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The Effect of Temperature and Radiation on the Cesium Adsorption Ability of IONSIV® IE-910 and IONSIV® IE-911

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SUMMARY

This study examined the ion exchange capacity (K_d) of crystalline silicotitanate (CST) in a simulated waste solution. The focus areas included the effect of temperature and radiation on cesium capacity. The test examined UOP IONSIV® IE-910 (pure form of CST) and UOP IONSIV® IE-911 (engineered form of CST) at temperatures of 22, 35, and 45 °C and IONSIV® IE-911 during irradiation conditions. The following conclusions summarize the results.

- The K_d values of IE-910 (lot # 993796040005) and IE-911 (lot # 999098810005) decreased with increasing temperature. K_d decreased by 56% and 35% for IE-911 and IE-910 as the temperature increased from 22 to 45 °C, respectively. Modeling predicted a 34.4% decrease.
- The K_d value of IE-911 proved significantly higher (by 15%) at 22 °C than predicted by the ZAM (Zheng, Anthony and Martin) equilibrium model.
- An unknown component of IE-911, possibly the binder, effectively absorbs cesium at 22 °C but adsorbs much less effectively at 45 °C.
- Radiation apparently affected K_d within the range of conditions tested. Comparison with the IONSIV® IE-911 thermal data suggest radiation decreased K_d by 20%. On the other hand, comparison with the ZAM model suggest a 30% decrease. However, we estimate the experimental error as high as ± 20%.

INTRODUCTION

Current support of the Salt Disposition Alternatives effort includes using crystalline silicotitanate (CST) ion exchange to remove cesium from highly alkaline High Level Waste (HLW) streams at the Savannah River Site (SRS). The evaluation includes determination of the equilibrium distribution coefficient (K_d) - the mass of absorbed cesium relative to the final concentration of cesium in the salt solution as illustrated in the following formula.

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

Preliminary test results of Phase III evaluation of salt processing alternatives suggested significantly lower cesium capacity for IONSIV® IE-911 at elevated temperatures than predicted by the Texas A&M University ZAM model (Zheng, Anthony and Martin) for IONSIV® IE-910.[1,2] The data suggested the need for additional testing of UOP IONSIV® IE-911 at 22, 35, and 45 °C to estimate the reproducibility of K_d measurements and indicate whether the low observed values at higher temperatures reflected production lot variations or resulted due to the binder. Phase III evaluations also suggested gas

[1] D. D. Walker, "Recovery Plan for the Non-Elutable Ion Exchange Salt Alternative", WSRC-RP-99-00568, Rev. 0, July 1999.
[2] D. D. Walker and W. D. King, "Cesium Removal From Simulated SRS High-Level Waste Using Crystalline Silicotitanate, WSRC-TR-98-00344, Rev. 1, October 1998.

generation rates in a fully loaded ion exchange column would result in bubble formation. Testing is needed to evaluate adsorption in an irradiated source to determine the effect of gas generation on equilibrium capacity.

EXPERIMENTAL PROCEDURE

Temperature Effects on K_d

Testing examined IONSIV® IE-910 lot # 993796040005 and IONSIV® IE-911 lot # 999098810005. Lab personnel weighed 0.1 grams of untreated IE-910 and IE-911 each into twelve (12) 60-mL plastic bottles. Personnel then added 25 mL of simulated average salt solution (see Table 1 for composition) to all the bottles except the IE-911 solutions. Due to an unfortunate mistake the IE-910 solutions did not have sufficient ^{134}Cs.

Table 1. Composition of Simulated Waste Used in the Experiments.

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

Testing used the three shakers listed in Table 2.

Table 2. Water Bath Shaker Settings

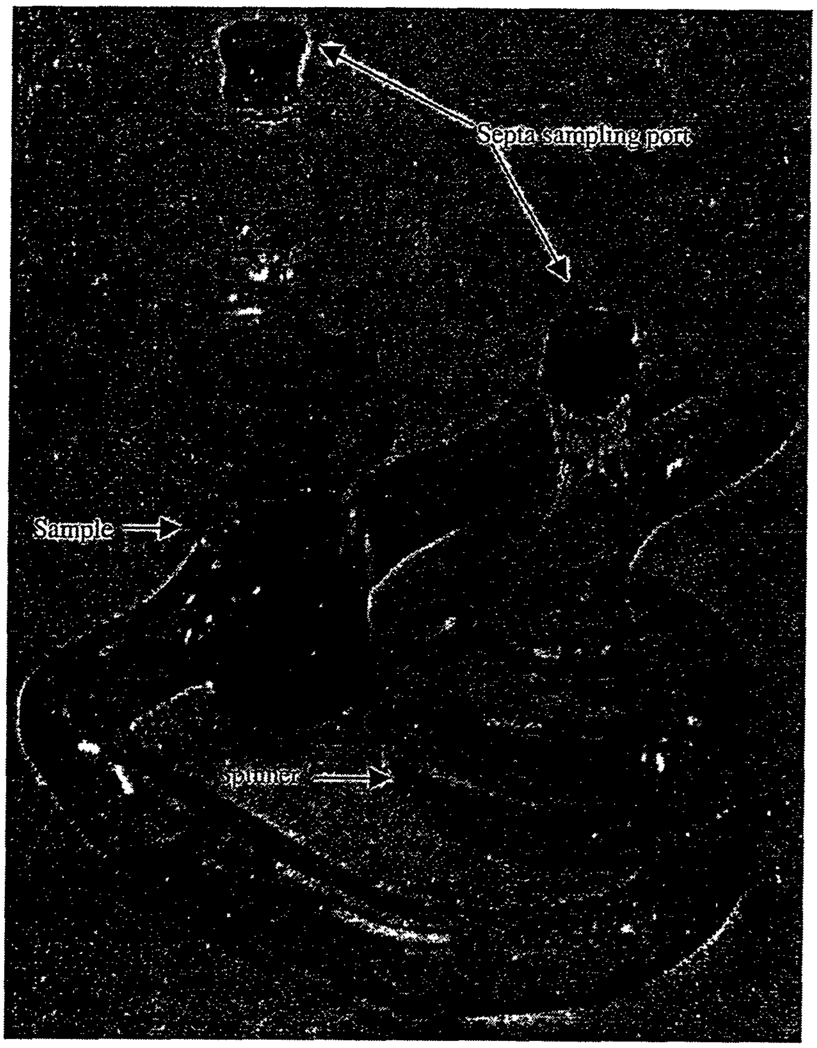
Shaker	Temperature (°C)
New Brunswick Scientific	22 ± 1.8*
Orbit Labline	35 ± 1.7
Orbit Labline	45 ± 1.3

* In one occasion the temperature rose to 26 °C for 6 hours.

Researchers then placed four samples of the IE-910 solution and four samples of the IE-911 solution on each shaker at the desired temperature. All three shakers rotated in an orbital motion at a rate of approximately 250 rpm. The testing continued for 3 weeks with samples taken periodically. The experimental protocol duplicated that used in previous testing.[3]

Radiation Effect

Testing examined IONSIV® IE-911 lot # 999098810005. Lab personnel filled a glass mixing vessel with 45-mL of average salt solution without cesium. We then weighed 0.2 grams of IE-911 into a mesh basket and inserted the basket into the vessel as shown below in the figure below.



Personnel placed the vessel on a stirrer and irradiated for 24 hours at 30 °C ± 1.4 °C in a cobalt source (Shepherd Model #109) at dose rate of 9.05 x 10^5 Rad/hr. Researchers then spiked the sample with 0.012 mL of 0.5 mCi/mL of $^{137}CsNO_3$ and irradiated for seven

[3] F. F. Fondeur, "The Effect of Pressure and Organic Constituents on the Cesium Ion Exchange Performance of IONSIV™ IE-911", WSRC-RP-99-00597, Rev. 0, July 1999.

days. Personnel periodically withdrew small amount of sample for analysis and added the same amount of salt solution (no Cs) back to the device. Personnel duplicated this same experimental procedure outside of the Gamma Cells as a control. The control experiment ran at 22 ± 1.8°C. Both the irradiated and control experiments had similar flow conditions but personnel made no attempt to measure the flow rate.

RESULTS & DISCUSSION

Gamma Counter Calibration

Personnel performed a calibration experiment of the gamma counter for different days. In these tests, researchers recorded the response of the gamma counter for samples containing six different concentrations of cesium. The cesium concentration ranged from the starting salt solution (19 mg/L) to the expected cesium concentration after exposing the solution to IE-911. Figure 2 provides the gamma counter response. The figure indicates a linear relationship between cesium concentration in salt solution and the in-house gamma counter response. Therefore, the authors substituted concentration ratio required in K_d calculation with the count ratio.

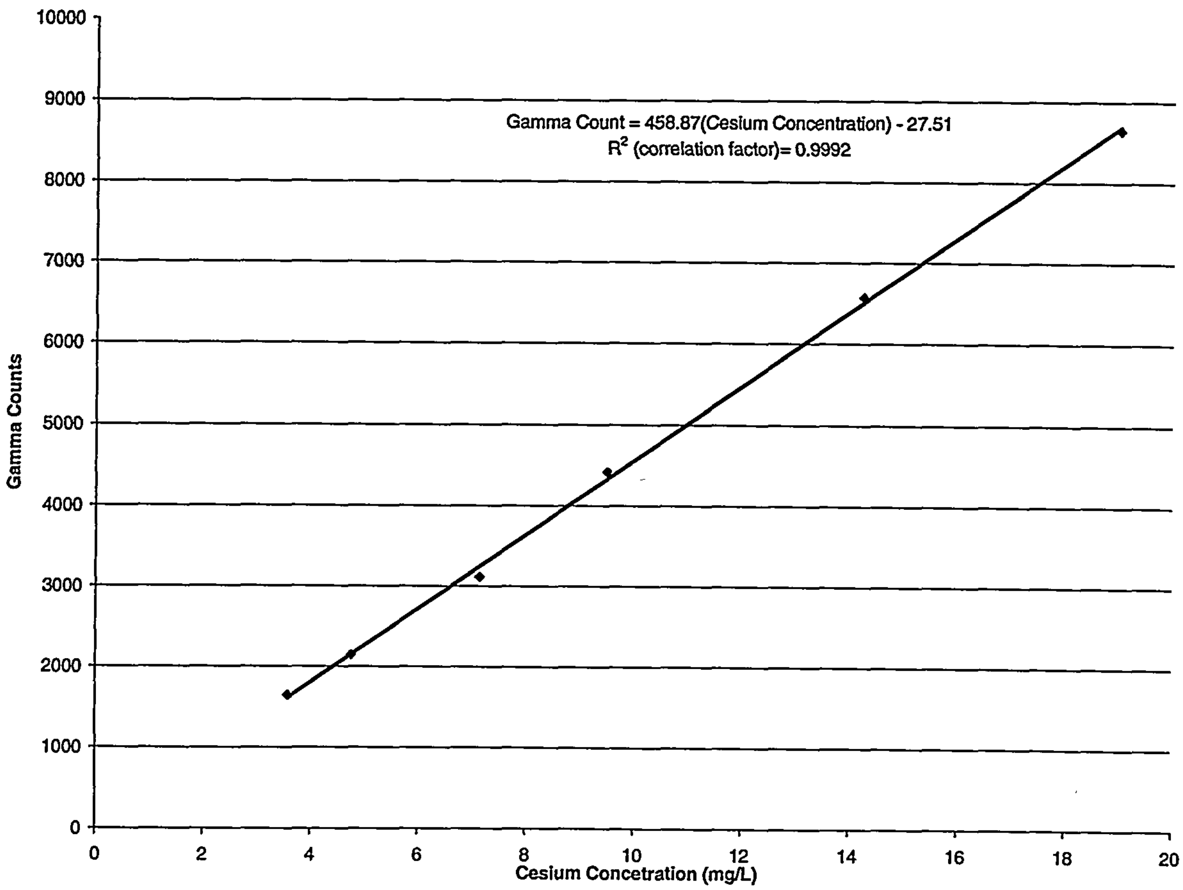


Figure 2. In house gamma counter response at different cesium concentrations.

In addition, personnel submitted samples to the Analytical Development Section (ADS) for gamma counting. The readings obtained by ADS agreed very well with the in-house gamma counter. The ADS values measured 2.32, 2.33 and 2.31 x 10^4 dpm/mL compared to 2.4 x 10^4 dpm/mL obtained from the in-house counter. Thus, the in-house gamma counter appears as precise as its counterpart in ADS. The authors used the counts from the in-house gamma counter to compute K_d values.

K_d Values of IE-910 and IE-911 as a Function of Temperature

Influence of Temperature

Personnel obtained filtered liquid samples from mixtures of untreated IE-910 and salt solution and from mixtures of IE-911 / salt solution after 48, 120 and 240 hours of contact for three different temperatures (22, 35 and 45 °C). Researchers placed the samples in the in-house gamma counter. Figure 3 plots cesium K_d values obtained from IE-910 in salt solution with an initial cesium concentration of 9 x 10^{-16} M and Figure 4 plots K_d values from the untreated IE-911 in salt solution at cesium concentration of 1.4 x 10^{-4} M. The appendix contains all the data. Due to experimental error the initial cesium concentration differed in these solution. If the IE-910 experiment had used the same initial cesium concentration (1.4 x 10^{-4} M) as the IE-911, lower K_d values would result. Looking at the figures, the K_d values appear nearly constant with time except for small amount of noise. The variances come from fluctuations of the in-house gamma counter and sampling errors. The figure indicates K_d values decreased with increasing temperature. Figure 5 shows the temperature effect on K_d values for IE-911. This figure plots the steady state average K_d values of IE-910 and IE-911 as a function of temperature.

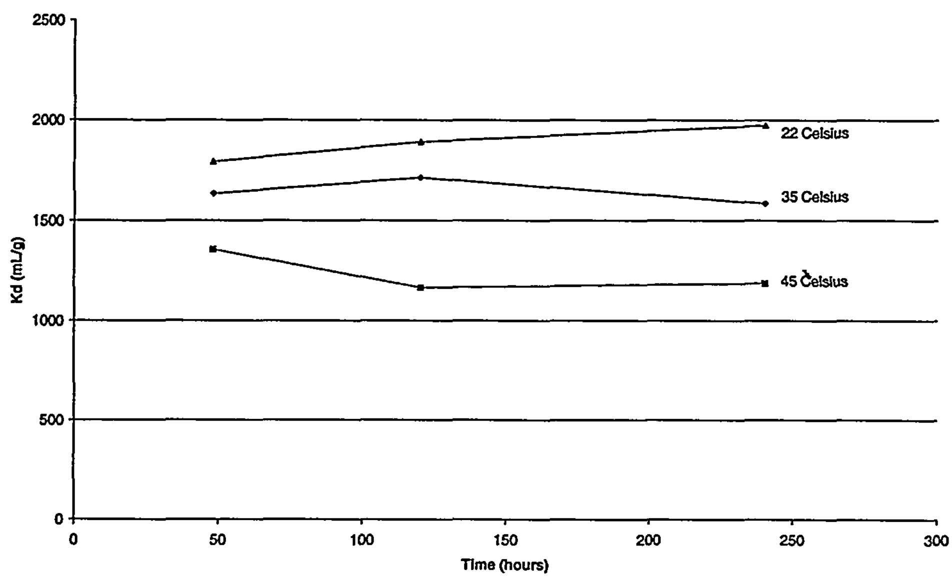


Figure 3. Cesium K_d values of IE-910 as a function of time at three different temperatures.

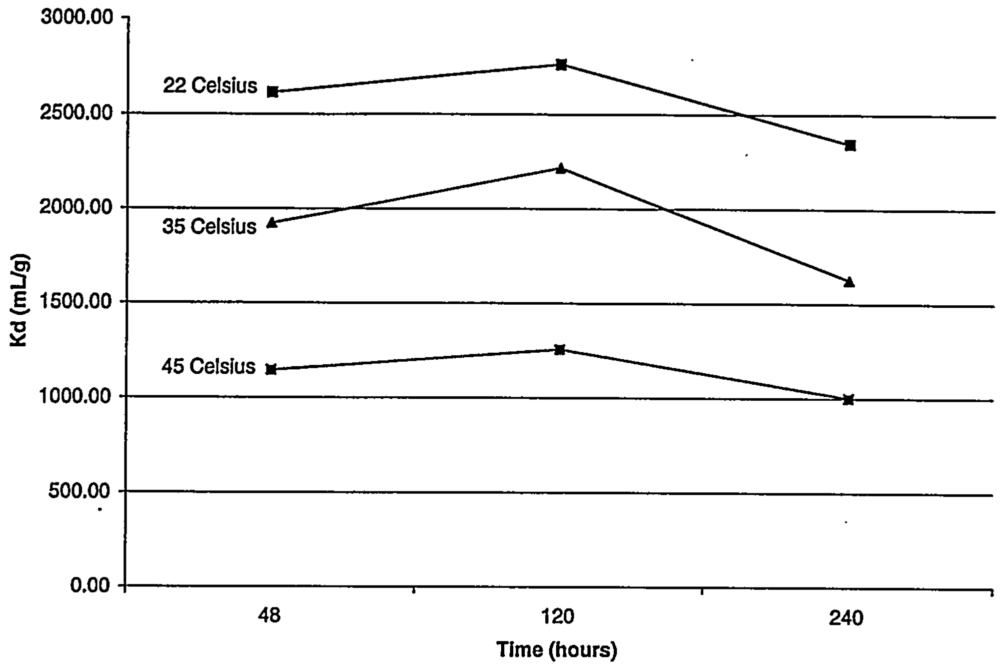


Fig. 4. Cesium K_d values of IE-911 as a function of temperature at three different temperatures

Also included in this figure is the predicted values for the sodium treated form of IE-910 from the ZAM (Z. Zheng, R. A. Anthony and J. E. Martin) model and sodium treated IE-911 test at ORNL. Looking at the figure, both IE-910 and IE-911 K_d values decreased with increasing temperature.

Returning to Figure 5, the K_d values from IE-911 proved higher than the corresponding values of IE-910. This trend suggests that another component of IE-911 absorbs cesium at lower temperature but at 45 °C absorbs less efficiently. Both IE-910 and IE-911 have similar K_d values at 45 °C but both prove lower than the predicted value of 1450 mL/g

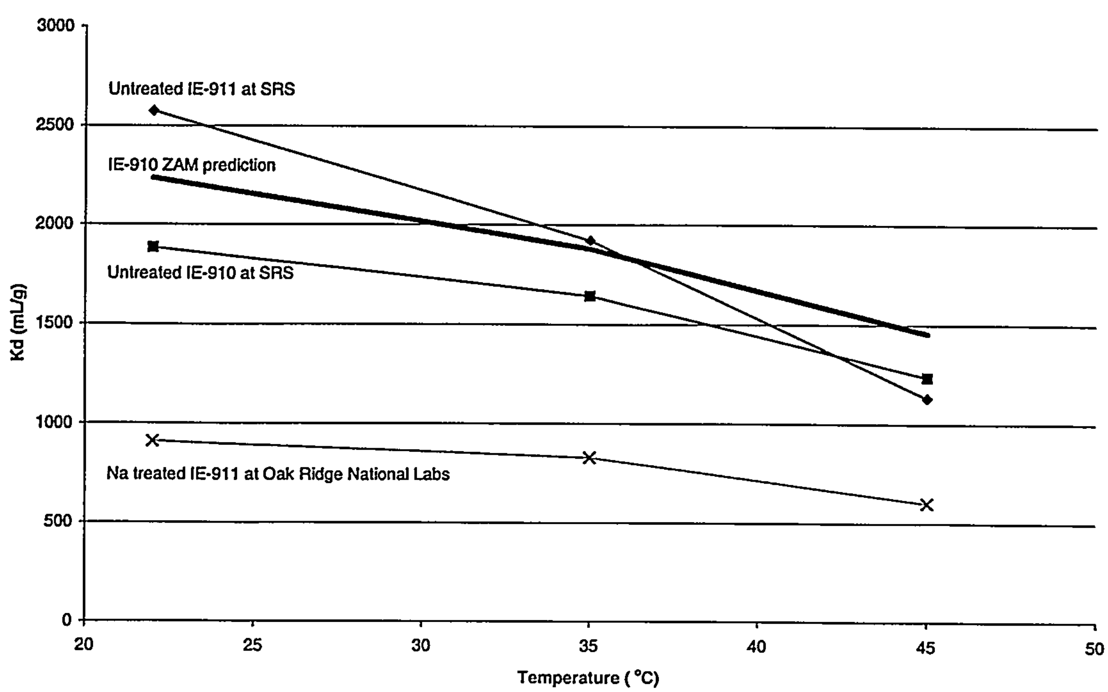


Figure 5. Cesium K_d values of IE-911; IE-910 as a function of temperature

from the ZAM (Z. Zheng, R. A. Anthony and J. E. Martin) program. Also from Figure 5, all the samples have similar temperature dependence except for the untreated IE-911 tested at SRS.

Radiation Effects on K_d Values

Personnel collected and filtered liquid samples from the testing device illustrated in Figure 1 and the similar one used as a control. Sampling occurred at 24, 48, 72 hours and 8 days. Personnel sent the samples to ADS for cesium analysis by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Atomic Absorption technique. Figure 6 provides the results. The figure shows four sets of curves. Two curves (one from ICP-MS and the other from AA) represent the cesium K_d values of IE-911 under radiation and the other two represent the control. As seen in this figure, both curves did not reach steady after 8 days. In addition, researchers did not adjust the cesium concentration was not adjusted for cesium removed during sampling and subsequently, dilution with salt solution. After 8 days, the K_d value of the irradiated experiment reached 1339 mL/g compared to 2340 mL/g value obtained in the control experiment. Since the control experiment ran at 22 °C and the irradiated one at 30 °C, the data contains an offset temperature.
We considered two methods to adjust the experimental data for the temperature offset. In the first method, we used the experimental data for IONSIV® IE-911 as shown in Figure 5 to adjust the measured K_d from the radiation test. Using the slope from Figure 5 (-66 mL/(g°C)) suggests a correction of 528 mL/g. Hence, the corrected K_d value at 22 °C is 1867 mL/g. Hence radiation decreased capacity by 20%. In the second method, we used the data from the ZAM model as shown in Figure 5. Using the ratio of K_d values at 22 °C and 30 °C (K_d(22 °C) / K_d (33 °C)), the corrected K_d is 1643 mL/g. Hence, radiation reduced the capacity by 30%. Both method of analysis suggests radiation reduced cesium capacity. We estimate the error based on routine analytical uncertainty as 20% (2σ). Further experiments should examine the role of radiation.

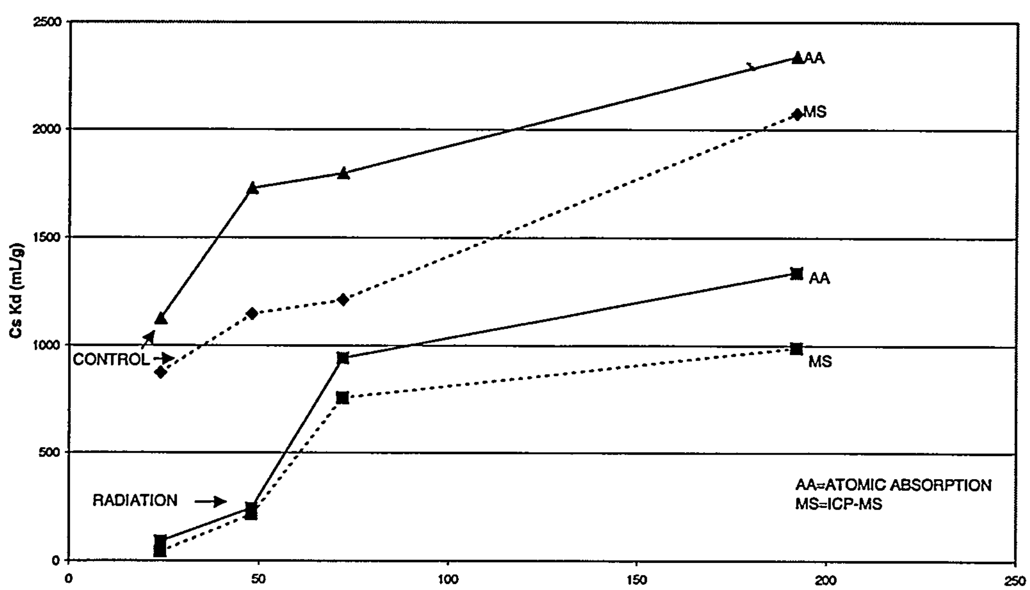


Figure 6. Cesium K_d values of IE-911 under radiation as a function of time

Conclusions

The study investigated the effect of temperature and radiation on cesium K_d values of IE-911. The results showed cesium K_d values decreased 56% for the IE-911 sample and 35% for IE-910 sample over the range from 22 to 45 °C. At 22 °C, the measured K_d's proved larger than predicted by the ZAM equilibrium model. Radiation affected Kd within the range of conditions tested. Data analysis with IONSIV® IE-911 thermal data suggest a 20% decrease in cesium capacity. On the other hand, data analysis with the model showed radiation decreased capacity by 30%. If the CST alternative is selected, the effect of radiation should be studied further.

Acknowledgement

The authors acknowledge Bill Sexton for conceptualizing and fabricating the device shown in Figure 1 for the irradiation test. We also thank Betty Croy, Jeanine Mills and Vicki Dukes for preparing the samples and carrying out the experiments.

Quality Assurance

Notebook WSRC-NB-99-00216 contains all the experimental data.

Appendix

Table 1. Measured K_d (mL/g) values as a function of temperature.

Temperature °C	IE-910	IE-911	ZAM model	ORNL
22	1885.00	2574	2235	910
35	1642.6	1921	1880	830
45	1236	1134	1455	600

Table 2. Measured K_d (mL/g) values of IE-910 as a function of time at different temperatures.

Hours	25 °C	35 °C	45 °C
48	1791	1632	1356
120	1891	1712	1165
240	1974	1584	1187
410	2616	14144	1161

Table 3. Measured K_d (mL/g) values of IE-911 as a function of time at different temperatures.

Hours	25 °C	35 °C	45 °C
48	2613.79	1922.92	1145.08
120	2760.75	2216.76	1256.42
240	2348	1624	1001
410	2688	1807	1042

Table 4. Measured K_d (mL/g) values of IE-911 as function of time under radiation.

Time (h)	Control No radiation	Irradiated
0	Not measured	Not measured
24	1125.7	89.4
48	1728.7	242.6
72	1798.5	942.3
192	2340.5	1339.7