PNWD-3265
WTP-RPT-037, Rev. 0

Batch Contact Testing of SuperLig® 644

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WTP
Project
Report

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under Contract 24590-101-TSA-W0000-0004

LEGAL NOTICE

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Batch Contact Testing
Using SuperLig® 644

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Test specification: N/A
Test plan: CHG-TP-41500-014, Rev. 0
Test exceptions: None
R&T Focus Area: Pretreatment
Test Scoping Statement(s): B-49

Battelle, Pacific Northwest Division
Richland, Washington 99352

Completeness of Testing

This report describes the results of work and testing specified by CHG-TP-41500-014, Rev. 0. The work and any associated testing followed the quality assurance requirements outlined in the Test Specification/Plan. The descriptions provided in this test report are an accurate account of both the conduct of the work and the data collected. Test plan results are reported. Also reported are any unusual or anomalous occurrences that are different from expected results. The test results and this report have been reviewed and verified.

Approved:

____ __________________

Gordon H. Beeman, Manager Date
WTP R&T Support Project

____ __________________

Research and Technology Manager Date

Summary

Objectives

Battelle, Pacific Northwest Division (PNWD) is contracted to Bechtel National Inc. (BNI) on the River Protection Project – Waste Treatment Plant (RPP-WTP) project to perform research and development activities. Unit operations of the WTP process include the separation of ^{137}Cs by ion exchange from the liquid portion of the waste. The SuperLig® 644 (SL-644) ion exchange resin was selected by the project to perform this ^{137}Cs separation.

The RPP-WTP is evaluating the SL-644 resin to determine its behavior under various potential processing conditions. Under test scoping statement S-142, a model is being developed at the Savannah River Technical Center (SRTC) that will be capable of predicting the response of SL-644 under various processing conditions. This investigation was conducted according to the test plan prepared by Rapko (2001) in response to the test requirements to investigate ion exchange resin performance delineated by Barnes et al. (2002) in Section 3.2.6.1 of the Research and Technology Plan and test scoping statement B-49. The results from these tests will be incorporated into the afore-mentioned model. Objectives as noted in test scoping statement B-49 were to:

- evaluate the impact of the solution's sodium-to-cesium ratio on the SL-644 Cs-distribution ratio
- evaluate the impact of the solution's potassium-to-cesium ratio on the SL-644 Cs-distribution ratio
- evaluate the impact of the solution's ionic strength on the SL-644 Cs-distribution ratio
- evaluate the impact of time on the SL-644 Cs-distribution ratio.
- evaluate the SL-644 uranium-distribution ratio
- evaluate the impact of changing hydroxide concentration on the SL-644 Cs-distribution ratio

These results were achieved.

Conduct of Testing

A batch of SuperLig® 644 was preconditioned by contact with distilled water, followed by contact with 0.5 M nitric acid. Excess nitric acid was removed by repeated contacts with deionized water, and the resin was dried to a constant weight. Approximately 0.1 g of resin was contacted with 10 ml of a cesium (^{137}Cs spiked)-containing test solution. Sample aliquots were taken before and after contact with the resin, and their activity was analyzed by gamma energy analysis using a liquid nitrogen cooled Ge detector.

Results and Performance Against Objectives

The variables tested and a summary of key findings are given below:

1) *Room-temperature cesium K_d*[(a)] *time-dependence measurements under the base experimental conditions (initial $[Na^+]/[Cs^+] = 11000$, 5 M total sodium, 0.25 M $[OH^-]$) used for subsequent batch contacts.* The primary purpose behind this measurement was to verify that subsequent room-temperature batch contacts were performed under equilibrium conditions. It was determined from the results reported in Section 3.1 that at a shaker speed of 225 rpm, 24 h would be sufficient to achieve an equilibrium K_d value of about 1600 ml/gram. Contact times of 72 h were used in subsequent measurements to assure that these measurements were made under equilibrium conditions. However, the measured maximum Cs K_ds are substantially greater in this set of tests than were found in later measurements under comparable conditions. The reasons for this discrepancy are unknown but may be related to resin degradation in air.

2) *Evaluation of the impact of changing $[H^+]$ or $[OH^-]$ under analogous conditions (5 M total sodium, initial $[Na^+]/[Cs^+] = 11,000$) to the conditions of the room-temperature kinetics measurements.* The results reported in Section 3.2 indicate that SuperLig® 644 has little affinity for cesium when the solution hydroxide concentration is less than 0.01 M (pH 12). This supports the planned use of 0.5 M nitric acid for elution of the SuperLig® 644 resin in the WTP. However, above 0.01 M hydroxide, the cesium distribution values increase as the hydroxide concentration increases. However, the observed behavior at hydroxide concentrations greater than 0.01 M do not agree well with those found in the kinetics test, and, in selected cases, the interpretation of these results is confounded by the data's poor reproducibility.

3) *Evaluation of the impact of varying $[Na^+]$ on the Cs K_d at a constant 0.25 M $[OH^-]$).* This data set, described in Section 3.3, was plagued by poor reproducibility. However, the filtering of outlying data shows an inverse correlation of the cesium K_d to the test solution's sodium concentration at a fixed initial sodium-to-cesium ratio. It should be noted that some of this filtering cannot be justified by statistical analysis of the data. This observed correlation is expected since sodium is a competing cation for the cation-exchange sites in SuperLig® 644 and is consistent with previous report behavior for a variety of cesium-selective cation-exchange resins. It appears that the cesium K_d can be correlated to the sodium concentration with a correlation of Cs $K_d = 882–144[Na^+]$ and a correlation coefficient of 0.986.

4) *Evaluation of the impact of varying $[Na^+]/[Cs^+]$ ratio on the Cs K_d at a constant 5 M $[Na^+]$, 0.25 M $[OH^-]$).* In Section 3.4, it was found that as the $[Na^+]/[Cs^+]$ ratio increases, the cesium K_d also increases. In addition, such similar behavior has been reported in prior research involving SuperLig® 644 batch contacts with actual Hanford tank supernatants. Alternatively, the data from this experiment can be expressed as a cesium isotherm at 5 M $[Na^+]$. Plotting the data as a cesium isotherm reveals a Type I relationship with only a slight negative deviation as the equilibrium cesium-solution concentration increases. The results at varying sodium concentrations can be added to this 5 M $[Na^+]$ data to generate a correlation of $\log (\text{Cs } K_d) = 1.06 – 0.378 \log$ equilibrium $[Cs^+]$ with a correlation coefficient of 0.979.

[(a)] K_d = distribution coefficient

5) *Evaluation of the impact of varying $[K^+]/[Cs^+]$ ratios on the Cs K_d at a constant 1 M $[K^+]$, 0.25 M $[OH^-]$).* In Section 3.5, it was found that, like with varying $[Na^+]/[Cs^+]$ ratios, as the $[K^+]/[Cs^+]$ ratio increases, the cesium K_d also increases. However, the magnitude of these changes is less than that observed for the analogous Na/Cs study, consistent with the idea that the binding affinities, which may be related to the relative size of the cations, for potassium and cesium are more closely equivalent than for sodium and cesium. Alternatively, the data from this experiment can be expressed as a cesium isotherm at 1 M $[K^+]$. Plotting the data as a cesium isotherm reveals an almost linear Type I relationship with a negative deviation only at the greatest cesium-solution concentrations examined.

6) *Measurement of the total ion-exchange capacity of SuperLig® 644.* In Section 3.6, an attempt was made to measure the total Cs ion-exchange capacity of SuperLig® 644. This was done by first converting the resin to the hydrogen form and then placing the resin in deionized water and titrating the suspension with CsOH. The solution pH was monitored with a pH electrode, and the titration continued until the solution pH was greater than 12, a pH regime where high Cs affinity has been observed (see also Section 3.2). A break point between pH 10 and 11 was observed, and, using this break as the equivalence point in the titration, a cation capacity for SuperLig® 644 of ca. 2 meq/g was calculated. However, the recorded values of pH were quite time dependent; significantly differing pH values for a given point in the titration can be recorded if differing time delays are used between the time of hydroxide addition and the time that the pH is recorded. In addition, even if phenolphthalein is used as an indicator (whose color change occurs over only slightly basic conditions), similar results are obtained. This approach still needs to be validated.

7) *Uranyl K_d time-dependence measurements with SuperLig® 644.* In Section 3.7, a solution 0.25 M in hydroxide and 1 M in sodium was spiked with uranyl solution of high specific activity, yielding a solution with an initial $[Na^+]$/[uranyl] ratio of 67,000. The uranyl K_d as a function of time was measured. It was observed that an approach to equilibrium appears to be much slower for uranyl than for cesium; indeed, even after 1 week of contact time, it is not clear that a steady K_d value for uranyl has occurred. Second, the uranyl K_ds measured are roughly comparable to those of cesium, although differences in $[Na^+]$/[uranyl] ratios and total sodium concentration interfere with any simple direct comparison.

8) *Measurement of the uranyl K_ds with SuperLig® 644 as a function of initial $[Na^+]$/[Uranyl] and $[K^+]$/[Uranyl].* In Sections 3.8 and 3.9, uranyl K_ds were measured as the alkali metal-to-uranyl ratio was varied. Unfortunately, the reproducibility of these measurements was so poor and so inconsistent with the results of the uranyl kinetics measurements that no conclusions are possible.

For each set of test results, the distribution values are presented both in a table and, except for Sections 3.8 and 3.9, graphically.

Quality Requirements

PNWD implemented the RPP-WTP quality requirements in a quality assurance project plan (QAPjP) as approved by the RPP-WTP quality assurance (QA) organization. The tests reported in Sections 3.1 through 3.5 and all analytical data collection were conducted in accordance with PNWD's quality assurance project plan, CHG-QAPjP, Rev.0, which invoked PNWD's Standards Based Management System (SBMS), compliant with DOE Order 414.1A Quality Assurance and 10 CFR 830, Energy/Nuclear Safety Management, Subpart A -- Quality Assurance Requirements. Due to a change in the contract QA requirements, the tests reported in Sections 3.6 through 3.9 were conducted in accordance with PNWD's quality assurance project plan, RPP-WTP-QAPjP, Rev.0, which invoked NQA-1-1989 Part I, Basic and Supplementary Requirements, and NQA-2a-1990, Subpart 2.7. These quality requirements were implemented through PNWD's Waste Treatment Plant Support Project Quality Assurance Requirements and Description Manual (WTPSP). The quality of the data gathered during the earlier experiments was not impacted by the change in requirements.

PNWD addressed verification activities by conducting an Independent Technical Review of the final data report in accordance with procedure QA-RPP-WTP-604. This review verified that the reported results were traceable, that inferences and conclusions were soundly based, and the reported work satisfied the Test Plan objectives. The review procedure is part of PNWD's WTPSP Manual.

Issues

No WTP design or operational issues have been identified.

References

Barnes S, R Roosa, and R Peterson. 2002. *Research Technology Plan,* 24590-WTP-PL-RT-01-002, Rev. 1, River Protection Project, Richland, Washington.

Rapko BM. 2001. “Equilibrium Batch Contact Testing for CH2MHill Inc.” CHG-TP-41500-014, Pacific Northwest National Laboratory, Richland, Washington.

Acronyms

ASTM	American Society for Testing and Materials
DI	deionized water
DSSF	double shell slurry feed
HLW	high-level waste
ICP-MS	inductively coupled plasma-mass spectrometry
LAW	low-activity waste
LSC	liquid scintillation counting
PNWD	Battelle, Pacific Northwest Division
QA	quality assurance
QAPjP	quality assurance project plan
RF	resorcinol-formaldehyde
SRTC	Savannah River Technology Center
WTPSP	Waste Treatment Plant Support Project Quality Assurance Requirements and Description Manual

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1.0 Introduction

1.1 Background

The U.S. Department of Energy plans to vitrify the waste from the 177 underground storage tanks at the Hanford Site. Vitrification will immobilize the tank waste for permanent disposal. In the proposed facility for immobilizing tank waste, the incoming tank waste will be split initially into a low-activity waste (LAW) solution stream and a high-level waste (HLW) solids stream for separate vitrification. To render the solution stream suitable for LAW vitrification, additional processing to remove radioactive cesium and technetium will be required (Barnes et al. 2001). Much recent work has investigated two ion exchange resins developed by IBC Advanced Technologies, Inc. for removing selected radionuclides from Hanford tank waste supernatants. SuperLig® 644 has been and is being investigated for removing cesium from alkaline, high-sodium solutions, including actual Hanford tank supernatants (King et al. 2000; Hassan et al. 2000; Hassan et al. 2001; Kurath et al. 2000a and 2000b; Kurath et al. 1999). Existing data up to year 2000 using both simulants and actual tank wastes have been evaluated and included in an ion exchange process model under continuing development at Savannah River Technology Center (SRTC) (Hamm et al. 2000).

It has been shown that batch-contact distribution data collected from simple binary systems can be incorporated in such a process model for use in more complex systems (Mehablia et al. 1994). Incorporating such information from previous batch-contact data is difficult because of changing conditions amongst prior testing with SuperLig® 644, such as differing resin batches and varying experimental designs. A need for additional, equilibrium-batch-contact data has been identified in order to continue to develop and extend the modeling for use under likely process conditions (Hamm et al. 2000; Barnes et al. 2001).

The work covered in this report measured a subset of the desired binary equilibrium-batch-contact data together with the appropriate controls (such as the batch-distribution kinetics) required to interpret the equilibrium-batch-contact data for SuperLig® 644.

1.2 Objectives

Battelle, Pacific Northwest Division (PNWD) is contracted to Bechtel National Inc. (BNI) on the River Protection Project – Waste Treatment Plant (RPP-WTP) project to perform research and development activities. Unit operations of the WTP process include the separation of ^{137}Cs by ion exchange from the liquid portion of the waste. The SuperLig® 644 (SL-644) ion exchange resin was selected by the project to perform ^{99}Tc separations.

The RPP-WTP is evaluating the SL-644 resin to determine its behavior under various potential processing conditions. Under test scoping statements S-142 and S-143, a model is being developed at the Savannah River Technical Center (SRTC) that will be capable of predicting the response of SL-639 under various processing conditions. This investigation was conducted according to the test plan prepared by Rapko (2001) in response to the test requirements to investigate ion exchange resin degradation delineated by Barnes et al. (2002) in Section 3.7.2.1 of the Research and Technology Plan and test scoping statement B-49. The results from these tests will be incorporated into the afore-mentioned model. Objectives as noted in test scoping statement B-49 were to measure the performance of SuperLig® 644 under the following conditions:

1) Room-temperature measurement of the approach to a constant (equilibrium) Cs K_d[(a)] under the experimental conditions used for most of the subsequent batch contacts. This assures that later measurements are made under equilibrium conditions.
2) Cesium capacity measurement by potentiometric titration.
3) Measurement of the effect of changing $[H^+]$ or $[OH^-]$ on the Cs K_d at 5 M $[Na^+]$.
4) Measurement of the effect of changing $[Na^+]$ (i.e., dilution effect) on the Cs K_d.
5) Measurement of the effect of changing $[Na^+]/[Cs^+]$ on the Cs K_d at 5 M $[Na^+]$.
6) Measurement of the effect of changing $[K^+]/[Cs^+]$ on the Cs K_d at 1 M $[K^+]$.
7) Room-temperature measurement of the approach to constant (equilibrium) uranyl K_d under the experimental conditions used for subsequent batch contacts. This assures that later measurements are made under equilibrium conditions.
8) Measurement of the effect of changing $[Na^+]/[Cs^+]$ on the uranyl K_d at 0.25 M $[OH^-]$.

   In addition, the following experiment was performed:

9) Measurement of the effect of changing $[K^+]/[Cs^+]$ on the uranyl K_d at 0.25 M $[OH^-]$.

1.3 Purpose

This report documents testing, results, and analysis associated with the measurement of kinetic and equilibrium batch contacts involving SL-644. The report is intended to aid the RPP-WTP project in developing the computer model to be used to predict performance of the Tc ion exchange system in the WTP over a wide variety of conditions.

1.4 Quality Assurance

PNWD implemented the RPP-WTP quality requirements in a quality assurance project plan (QAPjP) as approved by the RPP-WTP quality assurance (QA) organization. The tests reported in Sections 3.1 through 3.5 and all analytical data collection were conducted in accordance with PNWD's quality assurance project plan, CHG-QAPjP, Rev.0, which invoked PNWD's Standards Based Management System (SBMS), compliant with DOE Order 414.1A Quality Assurance and 10 CFR 830, Energy/Nuclear Safety Management, Subpart A -- Quality Assurance Requirements. Due to a change in the contract QA requirements, the tests reported in Sections 3.6 through 3.9 were conducted in accordance with PNWD's quality assurance project plan, RPP-WTP-QAPjP, Rev.0, which invoked NQA-1-1989 Part I, Basic and Supplementary Requirements, and NQA-2a-1990, Subpart 2.7. These quality requirements were implemented through PNWD's Waste Treatment Plant Support Project Quality Assurance Requirements and Description Manual (WTPSP). The quality of the data gathered during the earlier experiments was not impacted by the change in requirements.

(a) k_d = distribution coefficient

PNWD addressed verification activities by conducting an Independent Technical Review of the final data report in accordance with procedure QA-RPP-WTP-604. This review verified that the reported results were traceable, that inferences and conclusions were soundly based, and the reported work satisfied the Test Plan objectives. The review procedure is part of PNWD's WTPSP Manual.

2.0 Experimental

SuperLig® 644 was obtained from IBC Advanced Technologies, Inc., American Fork, Utah. The resin batch used for all testing described in this report was # 010319 SMC-IV-73. The material appears as purple irregular chips of varying sizes. The as-received material was passed through both 40 and 70 mesh (0.425 mm and 0.212 mm, respectively) sieves. Out of 391.3 g of resin sieved, 294.5 g was found to be greater than 40 mesh in size, 94 g was between 40 and 70 mesh in size, and 2.8 g was found to be less than 70 mesh in size. Only portions of the 94 g of material between 0.425 mm and 0.212 mm were used during these tests.

2.1 Preparation of Non-Radioactive Stock Solutions

Chemicals were obtained from standard commercial sources unless indicated otherwise. Deionized (DI) water was purified by passing in-house DI water through a commercial water purifier and was stored in plastic containers until used. Hydroxide concentrations for the stock solutions used in this work were verified by titration with a standard acid solution.

2.2 Preparation and Assay of ^{137}Cs-Spiked Cesium Stock Solutions

A 1 M solution of cesium nitrate spiked with ^{137}Cs was prepared as follows: to a 5-ml volumetric flask, 0.975 g (5.00 mmol) of reagent-grade cesium nitrate was added. Meanwhile, an aliquot of ^{137}Cs solution in dilute HCl (obtained from in-house stores) of approximately 5-mCi activity was removed and evaporated to dryness. The ^{137}Cs vial was rinsed with DI water, and these rinses were used to fill the volumetric flask to the 5-ml mark. Analysis of a sample aliquot indicated a solution activity of approximately 0.5 mCi/ml. Inductively coupled plasma-mass spectrometry (ICP-MS) analysis of the stock solutions gave a Cs concentration for this stock solution of 1.01±0.02 M. A targeted 0.01 M solution of cesium nitrate spiked with ^{137}Cs was prepared similarly except that 9.75 milligrams (0.05 mmol) of reagent-grade cesium nitrate was added to a 5-ml volumetric flask. Analysis of a sample aliquot of this solution also indicated an activity of approximately 0.5 mCi/ml. ICP-MS analysis of the stock solutions gave a Cs concentration for this stock solution of 0.0120±0.0002 M.

2.3 Preparation and Assay of the ^{233}Uranyl Stock Solutions

A known volume of $^{233}UO_2(NO_3)_2$ stock solution in dilute (1 mM) HNO_3 (obtained from in-house stores) was removed from its storage location in a glovebox and taken to a fume hood; a small portion was assayed for alpha activity. The solution was then diluted as needed with DI water. Two stock solutions were generated over the course of this work, but only one was diluted with DI water. Analysis of the activity of the final stock solutions, based on the assumption that all measured alpha activity was due to ^{233}U, indicated that these stock solutions were approximately 0.03 to 0.01 M in uranium.

2.4 Conditioning of As-Received SuperLig® 644

The SuperLig® 644 resin was conditioned starting with an initial contact with DI water in approximately a 10:1 (ml liquid/g resin) ratio performed in a polypropylene bottle. For this initial contact, the suspension was agitated in a rotary shaker at a rate sufficient to achieve a vortex for 20 min. The shaking was stopped, and the solids were isolated by filtration through a 0.45-µm Nylon® filter. The solids were then sluiced back into the bottle with the next contact solution. Following the initial DI contact, three 0.5 M HNO_3 contacts were performed, followed by four contacts with DI water. All of these contacts were at the same ratio as the initial contact, and each was agitated for at least 2 h. The pH of the DI water at the end of the fourth contact was approximately four and changed little from the pH of the previous DI water contact. The resin was then air dried for several days and placed in a plastic bottle until needed. The resin used for all the tests reported here was conditioned in one batch prior to the start of any of the tests.

2.5 F-Factor Measurements for Pretreated SuperLig® 644

In duplicate, approximately 0.1-g samples of the conditioned SuperLig® 644 were placed in tared, 20-ml glass vials and reweighed. These open vials were placed in a vacuum oven and heated to 48°C for 6 days. The samples were assumed to be dry by this time. The F-factor is simply the ratio of the final 48°C/vacuum-dried resin weight to the air-dried resin weight. Table 2.1 shows the results of the F-factor experiment, which yielded a calculated average F-factor of 0.8886 ± 0.0017.

Table 2.1. Results from F-Factor Experiment

	1st Sample	**2nd Sample**
Tare wt. (g)	17.3187	17.2793
Tare wt. + resin (g)	17.4244	17.3882
Initial wt. resin (g)	0.1057	0.1089
Final wt. after 6 days drying (g)	17.4125	17.3762
Final wt. resin (g)	0.0938	0.0969
F-factor	0.8874	0.8898

2.6 Batch-Contact Measurements – General Procedure

Step 1. Approximately 0.1 g of conditioned, air-dried SuperLig® 644 resin in the H^+ form was placed in a tared 20-ml glass liquid scintillation counting (LSC) vial and reweighed.

Step 2. Eleven ml of the test solution were placed in a second vial that was spiked with the appropriate Cs or uranyl stock solution. The spiked solution was agitated for at least 1 min, and a 1-ml aliquot (Cs) was removed and added to a tared 2-dram vial (Cs) or a tared 20-ml LSC vial containing 10 ml of Ultima Gold® LSC cocktail (uranyl) and reweighed.

Step 3. Ten ml of the spiked test solution were added to the vial containing the conditioned, air-dried, H^+ form, SuperLig® 644 resin, taking care not to disturb the resin so as to splash resin above the liquid. The vial was then sealed, placed in an orbital shaker, set to 25 ± 5°C, and shaken at 225 rpm. The sample temperature was monitored using a thermocouple placed in a 20-ml LSC vial containing 10 ml of DI water.

Step 4. At the conclusion of the shaking (generally 72 h unless indicated otherwise), the vial was removed, and the liquid was separated from the resin by filtration through a 0.2-µm Nylon® syringe filter.

Step 5. In the case of uranyl, a 1-ml aliquot of the filtered solution was removed, added to a tared vial containing 10 ml of Ultima Gold® LSC cocktail, and reweighed. For the cesium-spiked solution, a 1-ml aliquot was placed in a tared 2-dram vial and reweighed.

Step 6. In the case of uranyl, the sample's alpha activities were measured on a Packard Instruments liquid scintillation counter using an 18-nanosecond coincidence time over the region of 200 to 800 KeV. In the case of cesium, the concentration was determined from the area under the 661.7-KeV photopeak of its ^{137m}Ba daughter. The time between the separation of the resin from the test sample and the assay of the solution's activity was always greater than an hour and often not until hours to days later. This time is more than sufficient for the ^{137m}Ba daughter (half-life 2.52 min) to come to secular equilibrium with its ^{137}Cs parent. This activity was measured using a liquid-nitrogen-cooled Ge detector.

Step 7. K_d measurements were obtained according to the standard formula shown below (Brown et al. 1995):

$$K_d = \frac{(C_0-C_i)}{C_i} * \frac{V}{(M*F)} \tag{1}$$

where K_d = distribution coefficient (in ml solution/g 50°C, vacuum-oven-dried, H^+ form of resin)
C_0 = initial metal activity
C_i = final metal activity
M = mass of conditioned, H^+ form, air-dried resin (in grams) used in the batch-contact experiment
V = volume of test solution (in ml) used in the batch-contact experiment
F = F-factor.

Each experimental condition was examined in duplicate, except as noted. Uncertainties presented in the tables and plots are one standard deviation of the average K_d. These uncertainties are shown as error bars for every point that is an average in each plot. In some cases the error bars are so small they are indistinguishable from the point.

3.0 Results

As noted earlier, both column and batch-contact studies with SuperLig® 644 have been incorporated into a model (Hamm et al. 2000). Because of either the importance of the data or because of conflicting results, a need for additional equilibrium data was noted. The goal of this study was to provide a subset of the needed data.

The experimental approach was to start with a single batch of as-received resin with a specific particle size range. To that end, the as-received material was sieved, and the fraction from 40 to 70 mesh (0.212 to 0.425 mm) was collected. This resin was then conditioned by a water wash to remove any inert, water-soluble material that may have been present followed by repeated contacts with 0.5 M nitric acid. The purpose of the nitric acid contacts was to convert all of the material to a known (hydrogen) form to eliminate the presence of any potential competitor cations that might be contributed from the as-received resin during these (predominately) alkaline batch contacts. The resin was then air dried at room temperature in an attempt to get the resin to a stable environment with minimal resin degradation. This is important because testing did not begin until almost a month had passed from the time the resin was conditioned (late March 2001), and testing with this conditioned resin was continued intermittently over the following several months.

The batch contacts were performed with a volume of 10 ml of test solution to 0.1 g of pre-equilibrated SuperLig® 644 resin. The sieving limited the amount of resin available for testing much more severely than was initially anticipated and, because of competing demands for resin and the large number of batch contacts needed, 0.1 g per test was the most resin that could be used within these constraints. The batch contacts were agitated using a rotary shaker set to 225 rpm. This speed appeared to allow for maximum agitation of the system without splashing the resin onto the sides of the vial above the liquid line. Having resin above the liquid line would effectively alter the mass of resin in contact with the solution and would lead to variances in the effective V/m present for the test, which in turn would translate into variances in the observed K_d.

The initial set of contacts described in Section 3.1 was designed to determine the time needed for the resin under these experimental conditions to obtain a constant K_d (in effect to reach equilibrium). Subsequent batch contacts were performed at a time sufficient to assure equilibrium based on these initial test results.

For each type of measurement, the following are provided: the general experimental conditions, a table summarizing the experimental results, an accompanying graph of the experimental results, and any needed commentary. In general, aspects of the experimental design, such as the $[Na^+]/[Cs^+]$ ratio and the solution sodium concentration, have been kept constant to the extent practical to facilitate comparisons between sets of experiments.

3.1 The Effect of Contact Time on the Cesium K_d at 25°C

Samples of SuperLig® 644 were contacted with solutions that were 4.75 M in sodium nitrate and 0.25 M in sodium hydroxide (for a total sodium concentration of 5 M) at 25°C. The initial sodium-to-cesium ratio for these contacts was approximately 11,000 (a 5-µL spike of 1 M cesium stock solution into 11 ml of the 5 M sodium test solution) in this experiment, and the volume of solution (ml) to grams resin is 100. Duplicate samples were agitated in a rotary shaker at 225 rpm and removed from the shaker at varying intervals out to almost 1 week, and the activity of each filtered solution was assayed. The results of this experiment are summarized in Table 3.1 and in Figure 3.1.

Table 3.1. Results of 25°C Cesium K_d Time Dependence Tests with SuperLig® 644

Time (h)	K_d (Test 1)	K_d (Test 2)	Ave. K_d	SD Ave. K_d
2	1104	1016	1060	63
4	1375	1429	1402	39
6.5	1502	1507	1504	4
24	1684	1785	1735	72
48	1559	1654	1607	67
74	1544	1741	1642	139
97	1706	1407	1557	211
167.5	1491	1466	1478	17
SD = standard deviation Contacts performed from 04-30-01 to 05-01-01				

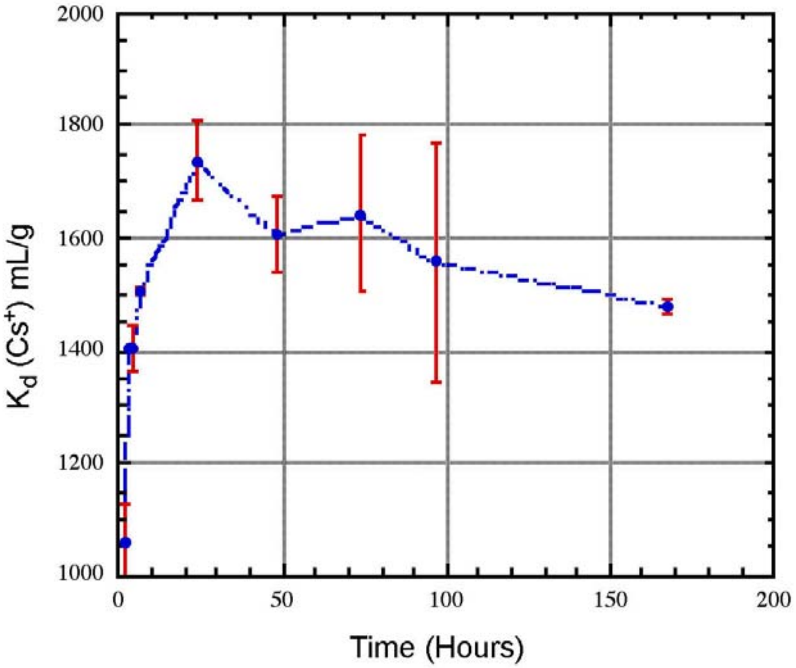

Figure 3.1. Plot of 25°C Cesium K_d Time Dependence Tests with SuperLig® 644 at 5 M Sodium

These test results clearly show that contact times of 24 h are sufficient to achieve a steady and maximum K_d value of approximately 1600 ± 120 ml/gram. There is some suggestion of decreasing K_ds after extended contact times beyond 72 h, but it should be noted that such a conclusion is based primarily on the final data point; within the large experimental uncertainties for most of the other post 24-h data, the K_d value remains the same as that found for the 24-h contact. Alternatively, the drop in cesium K_d at long contact times might be indicative of a competition with sodium ion, with the resin kinetics of the sodium ion being slower than that with cesium. Another possibility is that resin degradation is occurring upon prolonged contact with alkaline solution. This set of data by itself is insufficient to distinguish between these possibilities.

3.2 Impact of Changing $[H^+]/[OH^-]$ Ratio on the Cesium K_d with SuperLig® 644

The experimental procedure described in Section 3.1 was repeated, but in these experiments, while the total $[Na^+]$ was kept at approximately 5 M and the initial $[Na^+]/[Cs^+]$ ratio was kept as before at 11,000, the acidity/basicity of the solution was changed from $[H^+]$ of 0.5 M to $[OH^-]$ of 2.5 M. The results are shown in Table 3.2 and are plotted in Figure 3.2.

Table 3.2. Results of Changing $[H^+]/[OH^-]$ on the Cesium K_d with SuperLig® 644

Conditions	**[Na]/[Cs], Final***	**K_d (Test 1)**	**K_d (Test 2)**	**Ave. K_d**	**SD Ave. K_d**
2.5 M $[OH^-]$	2.40E+05	2694	1465	2080	869
1 M $[OH^-]$	7.81E+04	736	623	680	80
0.1 M $[OH^-]$	5.50E+04	401	401	401	1
pH 12	1.25E+04	16	13	15	2
pH 9	1.02E+04	-6	-8	-7	1
pH 7	1.08E+04	1	-4	-1	3
pH 5	1.11E+04	2	-1	1	2
pH 2	1.12E+04	-1	4	2	4
0.5 M $[H^+]$	1.08E+04	-1	-2	-2	0
Contacts performed from 06-11-01 to 06-14-01 * Based on the final average cesium concentration for Tests 1 and 2.					

A couple of points are worth making about these results. First, there appears to be a steady decrease in the Cs K_d from 2.5 M hydroxide to 0.01 M hydroxide, although the uncertainty in the 2.5 M data makes the magnitude of the change somewhat uncertain. Below pH 12 (0.01 M hydroxide), the cesium K_d is close to zero and remains that way as the test solution becomes increasingly acidic, all the way to 0.5 M nitric acid (see Table 3.2). This has the implication that the hydroxide-concentration adjustments in a feed solution may be a simple way to improve cesium complexation with SuperLig® 644. A further implication is that the low batch K_d value found for 0.5 M nitric acid supports its planned use for elution of the SuperLig® 644 resin in the WTP.

Attention should be made to the poor agreement between the results of the kinetic measurements and the results here under the more strongly basic conditions. The kinetics measurements were performed at 5

M total sodium and 0.25 M hydroxide. Here, although all alkaline measurements were also performed at 5 M total sodium, a lower Kd was observed at a higher (1 M) hydroxide concentration. At a comparable base concentration (0.1 M hydroxide in this test versus 0.25 M hydroxide in Test 1), the noted difference is even more striking. The 2.5 M hydroxide values here are higher than in the Section 3.1 tests, but the error associated with this measurement is large. Indeed, if the larger data point is ignored, then these cesium K_ds are comparable. The reasons for this are unknown; as discussed in Section 4, some possible influences could be poor resin stability and variable resin particle sizes used for the individual contacts.

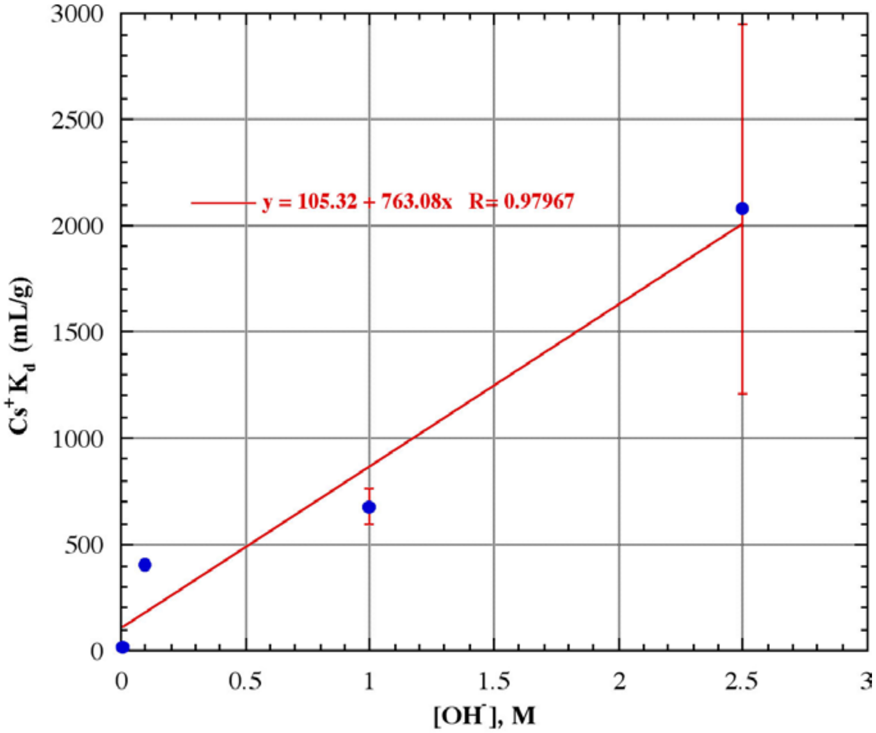

Figure 3.2. Results of Changing $[OH^-]$ on the Cesium K_d with SuperLig® 644. Note that below pH 12, the Cesium K_d is effectively zero.

3.3 Effect of Varying $[Na^+]$ on the SuperLig® 644 Cesium K_d at Constant Initial $[Na^+]/[Cs^+] = 5500$, $[OH^-] = 0.25$ M

For this series of experiments, the contact solution was kept at 0.25 M sodium hydroxide while the initial cesium nitrate and sodium nitrate concentrations were varied in tandem to maintain a constant initial ratio of 5500. The results are shown in Table 3.3 and Figure 3.3. It should be noted that because of the poor reproducibility in some of the data, this set of experiments was repeated, giving four independent contacts for each condition. If one removes selected data points that inspection suggests are widely different than the other measurements, a selected data set can be generated. The basis for selecting a subset of data is as follows. The large spread in the 1 M sodium data provides little information about behavior since the measured cesium K_d of 1971 ± 2237 would support almost any dependency generated by the remaining data. It is important to emphasize that because of the small number of measurements, this subset selection (the deletion of the 1 M sodium data) cannot be justified statistically. Application of a Q-test (Skoog and West 1976) allows rejection of the value from Test 2 in the 5 M sodium data. With these changes, the selected subset of data is shown in Table 3.4 and plotted in Figure 3.4. If the selected data are used, a linear decrease in the cesium K_d as the total sodium concentration is increased becomes more readily apparent.

Such a linear dependence of the cesium K_d on the total sodium concentration was reported previously during a study examining the behavior of various cation exchange resins for cesium removal (Brown et al. 1996). In this study using simulated and actual double-shell slurry feed (DSSF), the change in Cs K_d as a function of the total sodium concentration was examined at differing equilibrium sodium-to-cesium ratios. Ion exchange materials examined include resorcinol-formaldehyde (RF) resin, SuperLig® 644, CS-100 and crystalline silicotitanate. In all cases, the cesium K_ds decreased as the sodium-solution concentration increased from 0.2 to 5 M.

Table 3.3. Results of Changing Total [Na^+] on the Cesium K_d with SuperLig® 644, All Data

Total [Na^+], M	[Na]/[Cs], Final*	K_d (Test 1)	K_d (Test 2)	K_d (Test 3)	K_d (Test 4)	Ave. K_d	SD Ave. K_d
5	2.10E+04	189	628	197	192	301	218
2.5	2.82E+04	476	448	562	333	455	95
1	1.05E+05	856	5253	1450	323	1971	2237
0.25	4.85E+04	686	1397	613	827	881	356

Contacts performed from 06-11-01 to 06-14-01 and 07-10-01 to 07-13-01
* Based on the final average cesium concentration for tests 1 through 4.

Table 3.4. Results of Changing Total [Na^+] on the Cesium K_d with SuperLig® 644, Selected Data

Total [Na^+], M	K_d (Test 1)	K_d (Test 2)	K_d (Test 3)	K_d (Test 4)	Ave. K_d	SD Ave. K_d
5	189		197	192	193	4
2.5	476	448	562	333	455	95
0.25	686	1397	613	827	881	356

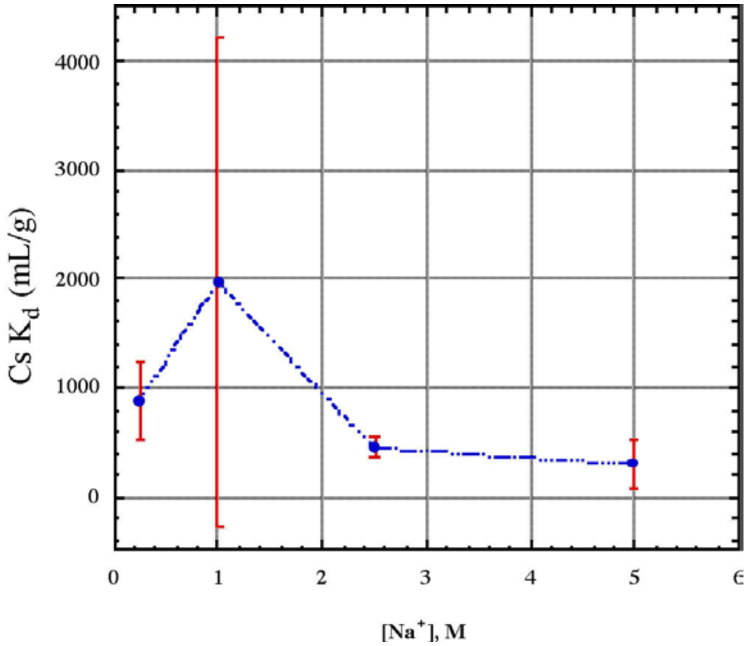

Figure 3.3. Results of Changing Total [Na^+] on the Cesium K_d with SuperLig® 644, All Data

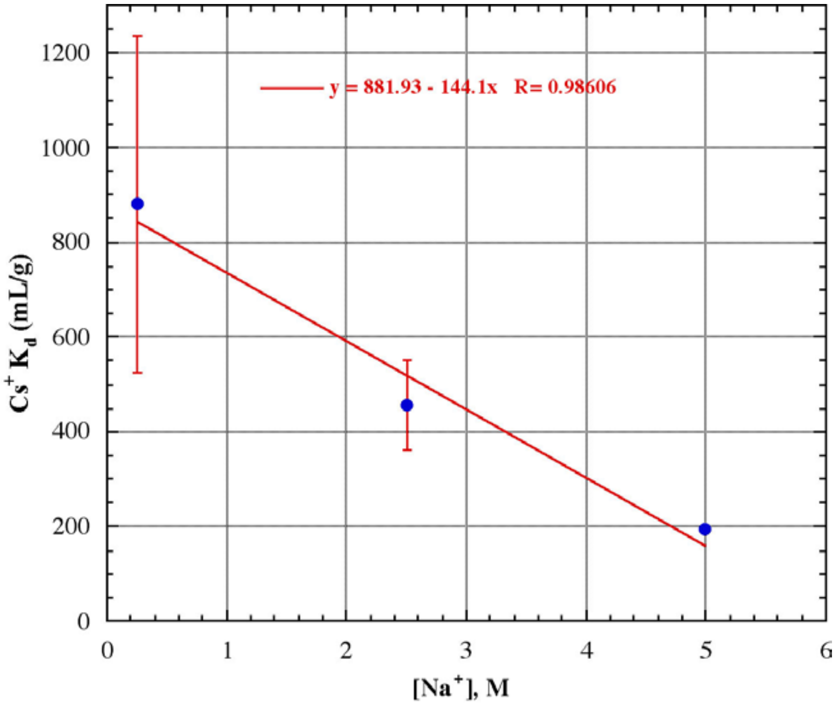

Figure 3.4. Results of Changing Total [Na^+] on the Cesium K_d with SuperLig® 644, Selected Data

3.4 Impact of Varying [Na^+]/[Cs^+] Ratio on the SuperLig® 644 Cesium K_d at 5 M [Na^+], [OH^-] = 0.25 M

In this set of tests, the initial test solution of 4.75 M $NaNO_3$/0.25 M NaOH was spiked with differing amounts of cesium nitrate, and the cesium K_d of the cesium-spiked solution was measured. The results are summarized in Table 3.5 and in Figure 3.5. These results indicate that the cesium K_ds decreased as the cesium concentrations increased. Furthermore, the Cs K_d shown in the first line of Table 3.5, a K_d of 220 at initial [Na^+]/[Cs^+] of 5500, is at least consistent with the independent test results from Section 3.3 under identical conditions.

It should be noted that similar behavior has been observed previously. In previous Battelle-Pacific Northwest Division (PNWD) studies (Kurath et al. 1999; Kurath et al. 2000a and b), SuperLig® 644 in the acid form was contacted with various Hanford tank waste supernatants spiked with various amounts of additional cesium nitrate, and the batch K_ds for Cs were measured. Similar to the behavior observed here, as the [Na^+]/[Cs^+] ratio increased, the cesium K_d also increased.

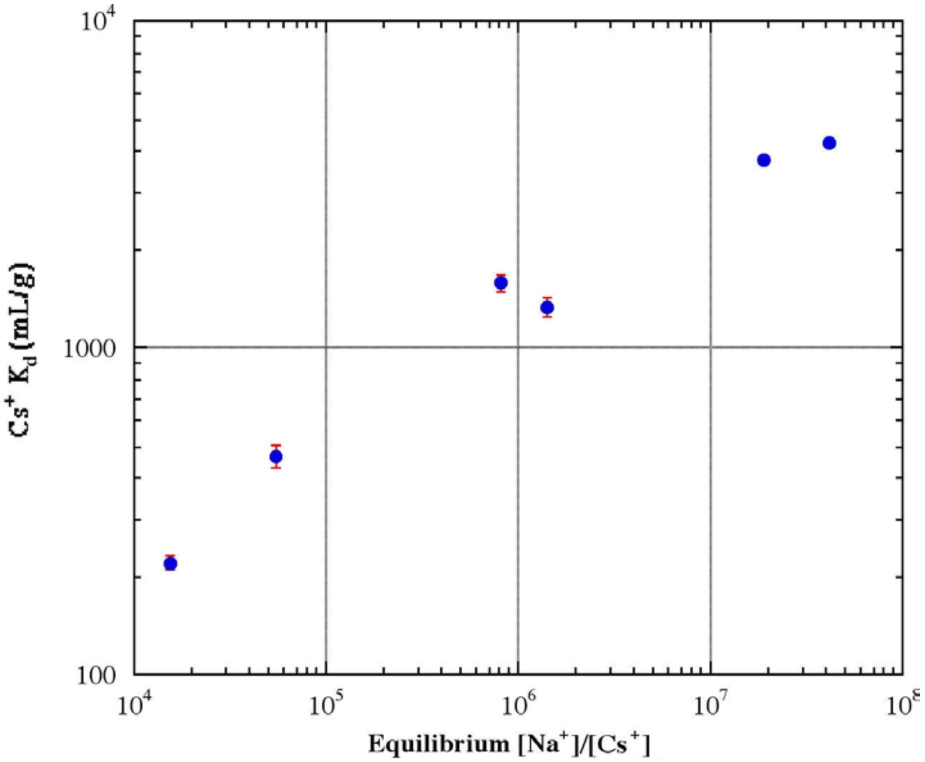

Figure 3.5. Impact of Varying Sodium/Cesium Ratios at 5 M Total Sodium on the Cesium K_d at 25°C

Table 3.5. Impact of Varying Sodium/Cesium Ratios at 5 M Total Sodium on the Cesium K_d at 25°C

Initial $[Na^+]/[Cs^+]$	Final $[Na^+]/[Cs^+]$	Total Cs (mmol) in Test	K_d (Test 1)	K_d (Test 2)	Ave. K_d	SD of Ave. K_d
5.5E+03	1.56E+04	9.1E-03	214	227	220	9
1.1E+04	5.53E+04	4.5E-03	439	491	465	37
5.5E+04	8.17E+05	9.1E-04	1648	1503	1575	102
1.1E+05	1.42E+06	4.5E-04	1265	1399	1332	95
5.5E+05	1.90E+07	9.1E-05	3747	3724	3735	16
1.1E+06	4.17E+07	4.5E-05	4131	4314	4222	130
Contacts performed from 06-18-01 to 06-21-01 * Based on the final average cesium concentration for Tests 1 and 2.						

The typical behavior of the response to SuperLig® 644 to these experimental conditions is made more obvious if the data are plotted as an isotherm, i.e., as the cesium concentration in the resin versus the cesium concentration in solution at equilibrium. This plot, shown in Figure 3.6, is indicative of a typical Type I isotherm with only a modest negative curvature. Indeed, the results from these 5 M $[Na^+]$ tests can be combined with the results in the previous section where the sodium concentration was varied from 0.25 to 5 M. A correlation of the Cs K_d to the equilibrium $[Cs^+]$ becomes apparent (Figures 3.7 and 3.8), with a correlation of log (Cs K_d) = 1.06 – 0.378 log equilibrium $[Cs^+]$.

In previous SRTC studies (Hassan et al. 2000; King et al. 2000), the behavior is more complex. With AN-102 supernatant (King et al. 2000), the cesium K_d also increased as the reported $[Na^+]/[Cs^+]$ ratio was decreased. For AN-103 supernatant, the cesium K_d increased initially as the reported $[Na^+]/[Cs^+]$ ratio was decreased, but then decreased again at the highest $[Na^+]/[Cs^+]$ ratio measured. However, direct comparisons between the results reported in this report with the results of the SRTC are more difficult because of a differing experimental design used for collecting most of their data, which was at $[Na^+]/[Cs^+]$ ratios greater than those observed in the actual tank supernatant. In the SRTC studies, as-received SuperLig® 644 was contacted with a particular Hanford tank supernatant, the Cs K_d was measured, and, as expected, the cesium concentration in solution was depleted. The Cs-depleted supernatant was then contacted with a new portion of as-received SuperLig® 644 resin, and the process was repeated. Unfortunately, recent results indicate that this as-received SuperLig® 644 resin contains a substantial fraction of potassium carbonate. Consequently, the potassium/cesium ratio as well as the sodium/cesium ratio were both increasing markedly and in a non-proportional manner during the SRTC experiments.

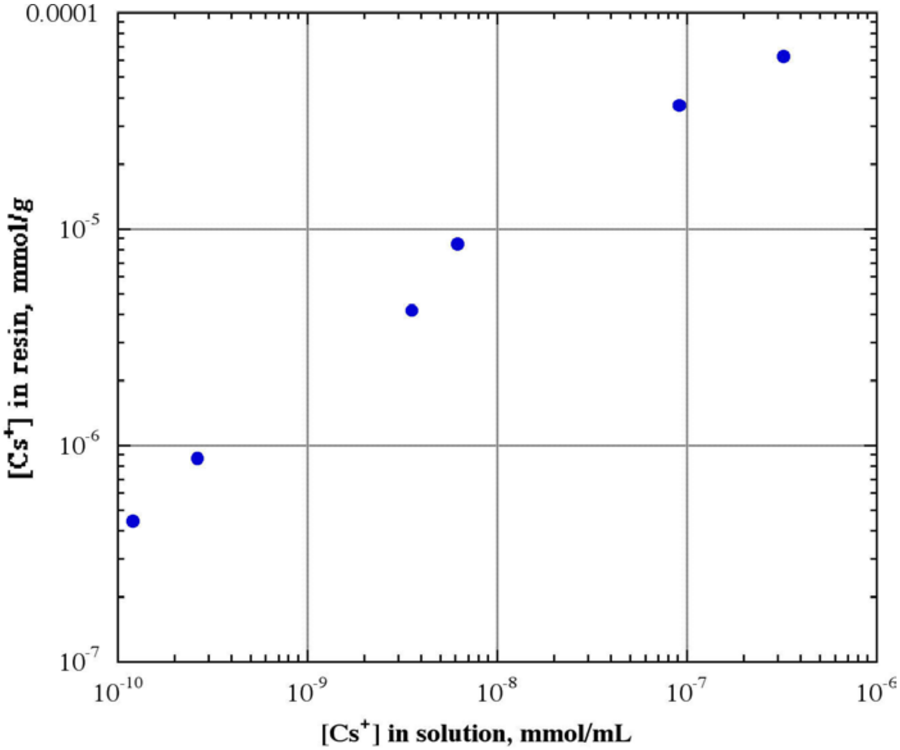

Figure 3.6. Cesium Isotherm Plot at 5 M Total Sodium at 25°C

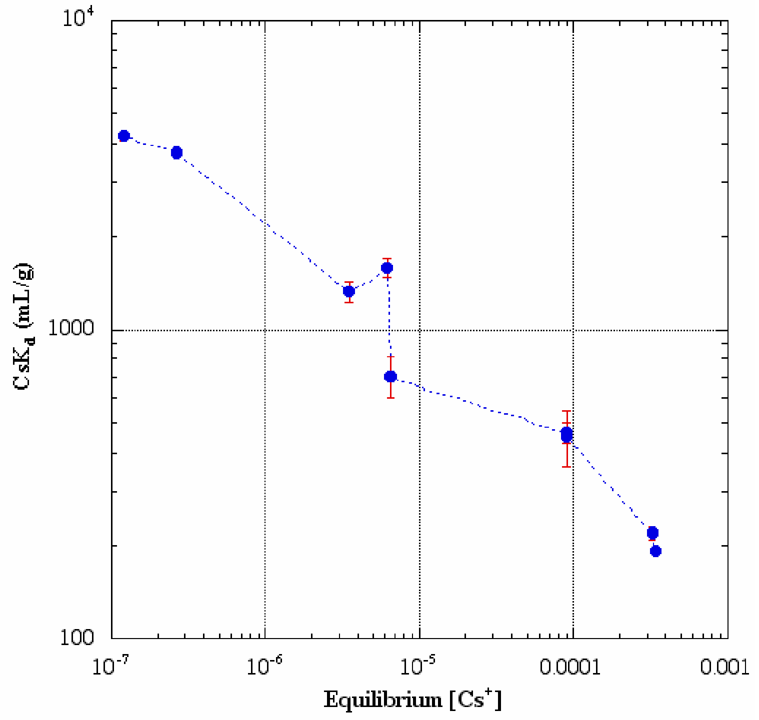

Figure 3.7. Cesium K_d Dependence on the Equilibrium [Cs^+] at 25°C

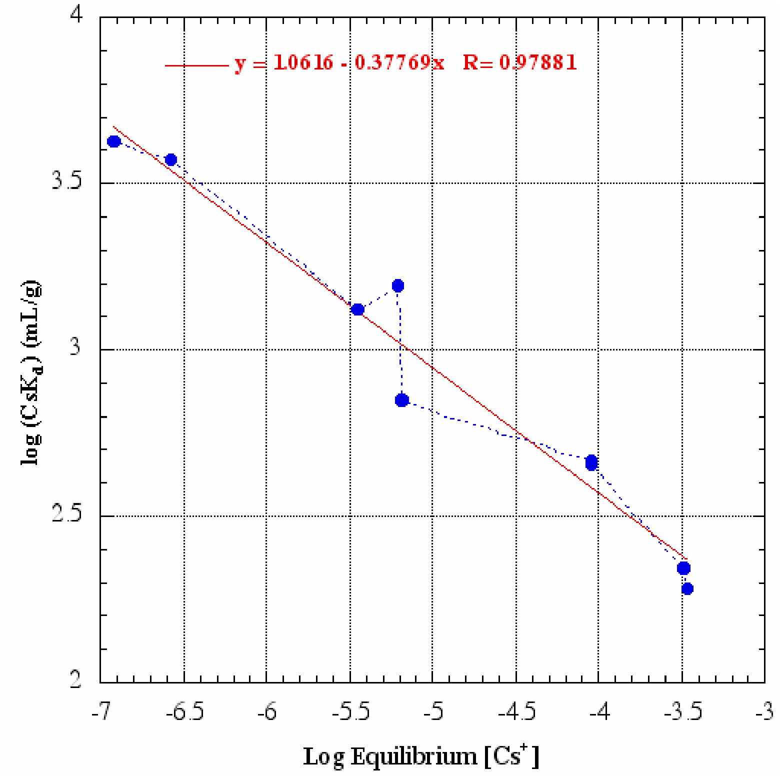

Figure 3.8. Cesium Kd Dependence on the Equilibrium [Cs^+] at 25°C – Alternative View

3.5 Impact of Varying $[K^+]/[Cs^+]$ Ratio on the SuperLig® 644 Cesium K_d at 1 M $[K^+]$, $[OH^-] = 0.25$ M

A set of batch contacts analogous to those reported in Section 3.4 was performed, only here the test solution was composed of 0.75 M KNO_3/0.25 M KOH. The results are listed in Table 3.6 and illustrated in Figure 3.9. Similar to the results observed in Section 3.4 where the sodium/cesium ratio at constant total sodium was varied, increasing concentrations of cesium result in a decreasing cesium K_d. However, the magnitude of the changes is less than that observed for the sodium/cesium system, and the changes level out at relatively lower $[K^+]/[Cs^+]$ ratios.

The cesium isotherm at 1 M potassium, Figure 3.10, like the cesium isotherm at 5 M sodium, indicates the response of a Type I isotherm. In this instance, the isotherm is almost linear, with only a slight negative curvature observed only at the highest cesium concentrations examined.

Table 3.6. Impact of Varying Potassium/Cesium Ratios at 1 M Total Potassium on the Cesium K_d at 25°C

Initial $[K^+]/[Cs^+]$	Final $[K^+]/[Cs^+]$*	Total Cs (mmol) in Test	K_d (Test 1)	K_d (Test 2)	Ave. K_d	SD of Ave. K_d
1.1E+03	1.65E+03	9.1E-03	58	53	56	3
5.5E+03	1.26E+04	1.8E-03	182	119	151	45
1.1E+04	3.17E+04	9.1E-04	276	127	201	105
5.5E+04	1.47E+05	1.8E-04	185	194	190	7
1.1E+05	3.24E+05	9.1E-05	247	193	220	38
5.5E+05	1.89E+06	1.8E-05	296	255	276	29

Contacts performed from 06-18-01 to 06-21-01
* Based on the final average cesium concentration for Tests 1 and 2.

3.6 Total Ion Exchange Capacity Measurement for SuperLig® 644

This experiment involved taking a known, approximately 0.1-g portion of conditioned SuperLig® 644, i.e., resin converted to the acid form, and titrating a suspension of the resin in DI water with standardized solutions of cesium hydroxide, with the solution pH being monitored with a pH electrode. The experimental design is a modification of American Society for Testing and Materials (ASTM) Procedure D 2187-94, Test Method F—Total Capacity of Cation-Exchange Resins. The principle behind the test, namely, converting all the cation exchange sites to the H^+ form followed by neutralization with strong base, remains the same. The major changes were 1) converting from sodium hydroxide to cesium hydroxide and 2) using a pH meter instead of an indicator. The reasons for these changes were first, that the introduction of cesium ion might provide a further driving force to the neutralization reaction with no adverse consequences associated with this substitution and second, that the use of a pH meter instead of an indicator might allow monitoring of the pH at which neutralizations are occurring. To see why this might be important, imagine that there are multiple (both strong and weak) cation exchange sites. One would need to know the pH regime at which the strong and weak sites deprotonated to choose an appropriate indicator. However, the direct monitoring of the pH allows direct observation of the breakpoints without such *a priori* knowledge.

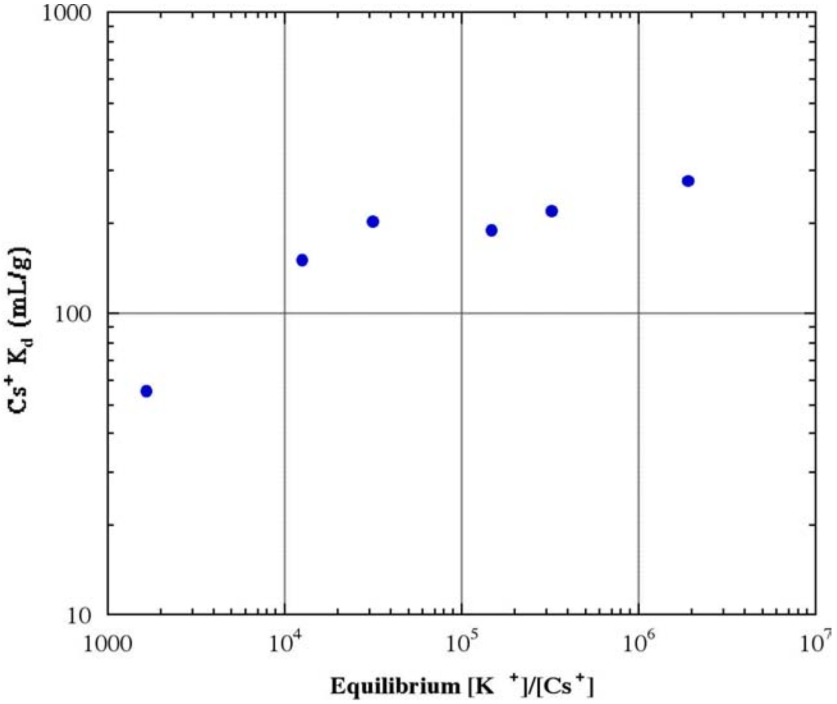

Figure 3.9. Impact of Varying Potassium/Cesium Ratios at 1 M Total [K^+] on the Cesium K_d at 25°C

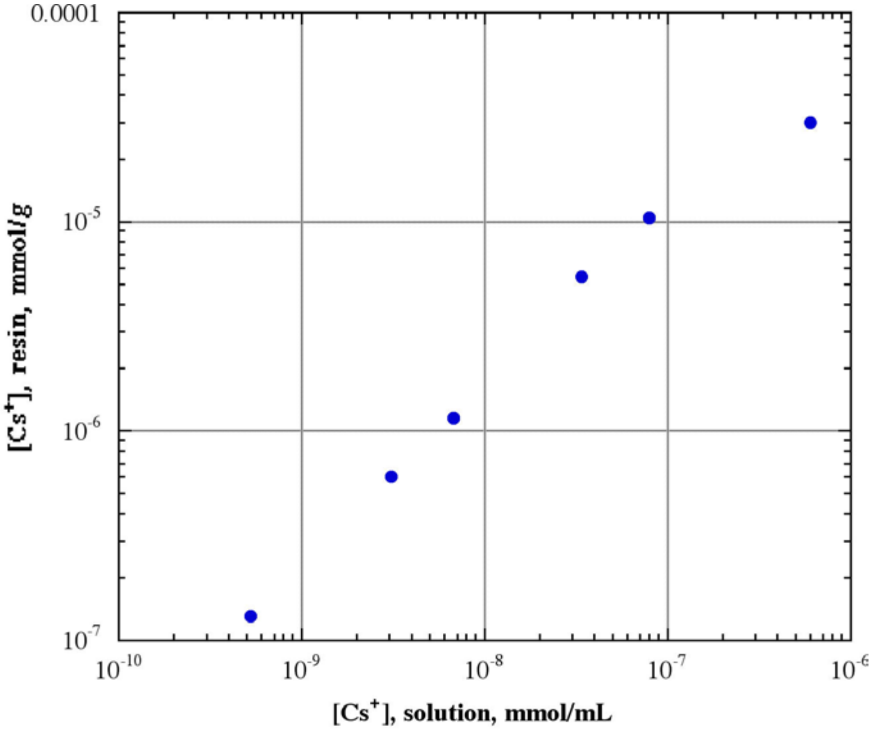

Figure 3.10. Cesium Isotherm Plot at 1 M Total Potassium at 25°C

The addition of 0.01 M cesium hydroxide was used until the pH became greater than 9.5, at which time the titrant was switched to 0.1 M CsOH to more conveniently access pH regions greater than 12. Choosing a wait interval between additions of titrant was problematic. Measurements indicate that a steady decrease in pH occurs over the course of hours to days. To perform the tests in a reasonable timeframe, a wait time of only 2 to 5 min per data point was used. After this time, the rate of pH change in the system dropped markedly. The results of a sample pH titration are shown in Table 3.7 and illustrated in Figure 3.11.

Table 3.7. Total Cation Exchange Capacity Measurement for SuperLig® 644

meq. [OH$^-$]	Initial pH	pH at 10 min	pH at 30 min	pH at 1 h	meq. [OH$^-$]	Initial pH	pH at 10 min	pH at 30 min	pH at 1 h
0	5.07	4.35	4.06	-	0.06591	9.4	8.5	-	-
0.001014	3.71	3.75	-	-	0.07098	9.7	9.3	8.4	-
0.002535	3.94	3.89	3.88	-	0.07605	9.5	8.7	-	-
0.004056	4.57	4.5	-	-	0.08112	9.4	-	-	-
0.00507	4.46	4.4	4.39	-	0.08619	9.4	-	-	-
0.006591	4.95	4.6	4.57	-	0.09126	9.4	-	-	8.9
0.008112	5.3	-	-	-	0.09633	9.5	-	-	9
0.009126	5.5	-	-	-	0.1014	9.55	-	-	-
0.01014	4.45	-	-	-	0.10647	9.24	-	-	-
0.012168	4.75	-	4.43	-	0.11154	9.3	-	-	-
0.014196	4.8	4.62	4.48	-	0.12168	9.5	-	-	-
0.016224	7	5	4.96	-	0.13182	9.58	-	-	-
0.018252	7.4	5.6	-	-	0.14196	9.6	-	-	-
0.02028	8.5	6.6	5.36	-	0.1521	9.6	-	-	-
0.022308	8.7	6.6	-	5.56	0.1707	10.21	-	-	9.9
0.024336	9.2	7.6	-	-	0.1985	10.76	-	-	-
0.026364	9.25	-	6.26	-	0.2450	11.17	-	-	-
0.028392	9.1	-	-	5.68	0.2914	11.38	-	11	-
0.03042	9.3	-	5.84	-	0.3378	11.53	-	-	11.2
0.032448	9.3	-	6.09	-	0.3843	11.56	-	-	11.3
0.034476	9.1	-	6.43	-	0.4307	11.54	-	-	-
0.036504	9.3	7.2	6.74	-	0.4771	11.53	-	11.48	-
0.038532	9.3	7.2	7.1	-	0.52354	10.93	-	-	-
0.041067	9.6	-	7.71	-	0.56997	11.38	-	-	-
0.04563	9.6	-	-	-	0.6164	11.65	-	-	11.46
0.047658	9.2	7.2	7.1	-	0.70926	11.8	-	-	11.67
0.0507	9.3	7.4	7.37	-	0.80212	11.91	-	-	11.79
0.053742	9.2	-	7.5	-	0.89498	11.97	-	-	-
0.05577	9.2	-	7.6	-	0.98784	12.1	-	-	-
0.058305	9.2	-	-	-	1.0807	12.2	-	-	-
0.06084	9.3	-	-	-	1.26642	12.2	-	-	-
0.063375	9.4	8.1	7.84	-	1.545	12.4	-	-	-

In general, the shape of the curve changes little as long as the same length of time between data points is taken. If the equivalence point is taken as shown in Figure 3.9, a capacity of 1.63 meq./g SuperLig®644 is obtained. Interestingly, if phenolphthalein is used as an indicator, and longer interval times are used, a capacity of ca. 2.2 meq./g SuperLig® 644 was obtained. The results of this experiment, although yielding a reasonable capacity for a typical organic ion exchange resin, remain to be validated and should be used with caution. A validation of the titration results might be performed in the following way: first, a known amount of SuperLig® could be placed in a column. An alkaline cesium solution of known concentration could then be slowly passed through the column. Adding ^{137}Cs would allow the cesium concentration in the effluent to be monitored. When the effluent concentration reaches that of the feed solution ($C/C_0 = 1$), the remaining cesium in solution could be flushed out with a strong sodium hydroxide solution. In Section 3.2, it was shown that the cesium Kd remains high at high concentrations of hydroxide so little of the cesium bound to the resin would be displaced. The cesium could then be eluted off with 0.5 M nitric acid until the bulk of the cesium ($C/C_0 < 0.01$) was removed. Again, the solution concentration could be monitored conveniently through the ^{137}Cs activity in the eluate. Finally, the eluate could be combined, assayed for cesium, and the total amount of cesium from the fully loaded column determined. Since the total amount of resin is known, the total cesium capacity could be readily calculated and compared to the titration results reported above.

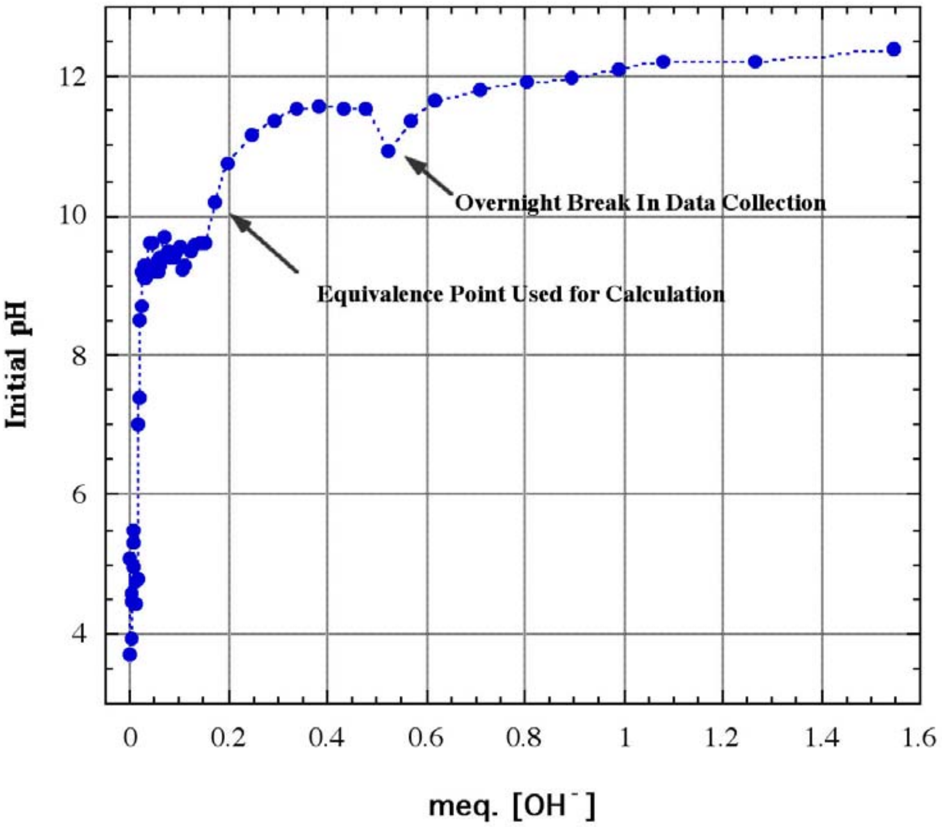

Figure 3.11. Total Cation Exchange Capacity Measurement for SuperLig® 644

3.7 The Effect of Contact Time on the Uranyl K_d for SuperLig® 644 at 1 M $[Na^+]$, 0.25 M $[OH^-]$, and 25°C

For this set of experiments the general procedure used in the cesium-testing analysis was followed after several modifications. First, because the binding affinity of SuperLig® 644 with uranyl ion was anticipated to be less than that of cesium, sodium might become a more effective competitor and mask the resin's affinity for uranyl ion. For this reason, the total sodium concentration was reduced to 1 M by using a test solution of 0.75 M $NaNO_3$/0.25 M NaOH. This was spiked with a stock solution composed of $^{233}UO_2(NO_3)_2$ in a dilute acidic solution. Preliminary tests indicated that uranyl solubility in the test solution was relatively poor and insufficient for concentrated solutions of uranyl ion to remain in solution under these experimental conditions. However, uranyl concentrations in low organic tank supernatants have been measured at the ppm level. To allow measurements with more dilute uranyl solutions, the higher specific activity ^{233}U isotope was used, and the procedure was adjusted to use 1-ml aliquots rather than the 0.1-ml aliquots in 10-ml LSC cocktail. With these changes, what appeared to be homogeneous uranyl-spiked test solutions were tested. The initial uranyl concentration in the solution, based on the initial solution activity and the specific activity of ^{233}U, is about 3.5 ppm or 1.5E-05 M.

The results of the time dependence on the uranyl K_d with SuperLig® 644 are summarized in Table 3.8 and presented graphically in Figure 3.12. The results indicate that the original assumption, that sodium ion would be an effective competitor with uranyl, is incorrect and that SuperLig® 644 binds uranyl ion effectively even in the presence of a substantial excess of sodium ion.

Table 3.8. Time Dependence of the Uranyl K_d with SuperLig® 644 at 1 M total $[Na^+]$, 25°C. Initial $[Na^+]/[UO_2^{2+}] = 67000$.

Time (h)	K_d(Test 1)	K_d(Test 2)	Ave. K_d	SD of Ave. K_d
2	70	78	74	6
4	106	108	107	1
8	173	193	183	14
24	613	537	575	54
48.5	1669	1596	1633	52
72	3090	3156	3123	47
96	3807	3945	3876	9
168	4285	-*	4285*	-*
* Data for duplicate not obtained due to limited resin supply. Contacts performed from 10-08-01 to 10-15-01.				

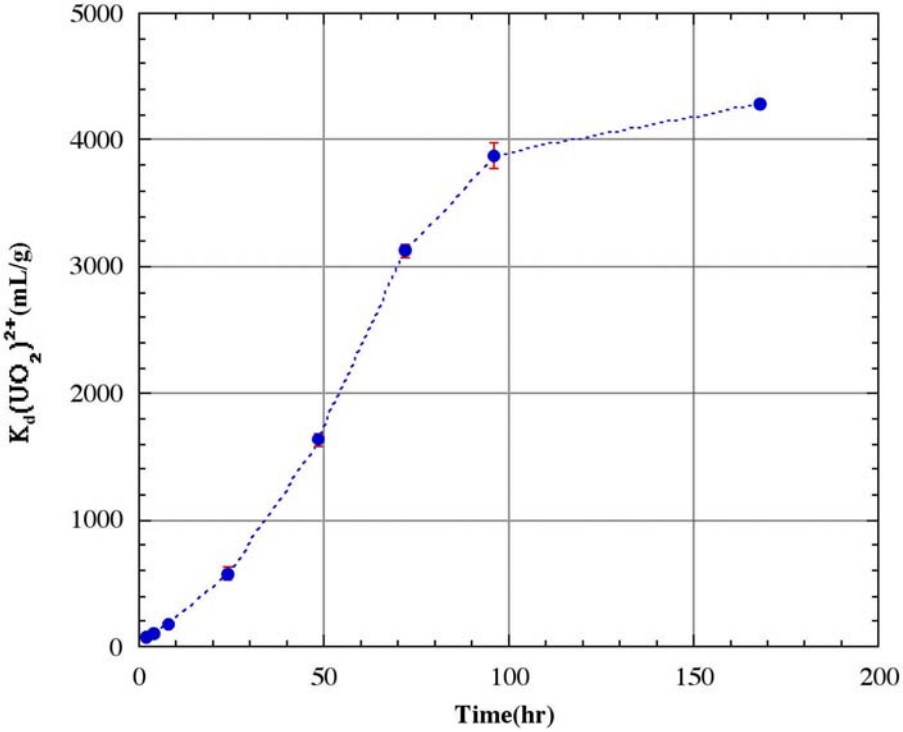

Figure 3.12. Time Dependence of the Uranyl K_d with SuperLig® 644 at 1 M total $[Na^+]$, 25°C. Initial $[Na^+]/[UO_2^{2+}] = 67000$.

3.8 The Effect of Varying $[Na^+]/[UO_2^{2+}]$ Ratio on the Uranyl K_d at 25°C

Experiments designed to test the influence of varying sodium/uranyl ratio were performed. Contact times of 1 week were used based on the results of the previous kinetics tests. Because of the limitations of resin as well as restrictions due to poor solubility of uranyl nitrate in 0.25 M sodium hydroxide, only two data points were collected. These two contacts contained differing concentrations of total sodium. Interpretation of these experiments is confounded by each data point's extremely poor reproducibility, which is puzzling given the good reproducibility in the kinetics experiments. Table 3.9 summarizes the experimental results.

Table 3.9. The Effect of $[Na^+]/[UO_2^{2+}]$ Ratio on the Uranyl K_d at 0.25 M Hydroxide, 25°C

Total $[Na^+]$, M	**Initial [Uranyl], M***	**Initial $[Na^+]/[UO_2^{2+}]$**	**Final $[Na^+]/[UO_2^{2+}]$****	**K_d (Test 1)**	**K_d (Test 2)**	**Ave. K_d**	**SD of Ave. K_d**
5	1.04E-06	4.79E+06	1.01E+07	196	62	129	95
0.25	1.06E-05	2.35E+04	1.84E+05	1444	124	784	933

* Obtained from the initial solution's total alpha activity and the specific activity of ^{233}U.

** Based on the final average uranyl concentration for Tests 1 and 2.

Contacts performed from 12-12-01 to 12-15-01

3.9 The Effect of Varying $[K^+]/[UO_2^{2+}]$ Ratio on the Uranyl K_d at 25°C

Experiments designed to test the influence of varying potassium/uranyl ratio also were examined. Because of the limitations of resin as well as restrictions due to poor solubility of uranyl nitrate in 0.25 M potassium hydroxide, only four data points were collected, and one of these contacts contained a differing concentration of total potassium. As with the sodium/uranyl tests, interpretation of these experiments is confounded by each data point's extremely poor reproducibility. Table 3.10 summarizes the experimental results.

Table 3.10. The Effect of $[K^+]/[UO_2^{2+}]$ Ratio on the Uranyl K_d at 0.25 M Hydroxide, 25°C

Total $[K^+]$, M	**Initial [Uranyl], M***	**Initial $[K^+]/[UO_2^{2+}]$**	**Final Ave. $[K^+]/[UO_2^{2+}]$****	**K_d (Test 1)**	**K_d (Test 2)**	**Ave. K_d**	**SD of Ave. K_d**
1	1.06E-06	9.40E+05	6.45E+06	48	1375	712	939
1	4.01E-06	2.49E+05	3.49E+05	37	47	42	7
1	1.04E-05	9.59E+04	2.65E+05	365	64	215	213
0.25	1.06E-05	2.35E+04	1.37E+05	170	876	523	500

* Obtained from the initial solution's total alpha activity and the specific activity of ^{233}U.

** Based on the final average uranyl concentration for Tests 1 and 2.

Contacts performed from 12-12-01 to 12-15-01

4.0 Discussion

This report summarizes a series of batch contacts with SuperLig® 644 that were used to measure how various system perturbations alter cesium and uranyl distribution values. Unfortunately, some of these experiments experienced considerable scatter in some of the data, although data from many experiments proved to be quite reproducible. It is worthwhile to conclude this report by considering possible sources for this behavior. This problem was not encountered during concomitant studies with SuperLig® 639 resin using the same protocols and personnel, even though SuperLig® 639 floated in most of the test solutions and so might be expected to give larger standard deviations. This implies that the poor reproducibility in some of the SuperLig® 644 data lies not with the test procedure but with some other factor. The resin batch used, the conditioning procedure employed, and the time of testing were the same for any given set of tests, which eliminates these possibilities as variables. With these external factors eliminated, inhomogeneity within the conditioned SuperLig® 644 resin itself remains as the most likely source. Although the same batch of SuperLig® 644 was used for all tests, and although it was sieved to a relatively uniform 0.212 to 0.425 mm of as-received material, no effort was made to homogenize the conditioned sample before transferring it into vials for testing. If this resulted in variability in the particle size distribution between the individual 0.1 g batch contact samples, and the cesium K_d varies with the particle size of the resin, the measured K_ds could be very different for samples that were otherwise experimentally identical.

One possible reason for a cesium K_d dependence on particle size would be poor stability of either the as-received or the conditioned resin. Air oxidation, for example, might occur more rapidly with smaller particle sizes because of the greater surface area per unit mass. Since the resin sat for at least several weeks from the time it was conditioned until the time the tests were performed, the rate of oxidation could still be significant even if slow. Furthermore, the tests occurred over a period of weeks to months, which might have contributed to some of the poor reproducibility from one set of tests to the other, as noted in the results section. Alternatively, a marked particle size dependence on the K_d could be a characteristic of the as-received SuperLig® 644 resin without invoking any subsequent alteration in the resin properties to explain the poor reproducibility in the batch-contact K_ds. No matter what the cause, an examination of possible sources that could contribute to Cs K_d variability is recommended for any future batch-contact tests with SuperLig® 644.

5.0 References

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Appendix A

Spreadsheets

Appendix A: Spreadsheets

RT Kinetics

Note: Work done from 06/11 - 06/14/01
Lot # 010319SMC-IV-23; H+ form; 40-70 mesh
Note: blank A = 2; blank B =0 so no correction needed for background activity
Note: material with particle size 40 to 70 mesh (0.210 mm to 0.425 mm); batch # 010319 SMC-IV-73

Note: initial volume 10 mL by pipette
Note: density of test solution (g/mL): 1.2685

Sample	Name	Time (hours)	Resin wt (g)	Intial aliquot (g)	Initial activity (cpm)	Initial activity (cpm/g)	Final aliquot (g)	Final activity (cpm)	Final activity (cpm/g)	Kd	Kd St Dev
1	H-1A	2	0.1005	1.2639	3740.6	2960	1.2588	343	272	1104	
2	H-1B	2	0.0996	1.2641	3802	3008	1.2615	379.8	301	1016	
ave										1060	63
1	H-2A	4	0.1006	1.2632	3932	3113	1.2671	296.8	234	1375	
2	H-2B	4	0.0997	1.2631	3676.7	2911	1.2637	269.2	213	1429	
ave										1402	39
1	H-3A	6.5	0.0996	1.261	3797.8	3012	1.2664	266.9	211	1502	
2	H-3B	6.5	0.1013	1.2629	3662.8	2900	1.2611	251.1	199	1507	
ave										1504	4
1	H-4A	24	0.1003	1.2619	3827.2	3033	1.2623	239.1	189	1684	
2	H-4B	24	0.0995	1.2643	3742	2960	1.2591	222	176	1785	
ave										1735	72
1	H-5A	48	0.1008	1.2434	3665.9	2948	1.2591	248	197	1559	
2	H-5B	48	0.1021	1.2617	3826.4	3033	1.2543	237.6	189	1654	
ave										1607	67
1	H-6A	74	0.1002	1.2567	3687.6	2934	1.2538	249.5	199	1544	
2	H-6B	74	0.1023	1.2187	3328.7	2731	1.2467	202.4	162	1741	
ave										1642	139
1	H-7A	97	0.1132	1.1813	3703.8	3135	1.2489	215.6	173	1706	
2	H-7B	97	0.1011	1.2238	3627.2	2964	1.2355	268.4	217	1407	
ave										1557	211
1	H-8A	167.5	0.1104	1.2635	3670.4	2905	1.2767	237.4	186	1491	
2	H-8B	167.5	0.106	1.2619	3679.1	2916	1.2656	249.2	197	1466	
ave										1478	17

Summary

2	1060	63
4	1402	39
6.5	1504	4
24	1735	72
48	1607	67
74	1642	139
97	1557	211
167.5	1478	17

Ionic Strength

Note: Work done from 06/11 - 06/14/01 and 7/10-7/13(*)
Lot # 010319SMC-IV-23; H+ form; 40-70 mesh
Note: blank A = 2; blank B = 3 so no correction needed for background activity
Note: material with particle size 40 to 70 mesh (0.210 mm to 0.425 mm); batch # 010319 SMC-IV-73

Note: initial volume 10 mL by pipette

Sample	Name	Conditions	Initial [Na], M	Initial [Cs], M	Initial [Na]/[Cs]	Final Cs, M	Final [Na]/[Cs]	Resin wt (g)	Intial aliquot (g)	Initial activity (cpm)	Initial activity (cpm/g)	Final aliquot (g)	Final activity (cpm)	Final activity (cpm/g)	Kd	Kd St Dev
1	K-1A	5 M Na, 10 microliters 1 M Cs	5	9.09E-04	=D7/E7	3.45E-04	1.45E+04	0.0973	1.2654	6610.9	5224	1.2315	2440	1981	189	
2	K-1B	5 M Na, 10 microliters 1 M Cs	5	9.09E-04	=D8/E8	1.26E-04	3.96E+04	0.1111	1.26	6603.9	5241	1.2481	908.2	728	628	
3	K*-1A	5 M Na, 10 microliters 1 M Cs	5	9.09E-04	=D9/E9	3.42E-04	1.46E+04	0.095	1.2664	7526.3	5943	1.2449	2782.2	2235	197	
4	K*-1B	5 M Na, 10 microliters 1 M Cs	5	9.09E-04	=D10/E10	3.29E-04	1.52E+04	0.1037	1.263	7305.7	5784	1.2203	2551.5	2091	192	
ave						2.85E-04	2.10E+04								301	218
						3.38E-04	1.48E+04								193	4
1	K-2A	2.5 M Na, 5 microliters 1 M Cs	2.5	4.55E-04	=D13/E13	8.12E-05	3.08E+04	0.1086	1.1337	3768.6	3324	1.1081	658.2	594	476	
2	K-2B	2.5 M Na, 5 microliters 1 M Cs	2.5	4.55E-04	=D14/E14	9.01E-05	2.77E+04	0.1016	1.129	3686	3265	1.1062	715.9	647	448	
3	K*-2A	2.5 M Na, 5 microliters 1 M Cs	2.5	4.55E-04	=D15/E15	7.54E-05	3.31E+04	0.1006	1.0654	4033	3786	1.1229	705.6	628	562	
4	K*-2B	2.5 M Na, 5 microliters 1 M Cs	2.5	4.55E-04	=D16/E16	1.18E-04	2.12E+04	0.0964	1.1363	4053	3566	1.1178	1034.8	926	333	
ave						9.12E-05	2.82E+04								455	95
1	K-3A	1 M Na, 2 microliters 1 M Cs	1	1.82E-04	=D19/E19	2.07E-05	4.84E+04	0.1025	1.05	1633.3	1556	1.0309	182.3	177	856	
2	K-3B	1 M Na, 2 microliters 1 M Cs	1	1.82E-04	=D20/E20	3.67E-06	2.73E+05	0.1041	1.0472	1262	1205	1.033	25.1	24	5253	
3	K*-3A	1 M Na, 2 microliters 1 M Cs	1	1.82E-04	=D21/E21	1.25E-05	7.99E+04	0.105	1.0527	1842.8	1751	1.0468	126.1	120	1450	
4	K*-3B	1 M Na, 2 microliters 1 M Cs	1	1.82E-04	=D22/E22	4.97E-05	2.01E+04	0.0927	1.0549	1771.3	1679	1.0436	479.2	459	323	
ave						2.16E-05	1.05E+05								1971	2237
1	K-4A	0.25 M Na, 50 microliters 0.01 M Cs	0.25	4.55E-05	=D25/E25	6.86E-06	3.64E+04	0.0923	1.0114	11506.2	11377	0.9967	1711.9	1718	686	
2	K-4B	0.25 M Na, 50 microliters 0.01 M Cs	0.25	4.55E-05	=D26/E26	3.26E-06	7.68E+04	0.1044	1.0069	11517.5	11439	0.9936	814	819	1397	
3	K*-4A	0.25 M Na, 50 microliters 0.01 M Cs	0.25	4.55E-05	=D27/E27	7.18E-06	3.48E+04	0.0978	1.017	12254.2	12049	1.0122	1926.4	1903	613	
4	K*-4B	0.25 M Na, 50 microliters 0.01 M Cs	0.25	4.55E-05	=D28/E28	5.45E-06	4.59E+04	0.1	0.9957	12300.4	12354	1.0001	1480.2	1480	827	
ave						5.69E-06	4.85E+04								881	356
						6.50E-06	3.91E+04								709	108

Final [Na]/[Cs]	Kd	Kd St Dev
1.45E+04	1.89E+02	
3.96E+04	6.28E+02	
1.46E+04	1.97E+02	
1.52E+04	1.92E+02	
2.10E+04	3.01E+02	2.18E+02
	1.93E+02	3.69E+00
3.08E+04	4.76E+02	
2.77E+04	4.48E+02	
3.31E+04	5.62E+02	
2.12E+04	3.33E+02	
2.82E+04	4.55E+02	9.46E+01
4.84E+04	8.56E+02	
2.73E+05	5.25E+03	
7.99E+04	1.45E+03	
2.01E+04	3.23E+02	
1.05E+05	1.97E+03	2.24E+03
3.64E+04	6.86E+02	
7.68E+04	1.40E+03	
3.48E+04	6.13E+02	
4.59E+04	8.27E+02	
4.85E+04	8.81E+02	3.56E+02
	7.09E+02	1.08E+02

H^+ Effect

Note: Work done from 06/11 - 06/14/01
Lot # 010319SMC-IV-23; H+ form; 40-70 mesh
Note: blank A = 1; blank B =4 so no correction needed for background activity
Note: material with particle size 40 to 70 mesh (0.210 mm to 0.425 mm); batch # 010319 SMC-IV-73

Note: initial volume 10 mL by pipette
Note: 5 M cesium, constant initial [Na]/[Cs]

Sample	Name	Conditions	Initial [Na]	Initial [Cs]	Initial [Na]/[Cs]	Final [Cs]	Final [Na]/[Cs]	Resin wt (g)	Intial aliquot (g)	Initial activity (cpm)	Initial activity (cpm/g)	Final aliquot (g)	Final activity (cpm)	Final activity (cpm/g)	Kd	Kd St Dev
1	J-1A	2.5 M OH	5	4.55E-04	1.10E+04	1.58E-05	3.16E+05	0.1157	1.2087	34415	28473	1.2127	1203	992	2694	
2	J-1B	2.5 M OH	5	4.55E-04	1.10E+04	3.05E-05	1.64E+05	0.1069	1.208	36472	30192	1.1965	2422	2024	1465	
ave						2.32E-05	2.40E+05								2080	869
1	J-2A	1 M OH	5	4.55E-04	1.10E+04	5.86E-05	8.53E+04	0.1032	1.2391	34795	28081	1.2315	4461	3622	736	
2	J-2B	1 M OH	5	4.55E-04	1.10E+04	7.04E-05	7.10E+04	0.0986	1.2387	36350	29345	1.2289	5585	4545	623	
ave						6.45E-05	7.81E+04								680	80
1	J-3A	0.1 M OH	5	4.55E-04	1.10E+04	9.04E-05	5.53E+04	0.1132	1.2509	33022	26399	1.2573	6599	5249	401	
2	J-3B	0.1 M OH	5	4.55E-04	1.10E+04	9.16E-05	5.46E+04	0.1111	1.252	36057	28800	1.2574	7297	5803	401	
ave						9.10E-05	5.50E+04								401	1
1	J-4A	0.01 M OH	5	4.55E-04	1.10E+04	3.93E-04	1.27E+04	0.1108	1.2516	37005	29566	1.2635	32290	25556	16	
2	J-4B	0.01 M OH	5	4.55E-04	1.10E+04	4.06E-04	1.23E+04	0.1006	1.2532	35146	28045	1.2649	31657	25027	13	
ave						3.99E-04	1.25E+04								15	2
1	J-5A	pH 9	5	4.55E-04	1.10E+04	4.82E-04	1.04E+04	0.1046	1.2537	35588	28386	1.2608	37933	30086	-6	
2	J-5B	pH 9	5	4.55E-04	1.10E+04	4.95E-04	1.01E+04	0.1157	1.2541	34569	27565	1.2621	37892	30023	-8	
ave						4.88E-04	1.02E+04								-7	1
1	J-6A	pH 7	5	4.55E-04	1.10E+04	4.50E-04	1.11E+04	0.1142	1.2564	37146	29565	1.2652	37060	29292	1	
2	J-6B	pH 7	5	4.55E-04	1.10E+04	4.73E-04	1.06E+04	0.1138	1.2576	34776	27653	1.2633	36327	28756	-4	
ave						4.62E-04	1.08E+04								-1	3
1	J-7A	pH 5	5	4.55E-04	1.10E+04	4.47E-04	1.12E+04	0.0954	1.2558	35231	28055	1.2624	34794	27562	2	
2	J-7B	pH 5	5	4.55E-04	1.10E+04	4.57E-04	1.09E+04	0.103	1.2614	36532	28961	1.261	36714	29115	-1	
ave						4.52E-04	1.11E+04								1	2
1	J-8A	pH 2	5	4.55E-04	1.10E+04	4.58E-04	1.09E+04	0.101	1.2503	35858	28680	1.2548	36266	28902	-1	
2	J-8B	pH 2	5	4.55E-04	1.10E+04	4.38E-04	1.14E+04	0.0921	1.2046	37628	31237	1.256	37848	30134	4	
ave						4.48E-04	1.12E+04								2	4
1	J-9A	0.5 M HNO3	4.5	4.09E-04	1.10E+04	4.15E-04	1.08E+04	0.1047	1.242	33533	26999	1.2495	34209	27378	-1	
2	J-9B	0.5 M HNO3	4.5	4.09E-04	1.10E+04	4.16E-04	1.08E+04	0.1006	1.2437	33477	26917	1.2482	34167	27373	-2	
ave						4.15E-04	1.08E+04								-2	0

H^+ Effect (Contd)

Name	Conditions	Final [Na]/[Cs]	Kd	Kd St Dev
J-1A	2.5 M OH	3.16E+05	2.69E+03	
J-1B	2.5 M OH	1.64E+05	1.46E+03	
		2.40E+05	2.08E+03	8.69E+02
J-2A	1 M OH	8.53E+04	7.36E+02	
J-2B	1 M OH	7.10E+04	6.23E+02	
		7.81E+04	6.80E+02	8.02E+01
J-3A	0.1 M OH	5.53E+04	4.01E+02	
J-3B	0.1 M OH	5.46E+04	4.01E+02	
		5.50E+04	4.01E+02	5.53E-01
J-4A	0.01 M OH	1.27E+04	1.59E+01	
J-4B	0.01 M OH	1.23E+04	1.35E+01	
		1.25E+04	1.47E+01	1.73E+00
J-5A	pH 9	1.04E+04	-6.08E+00	
J-5B	pH 9	1.01E+04	-7.96E+00	
		1.02E+04	-7.02E+00	1.33E+00
J-6A	pH 7	1.11E+04	9.20E-01	
J-6B	pH 7	1.06E+04	-3.79E+00	
		1.08E+04	-1.44E+00	3.33E+00
J-7A	pH 5	1.12E+04	2.11E+00	
J-7B	pH 5	1.09E+04	-5.76E-01	
		1.11E+04	7.67E-01	1.90E+00
J-8A	pH 2	1.09E+04	-8.57E-01	
J-8B	pH 2	1.14E+04	4.47E+00	
		1.12E+04	1.81E+00	3.77E+00
J-9A	0.5 M HNO3	1.08E+04	-1.49E+00	
J-9B	0.5 M HNO3	1.08E+04	-1.86E+00	
		1.08E+04	-1.68E+00	2.65E-01

Na/Cs Ratio

Cs Kds as f([Na]/Cs])

Note: Work done from 06/18 - 06/21/01
Lot # 010319SMC-IV-23; H+ form; 40-70 mesh

Note: initial volume 10 mL by pipette

Note: blank A = 0; blank B = 0 so no correction needed for background activity
Note: material with particle size 40 to 70 mesh (0.210 mm to 0.425 mm); batch # 010319 SMC-IV-73

Sample	Name	Initial [Na], M	Initial [Cs], M	[Na]/[Cs], initial	Final [Cs], M	[Na]/[Cs], final	Resin wt (g)	Intial aliquot (g)	Initial activity (cpm)	Initial activity (cpm/g)	Final aliquot (g)	Final activity (cpm)	Final activity (cpm/g)	Kd	Kd St Dev
1	L-1A	5	9.09E-04	5.50E+03	3.32E-04	1.51E+04	0.0916	1.2587	6738.1	5353	1.242	2427.8	1955	214	
2	L-1B	5	9.09E-04	5.50E+03	3.11E-04	1.61E+04	0.0954	1.2599	6832.4	5423	1.2407	2303.2	1856	227	
ave					3.22E-04	1.56E+04								220	9
1	L-2A	5	4.55E-04	1.10E+04	9.06E-05	5.52E+04	0.1029	1.2649	3821.7	3021	1.236	744.5	602	439	
2	L-2B	5	4.55E-04	1.10E+04	9.03E-05	5.53E+04	0.0924	1.2577	4064.7	3232	1.2381	795.3	642	491	
ave					9.05E-05	5.53E+04								465	37
1	L-3A	5	9.09E-05	5.50E+04	6.04E-06	8.28E+05	0.096	1.2584	728.9	579	1.2348	47.5	38	1648	
2	L-3B	5	9.09E-05	5.50E+04	6.20E-06	8.06E+05	0.1023	1.2615	743.3	589	1.2393	49.8	40	1503	
ave					6.12E-06	8.17E+05								1575	102
1	L-4A	5	4.55E-05	1.10E+05	3.79E-06	1.32E+06	0.0979	1.2588	11624.7	9235	1.2353	950.4	769	1265	
2	L-4B	5	4.55E-05	1.10E+05	3.29E-06	1.52E+06	0.1032	1.2601	11600.9	9206	1.2283	817.5	666	1399	
ave					3.54E-06	1.42E+06								1332	95
1	L-5A	5	9.09E-06	5.50E+05	2.60E-07	1.92E+07	0.102	1.258	3246.3	2581	1.2342	91.1	74	3747	
2	L-5B	5	9.09E-06	5.50E+05	2.67E-07	1.87E+07	0.0997	1.2613	3401.2	2697	1.2379	98.2	79	3724	
ave					2.64E-07	1.90E+07								3735	16
1	L-6A	5	4.55E-06	1.10E+06	1.25E-07	4.00E+07	0.0964	1.261	1685.5	1337	1.2576	46.2	37	4131	
2	L-6B	5	4.55E-06	1.10E+06	1.15E-07	4.33E+07	0.1001	1.2595	1733.9	1377	1.2298	43	35	4314	
ave					1.20E-07	4.17E+07								4222	130

Sample	Name	Initial [Na], M	Initial [Cs], M	Initial activity (cpm/g)	Final activity (cpm/g)	Resin wt (g)	final solids activity (cpm/g)	[Na]/[Cs], final	Kd	Kd St Dev
1	L-1A	5	9.09E-04	5.35E+03	1.95E+03	0.0916	3.71E+04	1.51E+04	213.5917819	
2	L-1B	5	9.09E-04	5.42E+03	1.86E+03	0.0954	3.74E+04	1.61E+04	226.6359144	
ave					1.91E+03		3.72E+04	1.56E+04	220.1138482	9.223594536
1	L-2A	5	4.55E-04	3.02E+03	6.02E+02	0.1029	2.35E+04	5.52E+04	439.1995299	
2	L-2B	5	4.55E-04	3.23E+03	6.42E+02	0.0924	2.80E+04	5.53E+04	490.9710032	
ave				3.13E+03	6.22E+02		2.58E+04	5.53E+04	465.0852665	36.60795981
1	L-3A	5	9.09E-05	5.79E+02	3.85E+01	0.096	5.63E+03	8.28E+05	1647.873721	
2	L-3B	5	9.09E-05	5.89E+02	4.02E+01	0.1023	5.37E+03	8.06E+05	1503.001459	
ave					3.93E+01		5.50E+03	8.17E+05	1575.43759	102.4401589
1	L-4A	5	4.55E-05	9.23E+03	7.69E+02	0.0979	8.65E+04	1.32E+06	1264.787291	
2	L-4B	5	4.55E-05	9.21E+03	6.66E+02	0.1032	8.28E+04	1.52E+06	1399.336625	
ave					7.17E+02		8.46E+04	1.42E+06	1332.061958	95.14074631
1	L-5A	5	9.09E-06	2.58E+03	7.38E+01	0.102	2.46E+04	1.92E+07	3746.787867	
2	L-5B	5	9.09E-06	2.70E+03	7.93E+01	0.0997	2.63E+04	1.87E+07	3724.025855	
ave					7.66E+01		2.54E+04	1.90E+07	3735.406861	16.09517274
1	L-6A	5	4.55E-06	1.34E+03	3.67E+01	0.0964	1.35E+04	4.00E+07	4130.679629	
2	L-6B	5	4.55E-06	1.38E+03	3.50E+01	0.1001	1.34E+04	4.33E+07	4313.925477	
ve					3.59E+01		1.34E+04	4.17E+07	4222.302553	129.5743819

Na/Cs Ratio (Contd)

Isotherm calc.

	molesCs/resin,final	molesCs/solution, final	final Cs in resin, moles/g(1)	final Cs in sol, moles/mL
1	5.77E-06	3.32E-06	6.30E-05	3.32E-07
2	5.98E-06	3.11E-06	6.27E-05	3.11E-07
ave	5.88E-06	3.22E-06	6.28E-05	3.22E-07
1	3.64E-06	9.06E-07	3.54E-05	9.06E-08
2	3.64E-06	9.03E-07	3.94E-05	9.03E-08
ave	3.64E-06	9.05E-07	3.74E-05	9.05E-08
1	8.49E-07	6.04E-08	8.84E-06	6.04E-09
2	8.47E-07	6.20E-08	8.28E-06	6.20E-09
ave	8.48E-07	6.12E-08	8.56E-06	6.12E-09
1	4.17E-07	3.79E-08	4.26E-06	3.79E-09
2	4.22E-07	3.29E-08	4.09E-06	3.29E-09
ave	4.19E-07	3.54E-08	4.17E-06	3.54E-09
1	8.83E-08	2.60E-09	8.66E-07	2.60E-10
2	8.82E-08	2.67E-09	8.85E-07	2.67E-10
ave	8.83E-08	2.64E-09	8.75E-07	2.64E-10
1	4.42E-08	1.25E-09	4.59E-07	1.25E-10
2	4.43E-08	1.15E-09	4.43E-07	1.15E-10
ave	4.43E-08	1.20E-09	4.51E-07	1.20E-10

K/Cs Ratio

Cs Kds as f([K]/[Cs])

Note: Work done from 06/18 - 06/21/01
Lot # 010319SMC-IV-23; H+ form; 40-70 mesh
Note: blank A = 0; blank B = 0 so no correction needed for background activity
Note: material with particle size 40 to 70 mesh (0.210 mm to 0.425 mm); batch # 010319 SMC-IV-73

Note: initial volume 10 mL by pipette
Note: density of test solution (g/mL):

Sample	Name	Initial [K], M	Initial [Cs], M	[K]/[Cs], initial	Final [Cs], M	[K]/[Cs], Final	Resin wt (g)	Intial aliquot (g)	Initial activity (cpm)	Initial activity (cpm/g)	Final aliquot (g)	Final activity (cpm)	Final activity (cpm/g)	Kd	Kd St Dev
1	M-1A	1	0.000909091	1.10E+03	6.10E-04	1.64E+03	0.0953	1.0657	7005.4	6574	1.0531	4642	4408	58	
2	M-1B	1	0.000909091	1.10E+03	6.06E-04	1.65E+03	0.1053	1.0638	6930.8	6515	1.0414	4523.7	4344	53	
ave					6.08E-04	1.65E+03								56	3
1	M-2A	1	0.000181818	5.50E+03	7.22E-05	1.39E+04	0.0938	1.0323	1293.6	1253	1.0405	517.5	497	182	
2	M-2B	1	0.000181818	5.50E+03	8.83E-05	1.13E+04	0.1	1.0564	1471.8	1393	1.0456	707.8	677	119	
ave					8.03E-05	1.26E+04								151	45
1	M-3A	1	9.09091E-05	1.10E+04	2.53E-05	3.96E+04	0.106	1.064	633	595	1.0366	171.5	165	276	
2	M-3B	1	9.09091E-05	1.10E+04	4.19E-05	2.39E+04	0.1042	1.063	719.9	677	1.0562	329.4	312	127	
ave					3.36E-05	3.17E+04								201	105
1	M-4A	1	1.81818E-05	5.50E+04	6.93E-06	1.44E+05	0.0989	1.0611	6019.2	5673	1.0435	2256.5	2162	185	
2	M-4B	1	1.81818E-05	5.50E+04	6.68E-06	1.50E+05	0.0996	1.0621	6184.7	5823	1.0411	2228.7	2141	194	
ave					6.81E-06	1.47E+05								190	7
1	M-5A	1	9.09091E-06	1.10E+05	2.87E-06	3.48E+05	0.0988	1.0555	3237.4	3067	1.0398	1007	968	247	
2	M-5B	1	9.09091E-06	1.10E+05	3.34E-06	2.99E+05	0.1002	1.0647	3356.9	3153	1.0419	1206.8	1158	193	
ave					3.11E-06	3.24E+05								220	38
1	M-6A	1	1.81818E-06	5.50E+05	5.24E-07	1.91E+06	0.0939	1.062	680.1	640	1.0385	191.5	184	296	
2	M-6B	1	1.81818E-06	5.50E+05	5.33E-07	1.87E+06	0.1064	1.0618	716.8	675	1.0385	205.7	198	255	
ave					5.29E-07	1.89E+06								276	29

Isotherm calc.

	molesCs/resin,final	molesCs/solution, final	final Cs in resin, moles/g(1)	final Cs in sol, moles/mL
1	2.99E-06	6.10E-06	3.14E-05	6.10E-07
2	3.03E-06	6.06E-06	2.88E-05	6.06E-07
ave	3.01E-06	6.08E-06	3.01E-05	6.08E-07
1	1.10E-06	7.22E-07	1.17E-05	7.22E-08
2	9.35E-07	8.83E-07	9.35E-06	8.83E-08
ave	1.02E-06	8.03E-07	1.05E-05	8.03E-08
1	6.56E-07	2.53E-07	6.19E-06	2.53E-08
2	4.90E-07	4.19E-07	4.71E-06	4.19E-08
ave	5.73E-07	3.36E-07	5.45E-06	3.36E-08
1	1.13E-07	6.93E-08	1.14E-06	6.93E-09
2	1.15E-07	6.68E-08	1.15E-06	6.68E-09
ave	1.14E-07	6.81E-08	1.15E-06	6.81E-09
1	6.22E-08	2.87E-08	6.30E-07	2.87E-09
2	5.75E-08	3.34E-08	5.74E-07	3.34E-09
ave	5.99E-08	3.11E-08	6.02E-07	3.11E-09
1	1.29E-08	5.24E-09	1.38E-07	5.24E-10
2	1.28E-08	5.33E-09	1.21E-07	5.33E-10
ave	1.29E-08	5.29E-09	1.29E-07	5.29E-10

[K]/[Cs], Final	Kd	Kd St Dev
1.64E+03	5.80E+01	
1.65E+03	5.34E+01	
1.65E+03	5.57E+01	3.25E+00
1.39E+04	1.82E+02	
1.13E+04	1.19E+02	
1.26E+04	1.51E+02	4.47E+01
3.96E+04	2.76E+02	
2.39E+04	1.27E+02	
3.17E+04	2.01E+02	1.05E+02
1.44E+05	1.85E+02	
1.50E+05	1.94E+02	
1.47E+05	1.90E+02	6.82E+00
3.48E+05	2.47E+02	
2.99E+05	1.93E+02	
3.24E+05	2.20E+02	3.78E+01
1.91E+06	2.96E+02	
1.87E+06	2.55E+02	
1.89E+06	2.76E+02	2.95E+01

Capacity

Note: Work done from 05/01 - 05/10/01
Note: material with particle size 40 to 70 mesh (0.210 mm to 0.425 mm); batch # 010319 SMC-IV-73
Note: sample dried at 50C, vacuum, so F factor = 1
Note: slow kinetics required ca. 4 hours per aliquot during titration

	weight SL-644 (g)	M CsOH	mLs to neutralize (phenolphthalein indicator)	meq./g
	0.12419	0.01014	27.2	2.22085514
	0.14312	0.01014	31	2.19633874
	0.13024	0.01014	28.7	2.23447482
ave.				2.2172229
SD				0.01577942

Uranyl Kd Kinetics

Note: Work done from 07/31 - 08/04/01
Lot # 010319SMC-IV-23; H+ form; 40-70 mesh
Note: blank A = 6.5; blank B =7 so no correction needed for background activity
Note: material with particle size 40 to 70 mesh (0.210 mm to 0.425 mm); batch # 010319 SMC-IV-73

Temperature = 22C
Note: initial volume 10 mL by pipette
Note: density of test solution (g/mL):

Sample	Name	Time (hours)	Resin wt (g)	Intial aliquot (g)	Initial activity (cpm)	Initial activity (cpm/g)	Final aliquot (g)	Final activity (cpm)	Final activity (cpm/g)	Kd	Kd St Dev
1	N-1A	2	0.09828	1.02973	73751	71622	1.02609	45622	44462	70	
2	N-1B	2	0.1021	1.03277	62300	60323	1.04124	36718	35264	78	
ave										74	6
1	N-2A	4	0.0921	1.02908	75896	73751	1.03139	40715	39476	106	
2	N-2B	4	0.09879	1.02254	76889	75194	1.02689	39602	38565	108	
ave										107	1
1	N-3A	8	0.09598	1.04286	75206	72115	1.03244	30033	29089	173	
2	N-3B	8	0.10994	1.02507	76378	74510	1.01339	26206	25860	193	
ave										183	14
1	N-4A	24	0.10213	1.03574	77112	74451	1.00978	11457	11346	613	
2	N-4B	24	0.10075	1.04438	76974	73703	0.99917	12679	12690	537	
ave										575	54
1	N-5A	48.5	0.10315	0.97521	73723	75597	1.01483	4707	4638	1669	
2	N-5B	48.5	0.09371	1.00048	75176	75140	1.02969	5414	5258	1596	
ave										1633	52
1	N-6A	72	0.09344	1.02868	74337	72264	0.99516	2698	2711	3090	
2	N-6B	72	0.09648	1.04026	71923	69139	0.99709	2457	2464	3156	
ave										3123	47
1	N-7A	96	0.10669	1.03622	75164	72537	1.00949	1974	1955	3807	
2	N-7B	96	0.10076	1.03402	75826	73331	0.99073	2000	2019	3945	
ave										3876	98
1	N-8A	168	0.09921	1.00766	59344	58893	1.00352	1524	1519	4285	
2	N-8B	168	0.09227								
ave										4285	

F-factor info for SuperLig 644 (H form)

	1st sample	2nd sample
inital wt	0.1057	0.1089
final wt	0.0938	0.0969
F-factor	0.8874	0.8898
F-factor ave	0.8886	
F-factor SD	0.0017	

Note: 15 microliter initial aliquot, gives ca. 75000 cpm.

Note: U-233 activity (g/dpm)	4.67465E-11
[U], M	1.50472E-05

Na vs Uranyl Kd

Note: Work done from 12/5 - 12/12/01
Lot # 010319SMC-IV-23; H+ form; 40-70 mesh
Note: blank A = 6.5; blank B =7 so no correction needed for background activity
Note: material with particle size 40 to 70 mesh (0.210 mm to 0.425 mm); batch # 010319 SMC-IV-73

Temperature = 22C
Note: initial volume 10 mL by pipette
Note: density of test solution (g/mL):

Sample	Name	[Na], M	Initial [uranyl], M	Initial [Na]/[Uranyl]	Final [uranyl], M	Final [Na]/[Uranyl]	Resin wt (g)	Intial aliquot (g)	Initial activity (cpm)	Initial activity (cpm/g)	Final aliquot (g)	Final activity (cpm)	Final activity (cpm/g)	Kd	Kd St Dev
1	O-1A	5	1.04327E-06	4.79E+06	3.87E-07	1.29E+07	0.09763	1.18885	5219	4390	1.20318	1959	1628	196	
2	O-1B	5	1.04327E-06	4.79E+06	6.89E-07	7.25E+06	0.09386	1.21235	5215	4302	1.20129	3415	2843	62	
ave					5.38E-07	1.01E+07								129	95
1	O-2A	0.25	1.06333E-05	2.35E+04	7.84E-07	3.19E+05	0.09786	0.96977	53349	55012	0.92279	3745	4058	1444	
2	O-2B	0.25	1.06333E-05	2.35E+04	5.06E-06	4.94E+04	0.10007	0.96199	52992	55086	0.96467	25295	26221	124	
ave					2.92E-06	1.84E+05								784	933
				U-233 activity (g/dpm)			4.6747E-11								

Final [Na]/[Uranyl]	Kd	Kd St Dev
1.29E+07	1.96E+02	
7.25E+06	6.15E+01	
1.01E+07	1.29E+02	9.47E+01
3.19E+05	1.44E+03	
4.94E+04	1.24E+02	
1.84E+05	7.84E+02	9.33E+02

K vs Uranyl Kd

Note: Work done from 12/5 - 12/12/01

Lot # 010319SMC-IV-23; H+ form; 40-70 mesh
Note: blank A = 6.5; blank B =7 so no correction needed for background activity
Note: material with particle size 40 to 70 mesh (0.210 mm to 0.425 mm); batch # 010319 SMC-IV-73

Temperature = 22C
Note: initial volume 10 mL by pipette

Note: density of test solution (g/mL):

Sample	Name	Initial [K], M	[uranyl], M	Initial [K]/[Uranyl]	Final [uranyl], M	Final [K]/[Uranyl]	Resin wt (g)	Intial aliquot (g)	Initial activity (cpm)	Initial activity (cpm/g)	Final aliquot (g)	Final activity (cpm)	Final activity (cpm/g)	Kd	Kd St Dev
1	P-1A	1	1.06333E-06	9.40E+05	7.49E-07	1.33E+06	0.09883	1.00026	4944	4943	0.97713	3404	3484	48	
2	P-1B	1	1.06333E-06	9.40E+05	8.64E-08	1.16E+07	0.09246	1.03101	5619	5450	1.00438	445	443	1375	
ave					4.18E-07	6.45E+06								712	939
1	P-2A	1	4.01258E-06	2.49E+05	2.98E-06	3.35E+05	0.10459	1.0019	18704	18669	0.97277	13499	13877	37	
2	P-2B	1	4.01258E-06	2.49E+05	2.76E-06	3.62E+05	0.10805	1.00968	21088	20886	0.96894	13923	14369	47	
ave					2.87E-06	3.49E+05								42	7
1	P-3A	1	1.04327E-05	9.59E+04	2.64E-06	3.79E+05	0.09114	0.98918	51079	51638	1.01272	13211	13045	365	
2	P-3B	1	1.04327E-05	9.59E+04	6.64E-06	1.51E+05	0.10056	1.0073	52963	52579	0.96763	32370	33453	64	
ave					4.64E-06	2.65E+05								215	213
1	P-4A	0.25	1.06333E-05	2.35E+04	4.24E-06	5.90E+04	0.1	0.96556	53328	55230	0.95374	20985	22003	170	
2	P-4B	0.25	1.06333E-05	2.35E+04	1.16E-06	2.16E+05	0.10498	0.97355	52565	53993	0.95451	5617	5885	876	
ave					2.70E-06	1.37E+05								523	500

U-233 activity (g/dpm) 4.6747E-11

Final [K]/[Uranyl]	Kd	Kd St Dev
1.33E+06	4.77E+01	
1.16E+07	1.38E+03	
6.45E+06	7.12E+02	9.39E+02
3.35E+05	3.72E+01	
3.62E+05	4.72E+01	
3.49E+05	4.22E+01	7.13E+00
3.79E+05	3.65E+02	
1.51E+05	6.40E+01	
2.65E+05	2.15E+02	2.13E+02
5.90E+04	1.70E+02	
2.16E+05	8.76E+02	
1.37E+05	5.23E+02	5.00E+02

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