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The Effect of Carbonate, Oxalate, and Peroxide on the Cesium Loading of IONSIV® IE-910 and IE-911[#]

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ABSTRACT

This study investigated the effect of salt solution chemistry on cesium loading of IONSIV® IE-911 (UOP LLC, Des Plaines, IL). The Savannah River Site (SRS) explored the use of this sorbent to remove cesium from the 35-million gallons of nuclear waste—supernatant and salt cake—stored on site. The proposed project has a cost estimated between \$1.14 to \$1.35 billion. The U.S. Department of Energy identified this technology as a backup in the Record of Decision.

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This study focused on salt solutions with different levels of carbonate, oxalate, and peroxide. The experiments examined the influence of these trace components on the performance of the sorbent, as even apparent minor variances in performance can dramatically influence the life-cycle cost of the project.

Cesium loading on IE-911 increased with carbonate content in the simulated salt solution. Over the range of concentration (0 to 0.7 M) expected in SRS waste, the cesium loading increased by 38%. The variance likely results from a shift in sodium activity in the solution for increasing carbonate concentration. Removing (0-M) oxalate from simulated "average" salt solution had no effect on cesium loading. Peroxide at 0.1 M decreased the cesium loading on IE-911 by 16%. The expected peroxide concentration in average SRS waste is estimated as 2.6×10^{-6} M. At this concentration level, interpolation of the data suggests no peroxide effect on cesium loading.

INTRODUCTION

More than 35-million gallons of liquid waste stored in carbon steel tanks at the Savannah River Site (SRS) require treatment prior to final disposition. The waste contains soluble radionuclides, in particular, cesium, along with high concentrations of sodium and potassium. Cesium is the primary radionuclide contributing to the activity of the liquid waste. Disposal of the bulk of the liquid as low-level waste requires removal of the cesium, as well as a large portion of the soluble actinides.

The SRS continues to examine two back-up processes for the removal of cesium from high-level waste. One such process uses nonelutable ion exchange with crystalline-silicotitanate (CST) particles as the ion-exchange media.[1] The design disposes of the cesium-loaded CST by vitrification within the Defense Waste Processing Facility. The sorbent, CST, derives from the intensive research for a new class of ion exchangers by personnel at Sandia National Labs (SNL) and Texas A&M University.[2–6] This material has shown a large affinity for cesium even in the presence of high-sodium concentrations.[7–11] Cesium exchanges with sodium ions residing inside the CST particles. The CST is a fine powder and cannot be used in column operations. UOP (Des Plaines, IL) developed a manufacturing process for an engineered form of CST, designated as IONSIV IE-911 for use in fixed-bed columns. The IONSIV IE-911 pellets are formed in a proprietary process that combines the granular titanate—designed as IONSIV IE-910 by UOP—with a binder. Column design requires knowledge of the equilibrium amount of cesium that adsorbs on IE-911. The typical measure of sorption involves the distribution coefficient (K_d), or the weighted (i.e., volume of salt solution per unit weight of solid) amount of adsorbed cesium relative to final salt solution cesium concentration.

$$K_d = \left(\frac{Concentration_{Initial}}{Concentration_{Final}} - 1\right) \times \frac{Volume\ of\ Salt\ solution}{Dry\ Weight\ of\ CST} \tag{1}$$

The SRS produces and stores a variety of liquid wastes with significant variation of composition. In addition, the highly caustic waste constantly absorbs carbon dioxide from the atmosphere. Therefore, the ion-exchange material, IONSIV IE-911, must remove cesium over a wide range of waste chemistry. The chemical elements present in the waste that were not previously tested for their effects on IONSIV IE-911 performance—at these ranges—carbonate, oxalate, and the radiolysis byproduct, peroxide. (The oxalate comes chiefly from previous additions of oxalic acid in various cleaning operations, as well as from the radiolysis of carbonate ions.) At least two possible mechanisms have been suggested that can affect cesium loading on IE-911. For example, the presence of carbonate and oxalate ions can perturb the ionic strength of the solution or they can absorb on (or surface precipitate on) the surface of the IE-911 granules blocking the entrance to the pores. In the case of peroxide, a possible reaction with titanium in IE-911 is envisioned.[12] This study examined the rate of cesium removal and capacity of IONSIV IE-911 in simulated wastes containing carbonate, oxalate, and peroxide.

EXPERIMENTAL

Solubility Test

Before conducting the cesium-removal tests, we determined the approximate solubility of sodium oxalate and sodium carbonate in waste compositions of interest. Personnel prepared 1.0-L samples of “average” salt solution (Table 1) with different amounts of sodium carbonate (corresponding to 0.5-, 0.7-, and 1.0-molar concentration). When adding carbonate, they deducted a proportional amount of nitrate to maintain electrical neutrality. During preparation, we maintained the concentration of sodium 5.6 molar, regardless of carbonate content. Personnel mixed the solution for 1 hour and allowed the solution to equilibrate for 48 hours. They then mixed again for another hour, filtered with a 0.2-micron filter, and analyzed a portion of the solution for sodium, potassium, cesium, and all the anions. Researchers used

Table 1. List of chemicals in average salt solution.

Chemical compound	Concentration (M)
Na^{+}...	0.56×10^{1}
Cs^{+}...	0.14×10^{-3}
H^{+}...	0.524×10^{-14}
Rb^{+}...	0.0
K^{+}...	0.15×10^{-1}
$SrOH^{+}$...	0.0
Sr^{2+}...	0.0
Ca^{2+}...	0.5×10^{-3}
OH^{-}...	0.19×10^{1}
$NO_3{}^{-}$...	0.218×10^{1}
$SO_4{}^{2-}$...	0.15
$Al(OH)^{4-}$	0.31
$CO_3{}^{2-}$...	0.16
NO_2^{-}...	0.51
Cl^{-}...	0.25×10^{-1}
F^{-}...	0.32×10^{-1}
$HPO_4{}^{2-}$...	0.1×10^{-1}
$C_2O_4{}^{2-}$...	0.8×10^{-2}

a similar procedure to make solutions with sodium-oxalate concentrations of 0.01, 0.001, and 0.0001 M.

IE-911 Pretreatment

Personnel placed about 5 g of IE-911 in a glass column suspending the sorbent on a mesh #2 filter. They passed distilled water in an up-flow motion through the sorbent bed at 4 cm/min until all the fines suspended above the bed disappeared. An additional 2-M sodium-hydroxide solution passed in a down-flow motion at 4 cm/min until the equivalent of 40-bed volumes flowed through the column. Finally, operators pumped distilled water in a down-flow motion at 4 cm/min until the pH of the liquid exiting the column fell within the range of 9 to 10. At this point, the bed was permitted to drain and placed in a dessicator until the sorbent reached a constant weight.

Simulated wastes were also prepared with 0- and 0.7-M sodium carbonate in "average" salt solution containing no oxalate. Again, the solutions

Table 2. The ionic strength of the simulants studied.

$CO_3{}^{2-}$ (M)	$C_2O_4{}^{2-}$ (M)	Ionic strength (M)
0	0.008	6.77
0.16	0.008	7
0.7	0.008	7.69
0.16	0	7

contained a sodium molarity of 5.6 M. The ionic strength of the solutions varied with the carbonate content, as indicated in Table 2.

K_d Test

Personnel placed about 0.1 g of pretreated IE-911 in 20 mL of solution and shook at 150 rpm for a finite time in an orbital shaker. The operators maintained the shaker temperature at 22 ± 1.3°C. At the end of the shaking test, researchers filtered the slurry using a 0.02-micron filter, and the filtrate was analyzed with a gamma spectrometer. The gamma-spectrometer response proved linear over the ^{137}Cs concentration range studied (Fig. 1). The limit of detection (LOD) for the in-house gamma spectrometer equaled 2×10^{-6}-M or 212-ppm cesium. The cesium concentrations always exceeded 212 ppm.

When determining cesium-removal efficiency, the investigators calculated the ratio of gamma counts for the initial (before contacting IE-911) and final solution. Using eq. (1) provides a K_d value to gauge the effect of carbonate, oxalate, and peroxide on cesium loading.

RESULTS AND DISCUSSION

Carbonate and Oxalate Solubility in Average Simulant

Sodium-carbonate solubility in “average” salt solution exceeded 1.0 molar. This may appear surprising since carbonates of alkaline metals, like cesium, potassium, and sodium carbonate, have low-solubility constant in water. Apparently, the large amount of free hydroxide stabilizes the compounds in the liquid. Sodium oxalate proved soluble to 0.002 M.

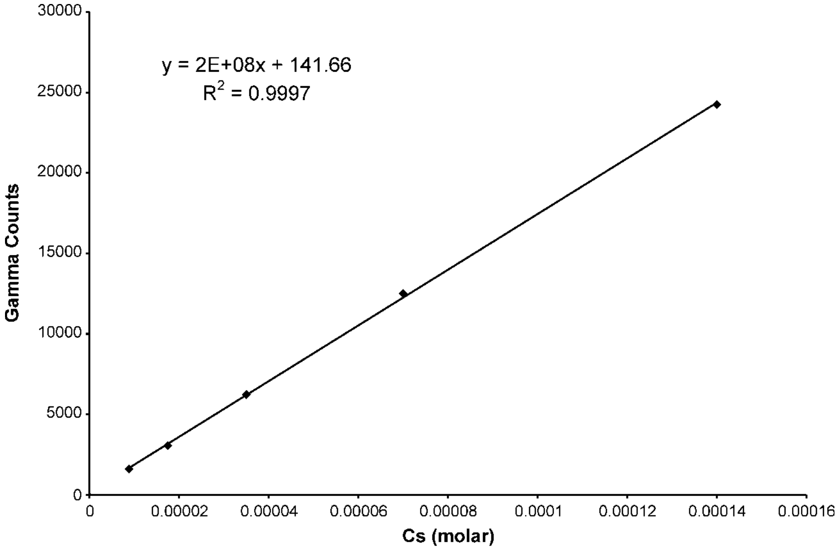

Figure 1. Linear performance of in-house gamma counter.

Cesium K_d Values of IE-911

Effect of Carbonates

Figure 2 shows the effect of (0- to 0.7-M) carbonate content in "average" salt solution on cesium K_d values. The higher the carbonate content, the higher the cesium K_d value achieved on IE-911. A similar experiment performed with samples of IE-910 examined whether this observation proves intrinsic to CST or whether the binder used in the IE-911 causes this behavior. Figure 3 provides the results. The figure affirms the observation of increasing cesium K_d values with increasing carbonate content. An F-test statistical evaluation of 12 samples—six treated in "average" salt solution with 0.16-M carbonate and six treated in "average" salt solution with 0.7-M carbonate—indicate that cesium K_d values increased in proportion with the carbonate content of the salt solution. One obtains the same conclusion when performing an F-test analysis of another six samples treated in "average" simulant with no carbonate vs the "average" simulant test. Next, we used the ZAM model[13] (a multi-component, ion-exchange model incorporating solution-equilibrium data developed by Zheng, Anthony, and Miller) to determine if activity coefficient

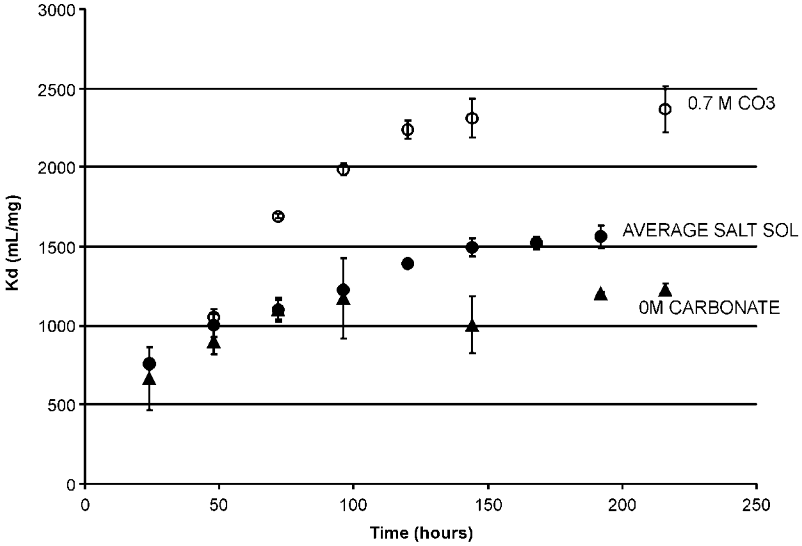

Figure 2. Cesium loading on IE-911 as a function of time and carbonate concentration in salt solution. Average salt solution contains 0.16-M carbonate.

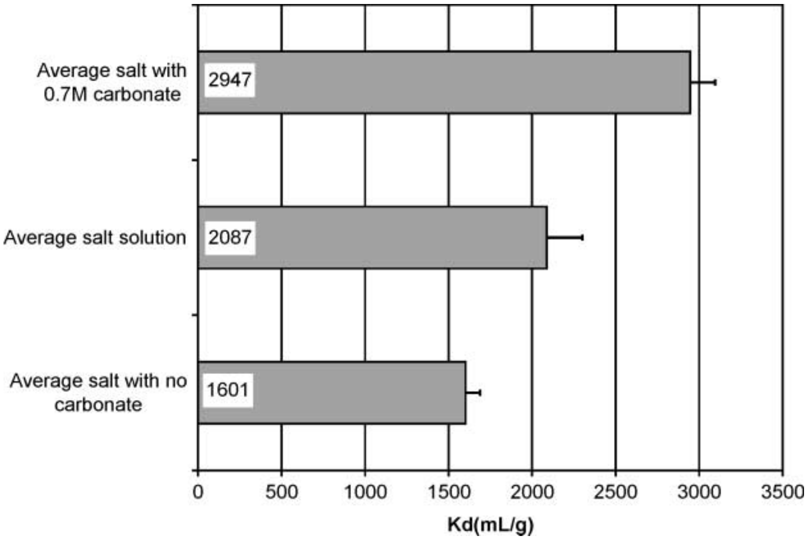

Figure 3. Cesium loading on IE-910 as a function of carbonate concentration in salt solution. Average salt solution contains 0.16-M carbonate.

Table 3. Langmuir isotherm parameters used in the ZAM model.

Salt solution	Measured Kd (mL/g)	Predicted Kd (mL/g)	K, equilibrium constant (L/mol)	Q_T (mmole Cs per g CST)
0 M CO_3^{2-}	1601	1980	3453	0.6
0.16 M CO_3^{2-}	2087	2260	3925	0.6
0.70 M CO_3^{2-}	2947	3410	5970	0.6
0 M $C_2O_4^{2-}$	1924	2260	3884	0.6

changes brought about by introducing carbonates into the salt solution can replicate (or explain) the experimental observation. Table 3 lists the results from the model. The predicted cesium K_d values increased with the carbonate content in the salt solution. The change in activity coefficient may explain the positive correlation between carbonate content and cesium K_d values.

Finally, the salt solutions containing carbonate were analyzed to determine the potassium, sodium, and cesium content. The results indicate no significant variation in the sodium, potassium, and cesium content of the salt solution in the presence of carbonates. This result indicates that the only possible explanation for the increase in cesium K_d values involves a lowering of either the sodium- or potassium-activity coefficient in solution, causing sodium ions to leave some of the sites in IE-911. These newly emptied sites become available for further cesium- and potassium-ion absorption. The investigators do not imply any special sequestration of sodium or potassium by the carbonate ions.

Effect of Oxalate

Figure 4 depicts the effect of oxalate on cesium removal. The figure shows the average result of two tests with the average waste simulant and two tests with the average waste with the oxalate removed. Although there is a difference observed in the kinetics of cesium sorption early in the tests, the equilibrium-distribution coefficient, K_d, is the same (~ 1600 mL/g) for all tests. This indicates that oxalate does not affect cesium loading in IE-911. A further verification that oxalate has no effect was obtained by performing similar tests with IE-910. Looking at Fig. 5, one concludes that there was no oxalate effect detected on cesium loading. Likewise, results from ZAM modeling indicates no effect on cesium loading (2106 vs 2260 mL/g). In fact, increasing oxalate concentration up to 0.1 M in the ZAM model had only a very small effect on cesium loading.

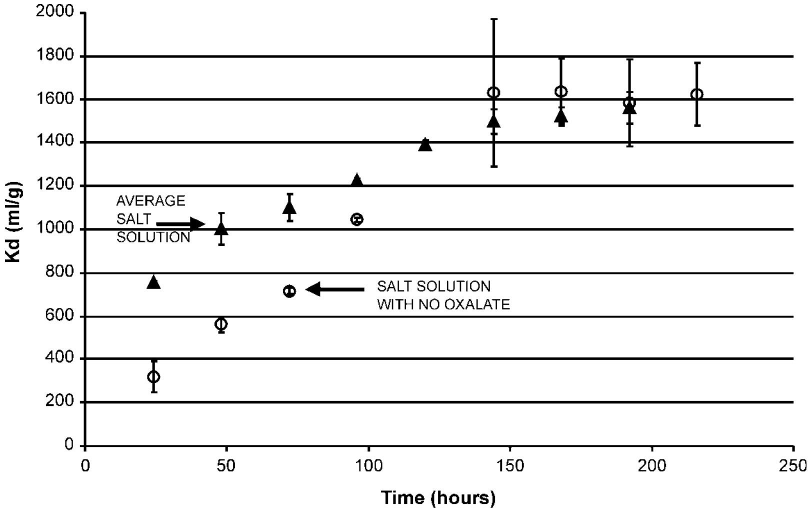

Figure 4. Cesium loading on IE-911 as a function of time and oxalate level.

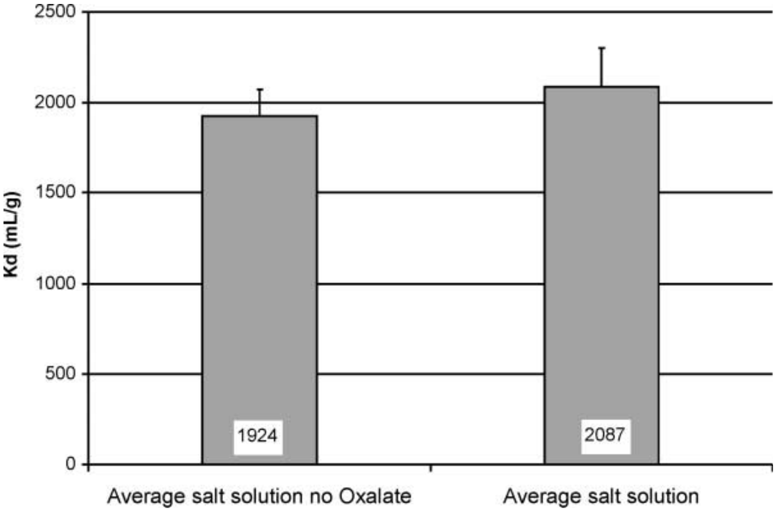

Figure 5. Cesium loading on IE-910 as a function of oxalate level. Average salt solution contains 0.002-M sodium oxalate.

Effect of Carbonate and Oxalate on Column Performance

The VERSE model[14] was run to simulate column performance for the three solutions studied assuming a 16-ft-long (plant-size) column with waste flow at 21 gal/min. The program used the cesium-loading parameters listed in Table 3. Figure 6 provides the results (column elution) of the modeling.

The larger the concentration of carbonate, the later the cesium breakthrough from the column occurred. The increase in cesium loading with carbonate content in the salt solution also results in a shorter mass-transfer zone length, as indicated in Table 4. For a given column diameter, the mass-transfer zone is the length of column whereby the cesium concentration drops from 5% to 95% (this percent drop depends on the objectives of the plant) of the feed concentration.

Effect of Peroxide

We conduced two simultaneous sets of experiments to examine the influence of peroxide. In one set of two experiments (called placebos), researchers injected "average" salt solution containing 0.005 g/mL of IE-911 (0.1 g of IE-911 in 20 mL of salt solution) every 5 hours with 100 μL of

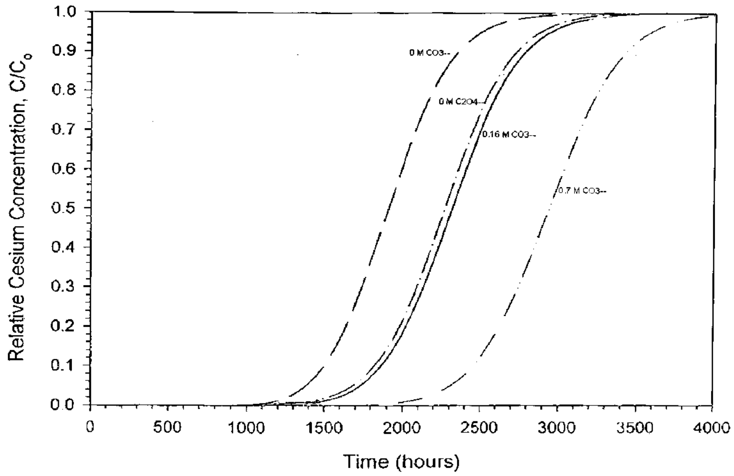

Figure 6. Cesium elution from a 16′-tall column as a function of carbonate and oxalate level. The average salt solution contains 0.002-M oxalate and 0.16-M carbonate.

Table 4. Effect of solution chemistry on mass-transfer zone.

Salt solution type	Ratio of mass-transfer zone to bed length
0 M CO_3^{2-}	0.83
0.16 M CO_3^{2-}	0.742
0.7 M CO_3^{2-}	0.635
0 M $C_2O_4^{2-}$	0.75

distilled water. In the other set, "average" salt solution containing 0.005 g/mL IE-911 was injected every 5 hours with 100 μL of 50 wt% peroxide solution. The peroxide concentration, as determined by permanganate titration, equaled 0.13 M immediately after injection. The peroxide concentration decreased to 0.0034 M after 5 hours. Both sets of experiments occurred on the same shaker. Figure 7 shows the data. The data points in Fig. 7 represent the average of duplicates. A look at the IE-911 data indicates a higher cesium loading in the placebo test relative to the peroxide test. A possible explanation for

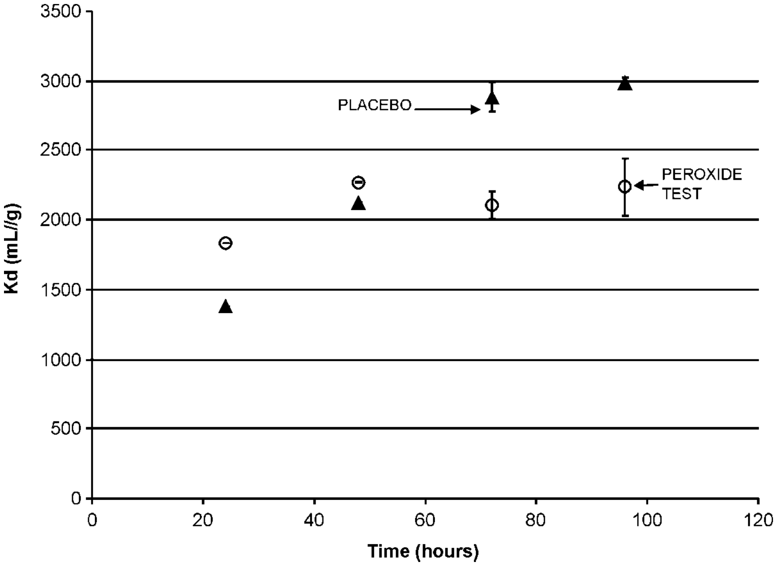

Figure 7. Cesium loading on IE-911 as a function of time and peroxide level in salt solution. Average salt solution contains no peroxide.

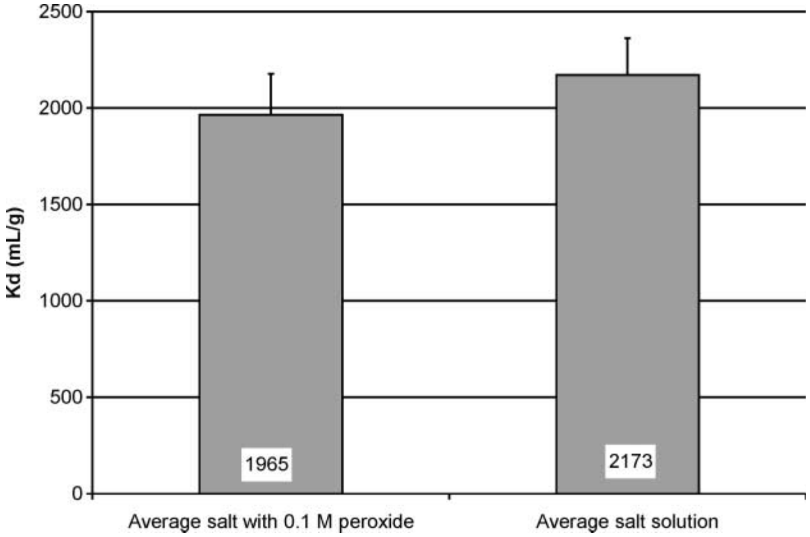

Figure 8. Cesium loading on IE-910 as a function of peroxide level in salt solution. Average salt solution contains no peroxide.

the peroxide effect is the complexation between peroxide and titanium from the IE-911 particles. This reaction can lead to the disintegration of the IE-911.[15]

We performed the same type of experiment with IE-910. Figure 8 displays that data. A look at the data indicates that the results from the average salt waste with 0.1-M peroxide are within the error bars of the results from the average salt solution. Therefore, no conclusion was determined from this test.

The tests used a conservative concentration of peroxide. Subsequently, an estimate of the expected peroxide level in a cesium-loaded plant column yielded a value of 2.6×10^{-6} M based on extrapolated radiolysis measurements in water at half the dose rate.[16] The estimated concentration value at 1 Mrad/h results from doubling the extrapolated value of peroxide production at 0.5 Mrad/h. At this peroxide concentration level and using the data from Fig. 7, one anticipates no effect on cesium loading of IE-911.

CONCLUSION

This study investigated the effect of changes in the solution chemistry on cesium loading. Experiments examined the influence of varying the concentration of carbonate, oxalate, and peroxide on cesium removal by either IONSIV IE-910 or IE-911. The study found that the amount of cesium loading on IE-911 varies proportionally with the amount of carbonate in solution. This correlation results from an increase in the ionic strength of the solution with carbonate content. Higher-ionic strength decreases the activity coefficient of competitors, such as sodium. The presence or absence of oxalate in solution had no effect on cesium loading. Peroxide at a 0.13-M concentration lowered cesium loading on IE-911. A plausible explanation is the destruction of the silicotitanate cell holding the cesium atom by peroxide.

REFERENCES

1. Anthony, R.G.; Dosch, R.G.; Gu, R.D.; Phillip, C.V. Use of silicotitanates for removing cesium and strontium from defense waste. Ind. Eng. Chem. Res. **1994**, *33*, 2702.
2. Anthony, R.G.; Dosch, R.G.; Philip, C.V. Method of Using Novel Silico-Titanates. US Patent Number 6,110,378, August 29, 2000.
3. Anthony, R.G.; Dosch, R.G.; Philip, C.V. Novel silico-titanates and their methods of making and using. World Intellectual Property Organization, PCT/US94/01718, September 1, 1994.
4. Poojary, D.M.; Cahill, R.A.; Clearfield, A. Synthesis, crystal structures, ion-exchange properties of a novel porous titanosilicate. Chem. Mater. **1994**, *6*, 2364.
5. Poojary, D.M.; Bortun, A.I.; Bortun, L.N. Structural studies on the ion-exchanged phases of a porous titanosilicate, $Na_2Ti_2O_3SiO_4{-}2H_2O$. Inorg. Chem. **1996**, *35*, 6131.
6. Sylvester, P.; Behrens, E.A.; Graziano, G.M.; Clearfield, A. An assessment of inorganic ion-exchange materials for the removal of strontium from simulated Hanford tank wastes. Sep. Sci. Technol. **1999**, *34*, 1981.
7. Anthony, R.G.; Philip, C.V.; Dosch, R.G. Selective adsorption and ion exchange of metal cations and anions with silico-titanates and layered titanates. Waste Manag. **1994**, *13*, 503.
8. Zheng, Z.; Gu, Z.D.; Anthony, R.G. Estimation of cesium ion exchange coefficients for concentrated electrolytic solutions when using silicotitanates. Ind. Eng. Chem. Res. **1995**, *34*, 2142.
9. Zheng, Z.; Philip, C.V.; Anthony, R.G. Ion exchange of group I metals by hydrous crystalline silicotitanates. Ind. Eng. Chem. Res. **1996**, *35*, 4246.

10. Gu, D.; Nguyen, L.; Philip, C.V.; Huckman, M.E.; Anthony, R.G.; Miller, J.E.; Trudell, D.E. Cs^+ ion exchange kinetics in complex electrolyte solutions using hydrous crystalline silico-titanates. Ind. Eng. Chem. Res. **1997**, *36*, 5377.
11. Huckman, M.E.; Latheef, I.M.; Anthony, R.G. Ion exchange of several radionuclides on the hydrous crystalline silicotitanates, UOP® IONSIV IE-911. Sep. Sci. Technol. **1999**, *34* (6–7), 1145.
12. Cotton, F.A.; Wilkinson, G. *Advanced Inorganic Chemistry: A Comprehensive Text*, 2nd Ed.; Interscience Publisher: John Wiley & Sons: New York, 1966; 803.
13. Zheng, Z.; Anthony, R.G.; Miller, J.E. Modeling multicomponent ion exchange equilibrium utilizing hydrous crystalline silicotitanates by a multiple interactive ion exchange site model. Ind. Eng. Chem. Res. **1995**, *14*, 119.
14. Whitley, R.D.; Wang, N.H.L. *User Manual—VERSE Simulation for Liquid Phase Adsorption and Chromatography Processes*; Purdue University, School of Chemical Engineering, 1998.
15. Welch, T.D.; Anderson, K.K.; Bostick, D.A.; Dillow, T.A.; Geeting, M.W.; Hunt, R.D.; Lenarduzzi, R.; Mattus, A.J.; Taylor, P.A.; Wilmarth, W.R. ORNL/TM-1999/103; Oak Ridge National Laboratory: Oak Ridge, TN, 2000.
16. Chatterjee, A.; Magee, J.L.; Dey, S.K. The role of homogeneous reactions in the radiolysis of water. Radiat. Res. **1983**, *96*, 1.