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C. A. Nash[a]; S. T. Isom[a]
[a] Savannah River National Laboratory, Savannah River Nuclear Solutions, LLC, Aiken, SC, USA

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Characterization of Spherical Resorcinol-Formaldehyde Resin Cesium Adsorption with Batch Contact Tests

C. A. Nash and S. T. Isom
Savannah River National Laboratory, Savannah River Nuclear Solutions, LLC, Aiken, SC, USA

Batch contact tests provided data that will be useful in cesium isotherm modeling of spherical resorcinol-formaldehyde ion exchange resin. This resin is the baseline for cesium removal from alkaline high sodium nuclear waste at the Hanford River Protection Project Waste Treatment Plant and is being considered for other applications. Batch contact work at 25°C found that increasing potassium concentration in alkaline solution simulating waste unexpectedly improves cesium adsorption when cesium concentration exceeds about 0.001 M. At lower cesium levels potassium competes with cesium for adsorption on the resin as expected. Additional batch work found that dimethylamine cation competes strongly with sodium adsorption with no significant reduction in cesium adsorption.

Keywords cesium; ion exchange; resorcinol-formaldehyde; spherical resin

INTRODUCTION

Spherical resorcinol-formaldehyde (sRF) ion exchange resin was developed for High Level Waste cesium removal by the United States Department of Energy's Hanford River Protection Project (RPP) (1). Cesium removal is one process within the Waste Treatment Plant (WTP) for high sodium alkaline liquid solutions. Batch contacts, column tests, and isotherm modeling are important in supporting waste treatment using sRF resin.

Resorcinol-formaldehyde resin was first patented at the Savannah River Site for cesium removal from nuclear waste (2). RPP research experience with hydraulic problems related to ground gel resins led to the requirement that the resin be made spherical (1,3,4). Microbeads AS in Skedsmokorset, Norway, produce the spherical form of the resin by a proprietary process.

The cesium removal performance of sRF resin has been the subject of much work in recent years. The resin has been tested with actual nuclear waste liquids as well as simulated waste in small ion exchange columns (5–7). The column campaigns included data on cesium elution from the loaded resins.

Modeling of cesium removal performance requires cesium isotherm data along with physical data on the resin. King, Duffey, and Malene (8) performed a systematic batch contact study with sRF that varied concentrations of sodium, potassium, cesium, and free hydroxide in simulated waste. The work included kinetics tests along with measurements of physical properties like particle size distribution, skeletal density, and drainable void. Potassium concentrations of zero, 0.09, and 0.7 M were tested. The high potassium value represents startup feed planned for the Hanford WTP and therefore saw much study with this resin. Much of the batch contact work by Nash, Duignan, and Duffey (7) used 0.7 M potassium in high sodium liquids for the same reason. However, the greatest volumes of waste supernate at both Hanford and Savannah River have less than 0.2 M potassium. This paper examines potassium effects in the vicinity of the lower potassium concentrations.

Savannah River modeling work uses an isotherm equation requiring concentrations of sodium, potassium, hydrogen ion (free hydroxide), and cesium along with solution temperature (9). Later work added rubidium concentration as an input (10). The modeling system included calculations of chemical activities in solution, a cesium adsorption isotherm, and column simulation. Complete solution composition is needed for the calculation of chemical activities. The modeling has been used to predict plant processing scenarios (11–13).

EXPERIMENTAL

Ion Exchange Resin

Batch 5E-370/641 of the spherical RF IX resin was purchased from Microbeads AS in Skedsmokorset, Norway, and shipped in hydrogen form. Resin was stored in hydrogen form under deionized water in sealed drums. The drums were filled with water as much as practical to displace air, and headspaces were filled with inert gas when practical.

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Address correspondence to C. A. Nash, Savannah River National Laboratory, Savannah River Nuclear Solutions, LLC, Aiken, SC 29808, USA. E-mail: charles.nash@srnl.doe.gov

Some of the drums of this batch were used in the 24'' IX column hydraulic test conducted in the fall of 2005 (4). Resin for this work was taken out of a drum not used in any previous work. To assure a representative supply of resin for laboratory work, the resin was removed from the drum in a manner consistent with ASTM method 2687 using the core-sampling technique. It was temporarily stored in an appropriate vessel submerged in deionized water.

Resin was pretreated per a standard procedure used at SRS. A supply of resin for the upcoming work was first gently agitated with five bed volumes of deionized water for half an hour. The resin was then drained and five bed volumes of 1.0 M NaOH were added. The resin was agitated gently several times and allowed to soak in this solution overnight. After the alkaline solution was removed, the resin was washed at least three times with 3 bed volume portions of deionized water, reducing pH to less than 12.5. The resin supply was then converted back to hydrogen form with 10 bed volumes of 0.5 M nitric acid for two hours or more. After the pH was found to be less than 1, the resin was washed at least three times with 3 bed volume portions of deionized water. It was stored underwater with an argon headspace while subsamples were removed later.

Resin ''F-factor,'' or dry resin weight fraction, was measured in triplicate each time a set of batch contacts was started. Free liquid was removed from a portion of moist resin by vacuum filtration. The damp sample was mixed while portions were removed for batch contact bottles and F-factor beakers. Batch contacts targeted phase ratio of approximately 100 mL/g by the addition of 0.2 g resin (dry hydrogen form basis) and 20 mL of test solution. Batch contact bottle headspaces were inerted with argon before closure and agitation. True phase ratios were calculated after F-factors were determined. Drying moist resin to constant weight at 50°C and less than 90 torr absolute pressure provided the desired dry resin weight fraction. F-factors for the sets of resins were always between 0.5 and 0.54 grams of dry resin per gram of moist resin. Standard deviations of the triplicate measurements were within 9% of the average measurement.

Special precautions were necessary to obtain accurate resin masses. 50-mL beakers were used because static electricity on glass Petri dishes, which were of larger diameter, affected the operation of the analytical balance. Static electricity generally caused an attraction between dry large-diameter glassware and the upper part of the balance chamber. Weight appeared to increase in an erratic fashion as the charge of static electricity dissipated. Handling glassware with metal tongs and aluminum foil greatly reduced the problem. Slow and careful handling of resin containers reduced the generation of static electricity on the glassware and resin beads. Electrical repulsion between resin beads could launch the beads from containers if the precautions were not taken.

Separate batches agitated for 48 or 72 hours provided indications of approach to equilibrium. A comparison of the data showed that this time frame for equilibration was sufficient. All batch contact work was performed in an agitated incubator which maintained batches at a temperature of 25 ± 2°C.

Resin loadings in this work were always calculated from a mass balance on the reduction of alkali metal concentration in batch contact solutions. Direct measurements of resin loadings would have been complicated by sources of the ions other than ions on resin sites. These sources would have included solution moistening the resin samples and pore fluids. It was not possible to wash the resin samples without changing the resin loading. Loadings (Q_{resin}), mmol/g, were calculated using the following:

$$Q_{resin} = \frac{(\text{Batch Liquid volume, mL}) * (\text{Concentration change, M})}{(\text{mass dry hydrogen form resin, g})}$$

Test Solutions

This work used three high sodium solutions simulating supernate at Savannah River. Table 1 provides compositions. ''Tank 2F'' refers to a composition of SRS Tank 241-2F supernate (11). ''SRS'' simulant is an average or typical composition of supernate at SRS. ''Modified Tank 2F'' solution was a simple variation on Tank 2F simulant where water and NaOH were used to reduce the total sodium concentration while boosting free hydroxide slightly. All solutions contained potassium and cesium, but these are not shown in Table 1 because of the wide variations used in the batch tests. Variations were made with solid nitrate salts or with concentrated nitrate solutions so that volume changes in the simulant adjustment were negligible.

Resin titrations were performed with deionized water having various levels of sodium or potassium hydroxide added. The alkali metal hydroxide was added to deprotonate sRF, a weak acid resin.

A series of batch contact tests used a simple solution that was 0.4 M in sodium hydroxide and 430 mg/L (0.00323 M) cesium as cesium nitrate to load resin with cesium. No rubidium was added to any of the batches. This solution was expected to provide relatively high cesium adsorption so that effects of competitors (potassium and organic amine cations) could be evaluated against the control. The high cesium adsorption was expected because of the relatively low ionic strength and high cesium

TABLE 1
Composition of high sodium simulant solutions

Component	Tank 2F simulant (M)	Tank 2F measurement (M)	SRS simulant (M)	Modified Tank 2F simulant
Sodium	6.0	6.26	5.55	4.9*
Nitrite	0.149	0.171	0.71	0.106
Nitrate	4.19	4.94	1.19	3.53
Phosphate	0.005	0.005	0.0	0.0036
Sulfate	0.032	0.033	0.34	0.024
Aluminum	0.26	0.32	0.20	0.228
Carbonate	0.13	N/M	0.20	0.093
Total OH^-	1.31	1.39	N/S	1.42
Free OH^-	0.76	0.80	2.11	1.00
Fluoride	0.0029	<0.013	0.0	0.002
Density**	1.306		1.242	1.239

*A verification measurement provided 4.96 M sodium.
**All densities were average measurements. Relative standard deviations of triplicate density measurements were all less than 0.14% of the average value.
N/M = not measured, and N/S = not specified.

concentration. However, the competitor added to each batch would be expected to interfere with cesium or sodium adsorption if it was indeed a significant competitor for resin sites.

RESULTS AND DISCUSSION

Batch Contacts with High Sodium Solutions

Figure 1 shows the cesium loading on sRF resin plotted against cesium concentration in the SRS simulant. The cesium level in the initial solution as well as potassium concentration was varied and the figure represents equilibrium values. Data at the lowest cesium concentrations show expected competitive behavior by potassium. Increasing potassium concentration in the solution reduces resin cesium loading, which is also represented by increased cesium remaining in solution. Points moving to the right at the lowest cesium concentration follow the operating line at that condition and represent potassium competition with cesium.

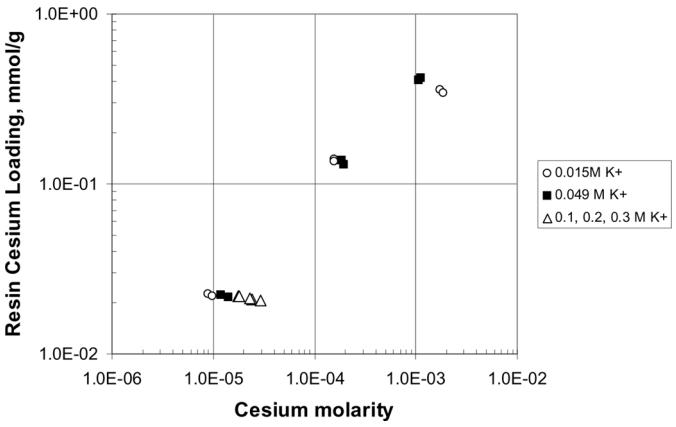

FIG. 1. Batch contact data for "SRS" simulant with varied cesium and potassium.

Data above a cesium concentration of 0.001 M show an unexpected reversal where the trend of cesium adsorption is more favorable at the higher potassium concentration. Table 2, presenting all cesium adsorption data with high sodium solutions, shows that the effect is still present when Tank 2 F and modified SRS solutions are used. In all cases the high cesium data sets show the unexpected effect of increased potassium on cesium adsorption.

Data in Table 2 show that less than 20% of the added potassium adsorbs on the resin. It also shows that the batch distribution coefficient K_d decreases with both increasing potassium and cesium except for the batch data at the highest cesium concentration. The analyses of concentration reported accuracy to be $\pm 10\%$. Batch distribution coefficients (K_d) are averages of two measurements, each being equilibrated to 48 and 72 hours. Reported errors thus consider any departure from equilibrium at the end of 48 hours. Error values increase with K_d because error in final cesium concentration has a higher impact at low cesium concentrations. Percent relative standard deviations (%RSD) are standard deviations of data pairs divided by their average value and expressed as a percentage.

Figures 2 and 3 of data from the other simulant formulations show the same unexpected effect of potassium at the highest cesium concentrations. Cesium adsorption is

TABLE 2
Batch contact data for SRS simulant, 5.55 M sodium

Phase ratio, mL/g	Contact agitation time, hr	Initial [Cs+], M	Final [Cs+], M	Initial [K+], M	Final [K+], M	Cs K_d mL/g	Average $K_d \pm$ %RSD	Resin Cs+ loading, mmol/g (%RSD 4% or less)
90.2	48	2.59E-04	8.88E-06	1.50E-02	1.34E-02	2539		2.25E-02
87.4	72	2.59E-04	9.86E-06	1.50E-02	1.32E-02	2208	$2373 \pm 10\%$	2.18E-02
90.1	48	1.70E-03	1.56E-04	1.50E-02	1.35E-02	893		1.39E-01
88.1	72	1.70E-03	1.55E-04	1.50E-02	1.42E-02	878	$886 \pm 1\%$	1.36E-01
90.2	48	5.73E-03	1.75E-03	1.50E-02	1.41E-02	204		3.58E-01
87.9	72	5.73E-03	1.85E-03	1.50E-02	1.39E-02	184	$194 \pm 7\%$	3.41E-01
89.8	48	2.59E-04	1.19E-05	4.85E-02	4.14E-02	1866		2.22E-02
87.5	72	2.59E-04	1.41E-05	4.85E-02	4.04E-02	1523	$1690 \pm 14\%$	2.14E-02
91.3	48	1.70E-03	1.84E-04	4.85E-02	4.78E-02	751		1.38E-01
86.7	72	1.70E-03	1.96E-04	4.85E-02	4.32E-02	664	$708 \pm 9\%$	1.30E-01
90.8	48	5.73E-03	1.12E-03	4.85E-02	3.89E-02	373		4.18E-01
87.4	72	5.73E-03	1.06E-03	4.85E-02	4.25E-02	384	$379 \pm 2\%$	4.08E-01
90.6	48	2.59E-04	1.78E-05	1.14E-01	1.16E-01	1230		2.18E-02
90.2	72	2.59E-04	1.82E-05	1.14E-01	1.07E-01	1192	$1211 \pm 2\%$	2.17E-02
89.7	48	2.59E-04	2.40E-05	2.13E-01	2.02E-01	878		2.11E-02
89.8	72	2.59E-04	2.32E-05	2.13E-01	2.03E-01	913	$896 \pm 3\%$	2.12E-02
89.8	72	2.59E-04	2.90E-05	3.12E-01	2.92E-01	713	713	2.06E-02

assisted by high potassium somewhere around the cesium level of 0.001 M. One possible explanation is that perhaps potassium in these high sodium solutions increases cesium chemical activity on the solution side, but this has not been investigated yet. Bray et al. (14) reported data on ground gel RF and neutralized current acid waste (NCAW) that appears to approach a similar result. In that report ground gel RF batch contacts measured cesium adsorption at varying potassium level and found a region where potassium competition appeared to vanish at a cesium level of 0.003 M with 3 M sodium solution. Potassium competed with cesium for adsorption sites as expected at lower cesium levels.

Resin Titration Batches

The sRF resin was equilibrated with sodium or potassium hydroxide at varying batch concentrations to provide fundamental characterization information on the resin. Figure 4 shows equilibrium levels of sodium and potassium from batch contacts that started with 0.012, 0.032, 0.052, and 0.069 M alkali metal hydroxide. Alkali metal concentrations were measured by inductively-coupled plasma emission spectroscopy (ICP-ES). The negative curvature would be unexpected if only one type of cation exchange site was active because the double effect of the increased metal and the increased hydroxide should show some region of positive curvature.

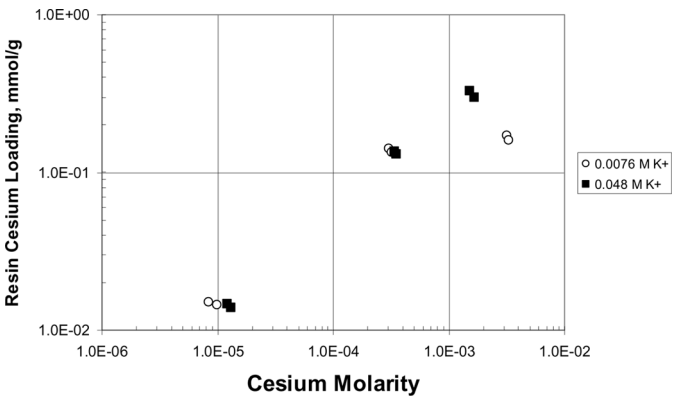

FIG. 2. Batch contact data for "Tank 2F" simulant.

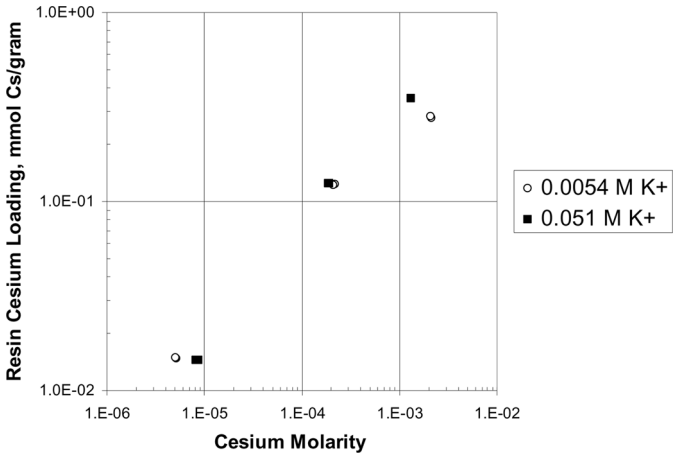

FIG. 3. Batch contact data for "Modified Tank 2F" simulant.

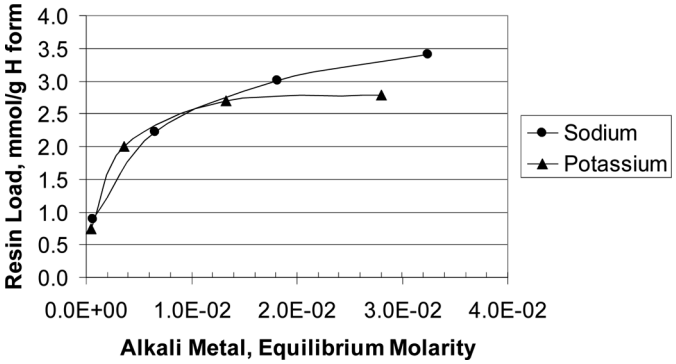

FIG. 4. Batch contact data for resin and alkali hydroxides.

A comparison of methods of reporting metal concentration by pH measurements with the ICP-ES measurements showed that the pH measured by either paper or by electronic pH meter added great scatter to the data. The pHydrion Ultrafine^{TM} papers and an IQ Scientific IQ-150 pH meter with a stainless steel probe were used on subsamples from the equilibrated batches. Figure 5 shows the results from following a simple equation to obtain the metal concentration from pH:

$$\text{Metal concentration, M} = 10^{**}(14 - \text{pH})$$

While the equation does not account for chemical activity in solution, it does allow the scatter from such methods to be visible. This work thus shows that use of ICP-ES is more reliable for resin titration work than pH-based methods of measurement.

Batch Contacts with Various Cation Competitors

While much work in the past has examined alkali metal adsorption on sRF resin, the current work has also explored organic amine cations. The motivations are that similar chemicals may be found in feeds for sRF applications and also that other cations may be useful for sRF applications where the use of elution acid is not desired. Seven batches starting with a base solution that was 0.4 M in NaOH and 430 mg/L cesium as cesium nitrate compared effects of various single competitors to cesium and sodium. Figure 6 shows the results. All but the control batch number 7 had additives as listed. The most notable effect is that the dimethylamine and to some extent the trimethylamine cations appear to compete strongly with sodium.

None of the added amines affected the cesium adsorption to a great extent. Resins of all batches outside of numbers 5 and 6 ended with cesium loadings of $0.290 +/- 0.004$ mmol/g. This suggests that amines should not impact sRF cesium removal processes, though some of them may stay adsorbed to the resin or follow adsorbed sodium during elution. Batch 5 and 6 resins had cesium loadings of 0.276 and 0.260 mmol/g, respectively, showing that potassium demonstrated some measurable competition with cesium.

The sodium loading at the initial sodium concentration of 0.4 M as NaOH shows that the resin total capacity is at least 4.5 mmol/g. Control batch 7 results are the average of four batches. Nash et al. (7) had found a best estimate total of 6 ± 0.8 mmol/g when much higher sodium concentrations were explored.

Sodium in batches 5 and 6 shows expected behavior in that increasing the potassium level in the batch to 0.4 M noticeably drives down the sodium loaded on the resin. The potassium loadings calculated for batch 5 and 6 resins appear to go down with increasing potassium. This is not expected. Effects of measurement error are one possible explanation. The final potassium concentration in solution was measured with an estimated accuracy of 7%. However, applying this uncertainty to the difference in initial and final potassium concentrations leads to the broader error ranges shown. The broad error ranges for sodium also come from differences between larger numbers. Cesium loading estimation had high precision because most batch contacts showed a 97% drop in cesium level. The cesium measurement error of 10% or less thus had much less impact on the resin cesium loading calculation.

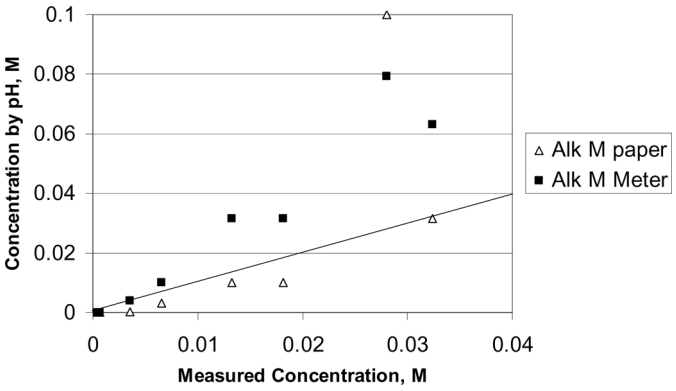

FIG. 5. Comparison of metal concentration by different measurements.

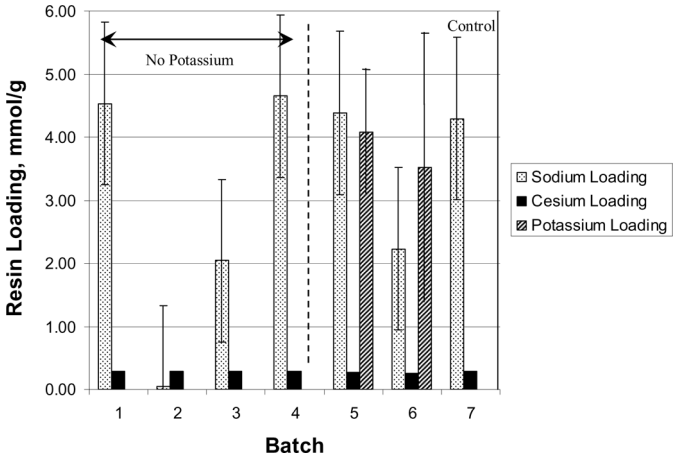

FIG. 6. Alkali metal loadings on sRF resin with different competitors.

Initial Concentration of Each Additive/Competitor:

1 – 0.1 M Methylamine Hydrochloride
2 – 0.1 M Dimethylamine Hydrochloride
3 – 0.1 M Trimethylamine Hydrochloride
4 – Tetrabutylamine phosphate
5 – 0.2 M Potassium Nitrate
6 – 0.4 M Potassium Nitrate
7 – Control, no additive

CONCLUSIONS

Batch contact data with SRS supernate simulants provided relatively low potassium data that will be useful in sRF resin isotherm modeling. The range of potassium level is typical of most SRS and Hanford supernate compositions. Potassium competes with cesium at waste-typical cesium concentrations. Exploration of resin behavior discovered part of a region where potassium assists cesium adsorption when cesium exceeds 0.001 M. Isotherm modeling will have to account for this if calculations above this cesium concentration cannot be avoided.

Resin titration data showed rapid deprotonation of resin sites as alkali metal hydroxide level increased to 0.01 M and above.

A screening of cationic organic amine competitors discovered that dimethylamine and to some extent trimethylamine completed strongly with sodium under conditions of low ionic strength (<0.4 M NaOH). Potassium did not show this effect on sodium. None of the competing cations affected cesium adsorption to a notable extent.

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