin thereby decreasing the replacement frequency. Additional chemical stability tests should be performed under more realistic plant conditions in the pilot-scale unit, if SuperLig® 632 resin is selected for use.

The presence of color in any resin effluent solution should be considered to contain cesium (SuperLig® 632 or 644) or technetium (SuperLig® 639) selective chelating agents. Introducing these solutions to the feed solution may prohibit uptake of the radioisotope by the ion exchange resin due to competition from the soluble chelant. If mixing of these solutions is inevitable, testing should be performed to determine if this potential effect will impact column performance. The absence of color in ion exchange column effluent may not indicate that chelating materials are absent, and mixing ion exchange resin effluent solutions with the feed should be avoided in all cases unless proven inconsequential.

Pretreatment of SuperLig® 632 and 639 can be performed as recommended by the vendor, as limited swelling of these resins is observed. Pretreatment should include washing new resin with acid to prevent bubbling, or allowing for re-packing the bed after the first acid elution. After any acid treatment, acidic sites on the resin must be completely neutralized prior to introduction of feed solution. Also, osmotic shock to the resin should be minimized by gradual changes in liquid composition. The recommended pretreatment for SuperLig® 632 is included below. However, this procedure has not

been verified with all waste envelope types, so additional studies are needed for confirmation. SuperLig® 639 pretreatment can be limited to steps 4-7.

1. Place new SuperLig® 632 resin in a bottle of water, soak 1 hour
2. Decant water and carefully replace with 0.5 M HNO₃ (10:1 Liquid:resin volume), (LOOSELY CAP TO VENT CO₂ GAS) gently shake for 2 hours
3. Decant acid, replace with water, gently shake for 1 hour
4. Decant water, replace with 1 M NaOH (10:1 v/v), gently shake for 2 hours
5. Slurry resin into column
6. Pump through 1-2 CV of fresh 1 M NaOH
7. Introduce feed

Pretreatment of new or used SuperLig® 644 should be initiated within 24 hours prior to any column runs. It appears that a concentration of 0.25 M sodium hydroxide is adequate for swelling the resin. The pretreatment sequence is summarized below, where steps 1 to 5 apply only to packing a new column and steps 4 and 5 apply only to laboratory scale columns.

1. Soak in 1.0 M NaOH (~10:1 vol:vol) for 2 hrs (gentle shaking)
2. Decant NaOH and add d.i. water
3. Slurry resin into column
4. Tamp resin with glass rod
5. Pack top of resin with glass wool (and glass beads if necessary)
6. Pump 3 column volumes (C.V.) of 0.5 M HNO₃ in 1 hour
7. Pump 3 C.V. of d.i. water in 1 hour
8. Pump 6 C.V. of 0.25 M NaOH in 1 hour
9. Pump 3 C.V. of d.i. water in 1 hour
10. Initiate column run

DESIGN CHECK

M.C. Thompson 3/29/99
M.C. Thompson Date
Chemical and Hydrogen Technology

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Figure 1(a). Pretreatment of "as received" superlig 644 resin - acid/caustic cycle

1 = 0.25 M NaOH
2 = de-mineralized water
3 = 0.5 M HNO₃
4 = de-mineralized water
5 = 0.25 M NaOH

—○— column 1
—▽— column 2

column i.d.=2.5 cm
resin = superlig 644
batch # = 644BZ

Figure 1(b). Pretreatment of "as received" Superlig 644 resin -caustic/acid/caustic cycle

- 1 = 0.25 M NaOH
- 2 = de-mineralized water
- 3 = 0.5 M HNO₃
- 4 = de-mineralized water
- 5 = 0.25 M NaOH

column i.d.=2.5 cm

—○— SuperLig 644 batch #981020mb48-563

Figure 2. Pretreatment of "as received" SuperLig 639

1 = 0.25 M NaOH
2 = de-mineralized water
3 = 0.5 M HNO₃
4 = de-mineralized water
column i.d.=2.5 cm
resin = superlig 639
batch # = 980624001DC

—○— SuperLig 639 resin

Figure 3. The effect of varying concentration of base on resin volume changes

1 = 0.25 M NaOH

2 = 0.5 M NaOH

3 = 1.0 M NaOH

4 = 3.0 M NaOH

5 = 5.0 M NaOH

6 = 7.0 M NaOH

7 = 8.0 M NaOH

8 = 9.0 M NaOH

9 = 10 M NaOH

10 = de-mineralized water

11 = 0.5 M HNO3

12 = de-mineralized water

column i.d.=2.5 cm

resin = superlig 632

weight = 17.219 g

batch # = 981015smc-11-80

—△— superlig 632

Figure 4. The effect of varying concentration of base on resin volume changes

1 = 0.5 M NaOH
 2 = 1.0 M NaOH
 3 = 3.0 M NaOH
 4 = 5.0 M NaOH
 5 = 7.0 M NaOH
 6 = 8.0 M NaOH
 7 = 9.0 M NaOH
 8 = 10 M NaOH
 9 = Di-H₂O
 10 = 0.5 M HNO₃
 11 = Di-H₂O
 12 = 0.25 M NaOH

column i.d.=2.5 cm
 resin = superlig 644
 resin wt. = 23.004 g (column #1)
 resin wt. = 23.002 g (column #2)
 batch # = 644BZ

—○— column (1)
 —◇— column (2)

Figure 5. Dependence of resin swelling and shrinking on sodium hydroxide concentration

column i.d.=2.5 cm
resin = superlig 644
resin wt. = 23.004 g (column #1)
resin wt. = 23.002 g (column #2)
batch # = 644BZ

Figure 6. The effect of ionic strength of external solution on resin bed volume

1 = 0.25 M NaNO₃/0.25 M NaOH
 2 = 0.75 M NaNO₃/0.25 M NaOH
 3 = 2.75 M NaNO₃/0.25 M NaOH
 4 = 4.75 M NaNO₃/0.25 M NaOH
 5 = 0.25 M NaOH
 6 = 0.375 Na₂SO₄/0.25 M NaOH
 7 = 2.375 Na₂SO₄/0.25 M NaOH
 8 = Di-H₂O
 9 = 0.5 M HNO₃
 10 = Di-H₂O
 11 = 0.25 M NaOH

column i.d. = 2.5 cm
 resin = superlig 644
 resin wt. = 23.004 g (column #1)
 resin wt. = 23.002 g (column #2)
 batch # = 644BZ

—○— column 1
 —▽— column 2

Figure 7. Effect of ionic strength of the external solution on resin volume changes

- 1 = 0.25 M NaOH
- 2 = 0.25 M NaNO₃/0.25 M NaOH
- 3 = 0.75 M NaNO₃/0.25 M NaOH
- 4 = 2.75 M NaNO₃/0.25 M NaOH
- 5 = 4.75 M NaNO₃/0.25 M NaOH
- 6 = 0.25 M NaOH
- 7 = 0.375 M Na₂SO₄/0.25 M NaOH
- 8 = 2.375 M Na₂SO₄/0.25 M NaOH
- 9 = de-mineralized water
- 10 = 0.5 M HNO₃
- 11 = de-mineralized water
- 12 = 0.25 M NaOH (extended storage)

column i.d.=2.5 cm
 resin = superlig 632
 weight = 17.219 g
 batch # = 981015smc-11-80

—○— superlig 632

Figure 8. Dependence of resin swelling and shrinking on ionic strength

column i.d.=2.5 cm
resin = superlig 644
resin wt. = 23.004 g (column #1)
resin wt. = 23.002 g (column #2)
batch # = 644BZ

Figure 9. Buoyancy effect of simulant on superlig 644 resin volume changes

1 = 5 M Na⁺/0.75 M OH⁻
 2 = 6 M Na⁺/0.75 M OH⁻
 3 = 7 M Na⁺/0.75 M OH⁻
 4 = 5 M Na⁺/2.0 M OH⁻
 5 = 6 M Na⁺/2.0 M OH⁻
 6 = 7 M Na⁺/2.0 M OH⁻

7 = De-mineralized water
 8 = 0.5 M HNO₃
 9 = De-mineralized water
 10 = 0.25 M NaOH

column i.d.=2.5 cm
 resin = superlig 644
 resin wt. = 23.004 g column 1
 resin wt. = 23.002 g column 2
 batch # = 644BZ

—◇— column 1
 —○— column 2

Figure 10. Effects of sodium ion concentration in simulant on resin swelling and shrinking