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Ion Exchange of Cesium by Crystalline Silico-titanates

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ABSTRACT

The crystalline silico-titanates developed by the Department of Chemical Engineering at Texas A&M University, Sandia National Laboratories and UOP exhibits extremely high ion exchange selectivity for removing cesium from aqueous defense wastes. Based on experimental data and structure studies, a competitive ion exchange model was proposed to predict the ion exchange performance in different simulated waste solutions. The predicted distribution coefficients were within 10% of the experimentally determined values.

INTRDUCTION

The Hanford Reservation in Washington incorporates 176 tanks that store more than 65 million gallons of radioactive wastes. These wastes are a byproduct of the production of nuclear materials during the past half century, and consist of complex and sometimes unstable mixtures of sludges, saltcakes, slurries and supernate. ^{137}Cs is one of the major radioactive elements in the wastes, which are highly concentrated sodium solutions. The supernate contains a trace amount of cesium in a caustic matrix with more than 5 M sodium. An ion exchanger with high selectivity for cesium together with stability in caustic and radioactive solutions is required to reduce the volume of the waste.

The crystalline silico-titanates, denoted as TAM5 or UOP IONSIV® ion exchanger type IE 910, developed by Department of Chemical Engineering at Texas A&M University, Sandia National

Laboratories and UOP exhibits extremely high ion exchange selectivity for cesium [1,2,3,4]. Marsh et al. [5] tested sixty-three materials for cleanup of cesium and concluded that TAM5 is the best. To design and optimize ion exchange equipment, knowledge of the cesium distribution coefficient, the equilibrium ratio of cesium concentration in the exchanger phase to that in the aqueous phase, is needed. Due to the wide variety of waste composition and possible competitive exchange with potassium and rubidium in the solutions, direct experimental measurement of all possible applications requires extensive laboratory work. An equilibrium model which is able to predict the cesium ion exchange performance in different solutions is necessary.

TAM5 is an inorganic ion exchanger with well defined crystal structure. It contains sodium which is exchangeable and has many unique ion exchange properties. Multiple ion exchange sites exist in the material, but only part of them are available for cesium. All Group I metals are exchangeable; therefore, competitive exchange must be considered as the waste solutions usually contains potassium and/or rubidium.

Based on the data on ion exchange performance and structure studies, an ion exchange equilibrium model has been developed to estimate the competitive effect of other cations on the cesium distribution coefficient. Distribution coefficients estimated for Hanford (DSSF and NCAW), ORNL and other waste simulants match the experimental data within 10%.

ION EXCHANGE EQUILIBRIUM

Ion exchange is a stoichiometric process, where an ion removed from the solution is replaced by another ion from the solid. This is normally represented as follows:

$$\nu_B A + \nu_A \overline{B} \leftrightarrow \nu_B \overline{A} + \nu_A B \qquad (1)$$

where, A and B are ions in the liquid phase; $\overline{A}$ and $\overline{B}$ are ions in the solid phase; ν_A and ν_B are stoichiometric coefficients, and equal to the absolute values of valences of the counter ions. The activities of the cations are related by an equilibrium constant as follows:

$$K_{eq} = \frac{(\overline{a_A}^{\nu_B})\ (a_B^{\nu_A})}{(\overline{a_B}^{\nu_A})\ (a_A^{\nu_B})} \qquad (2)$$

where K_{eq} is the thermodynamic equilibrium constant; $\overline{a}_A$ and $\overline{a}_B$ are the activities in the solid phase of counter ions A and B; a_A and a_B are the activities in the liquid phase of A and B.

For ion exchange between Group I metals, ν_A and ν_B are unity, and Equation (2) can be written as follows:

$$K_{eq} = K_{d_A} \frac{(\overline{\gamma_A})\ (C_B\, \gamma_B)}{(q_B\, \overline{\gamma_B})\ (\gamma_A)} \qquad (3)$$

where $\overline{\gamma}_A$ and $\overline{\gamma}_B$ are the activity coefficients in the solid phase of counter ions A and B; γ_A and γ_B are the activity coefficients in the liquid phase of A and B; C_B and q_B are the concentrations of B in the liquid phase and solid phase; K_{dA} is the distribution coefficient of A which is defined as:

$$K_{d_A} = \frac{q_A}{C_A} \qquad (4)$$

where q_A and C_A are the concentrations of A in the solid and liquid phases.

EXPERIMENTS

Titration by Acid. Titration by acid is basically ion exchange of a cation with a proton. A pH change in the aqueous phase can be observed as acid is added to the solution. The experiment was a multiple-cup batch experiment. Twenty-two HCl solutions with different concentrations were prepared. The HCl solutions were then mixed with TAM5 in plastic vials. The mixtures were shaken for twenty-four hours, and then filtrated to obtain the liquid free of solid. The sodium concentration in the liquid was determined by using Atomic Absorption Spectrophotometer (AA). The H^+ or OH^- concentration was calculated by material and charge balances.

Cesium Ion Exchange Performance. These were batch experiments in which solid and simulated waste solution were mixed in a plastic vial and shaken for twenty-four hours. Then, the sample was filtrated to obtain the clean solution. Cesium content in the liquid was analyzed by AA, and cesium content in the solid was calculated by material balance.

EXPERIMENT RESULTS

The titration curve is similar to the curve measured by Stephens et al. [6] for hydrous titanium oxide, which shows two step changes for pH revealing two ion exchange sites. The material is easily hydrolyzed; the pH was 11.6 when it was mixed with water. All the sodium cations in the solid are exchangeable with protons. The total ion exchange capacity is about 4.6 meq/g.

The cesium ion exchange isotherm was determined by measuring the ion exchange performance in different simulated solutions with various amounts of cesium as $CsNO_3$. The isotherm for a solution with 5.7 M Na^+, 5.1 M NO_3^- and 0.6 M OH^- was presented by Zheng et al. [7]. Compared with the total ion exchange capacity, the cesium ion exchange capacity in the 5.7 M Na^+ solution was reported as 0.57 meg/g. Therefore, cesium is only accessible to some of the ion exchange sites. A Mass-action plot (Figure 1)[8] and a Kielland's plot (Figure 2)[8] of the cesium ion exchange isotherm shows that the solid phase exhibits an ideal behavior, i.e. the rational selectivity is a constant. The rational selectivity is defined as follows:

$$K_{rB}{}^{A} = \frac{(q_A)\,(C_B\,\gamma_B)}{(q_B)\,(C_A\,\gamma_A)} \qquad (5)$$

where $K_{rB}{}^{A}$ is the rational selectivity.

Ideal behavior was found, also, for ion exchange experiments with rubidium and potassium. The ideal behavior of the solid simplifies the work of modeling the equilibrium behavior in a competitive ion exchange system, and allows estimation of the equilibrium constants from binary ion exchange in simple simulated solutions.

EQUILIBRIUM MODEL

The equilibrium model consists of equations for ion exchange equilibrium in the form of Equation (5) for all the competitive cations, water dissociation, and the material, charge and site balances. These equations can be solved simultaneously by Newton-Raphson method to calculate the equilibrium state.

CALCULATION RESULTS AND DISCUSSION

To calculate the ion exchange equilibrium, the activity coefficients in the liquid phase must be estimated due to the high nonideality of the electrolyte solution. Bromley's model [9] for activity coefficients in electrolyte solution was chosen because of its simplicity and accuracy.

The equilibrium constants, K_{eq}s, were determined by using data from well defined binary solutions. The isotherm in a solution of 5.7 M $NaNO_3$ (Figure 3) was used to determine K_{eq} of cesium in a neutral solution, and the result is 8.5×10^4 which is much higher than K_{eq} reported by Zheng et al. [7] for a basic solution. The data from Zheng et al. [7] were then used in conjunction with the data presented in Figure 3 to obtain a new equilibrium value for the basic solution of 5.7 M Na^+, 5.1 M NO_3^- and 0.6 M OH^-. The new K_{eq} for cesium ion exchange in a basic solution of 1.9×10^4 was obtained. This value is obviously less than 4.4×10^4 previously reported by Zheng et al. [7]. Because the titration curve indicates the presence of two sites and easy hydrolysis, TAM5 appears to be partially hydrolyzed in the solution with 0.6 M OH^-, which caused the higher K_{eq} reported Zheng et al. [7]. An indication of the goodness of fit of the model for the two simulants is illustrated in Figure 4, which shows a comparison of calculated and observed distribution coefficients for neutral and basic solutions.

By using the equilibrium constants determined in the simple simulants, calculations were performed for competitive ion exchange in complex solutions. Distribution coefficients for cesium were calculated for several typical waste simulants. These are NCAW [3], DSSF and ORNL [10] simulants. The compositions of these solutions are listed in Table 1. Both the experimental K_d for cesium and the calculation results are shown in Figure 5. The calculated result matches the experimental results excellently for NCAW and ORNL solutions. The calculated K_d for cesium for DSSF simulants were lower than experimental data but still within 10%. The differences between the calculated and the experimental results are caused by over correcting for the potassium competitive effect, as DSSF simulants contain high levels of potassium.

CONCLUSION

TAM5 is extremely selective for cesium removal. Two kinds of ion exchange sites exist in the material and only part of these sites are available for cesium exchange. TAM5 shows ideal behavior in ion exchange between alkali metals, and this makes the rational selectivities the same as thermodynamic constants. The rational selectivities can be measured in binary ion exchange systems in simple solutions and directly used for competitive ion exchange in complex solutions. The model of competitive ion exchange by TAM5 includes the ion exchange equilibrium equations, charge, material,and site balances and water dissociation. By using Bromley's model for activity coefficients in electrolyte solutions, the cesium ion exchange performance was estimated within 10%.

ACKNOWLEDGEMENTS

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Table 1. Compositions of NCAW, DSSF and ORNL simulants

	NCAW			DSSF			ORNL	
	1M Na^+	3M Na^+	5M Na^+	3.75M Na^+	5M Na^+	7M Na^+	Sup.	NGL.
Na^+ (M)	1.00	3.00	5.00	3.75	5.00	7.00	4.52	1.62
K^+ (M)	0.024	0.072	0.120	0.506	0.675	0.945	0.240	-
Rb^+ (M)	1.0e-5	3.0e-5	5.0e-5	-	-	-	-	-
Cs^+ (M)	1.0e-4	3.0e-4	5.0e-4	3.8e-5	5.0e-5	7.0e-5	8.7e-6	5.2e-7
Sr^{2+} (M)	-	-	-	-	-	-	6.4e-6	6.2e-8
$Al(OH)_4^-$ (M)	0.086	0.258	0.430	0.386	0.515	0.721	-	0.005
OH^- (M)	0.260	0.780	1.30	0.938	1.25	1.75	0.335	0.220
CO_3^{2-} (M)	0.046	0.138	0.230	0.079	0.105	0.147	0.140	0.587
F^- (M)	0.018	0.053	0.089	-	-	-	-	-
Cl^- (M)	-	-	-	0.054	0.071	0.100	0.100	0.059
PO_4^{3-} (M)	-	-	-	0.008	0.010	0.014	-	-
NO_2^- (M)	0.086	0.258	0.430	0.809	1.08	1.51	-	-
NO_3^- (M)	0.338	1.01	1.69	1.89	2.51	3.52	4.16	0.061
AlO_2^-(M)	-	-	-	-	-	-	-	0.012

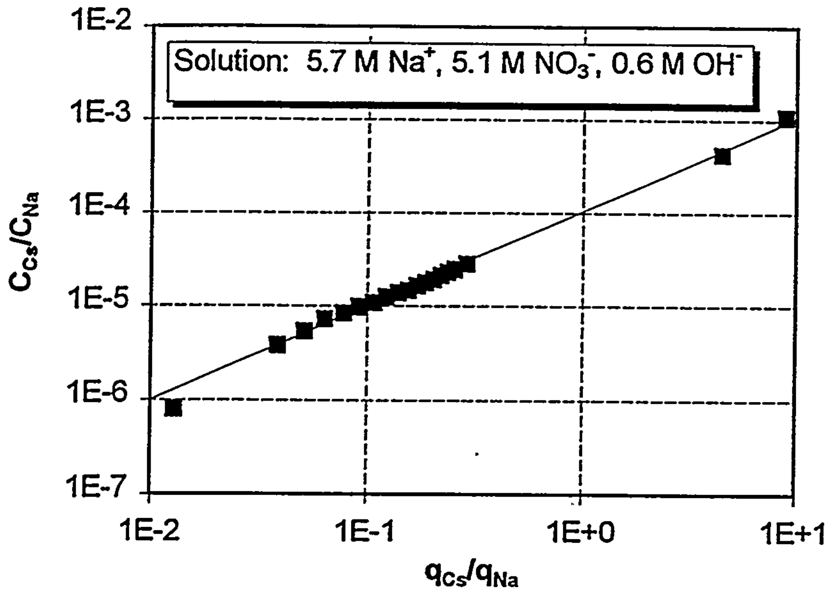

Figure 1. Mass Action Plot Cs^+/Na^+ ion exchange.

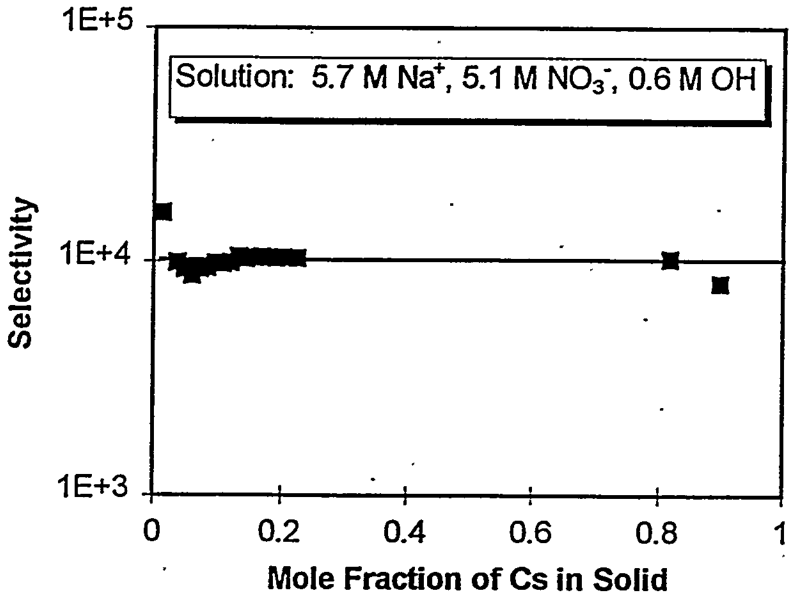

Figure 2. Kielland's Plot Cs^+/Na^+ ion exchange.

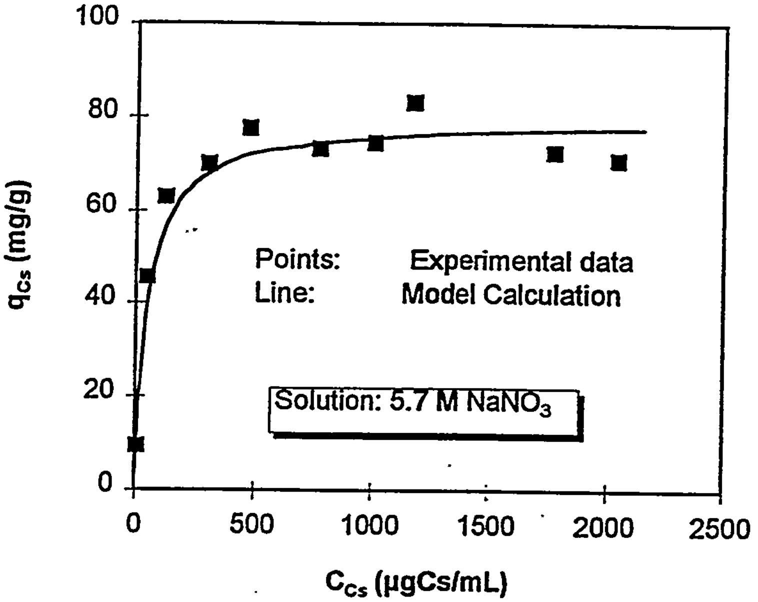

Figure 3. Using Cs^+/Na^+ ion exchange data in neutral solution to fit the model parameter.

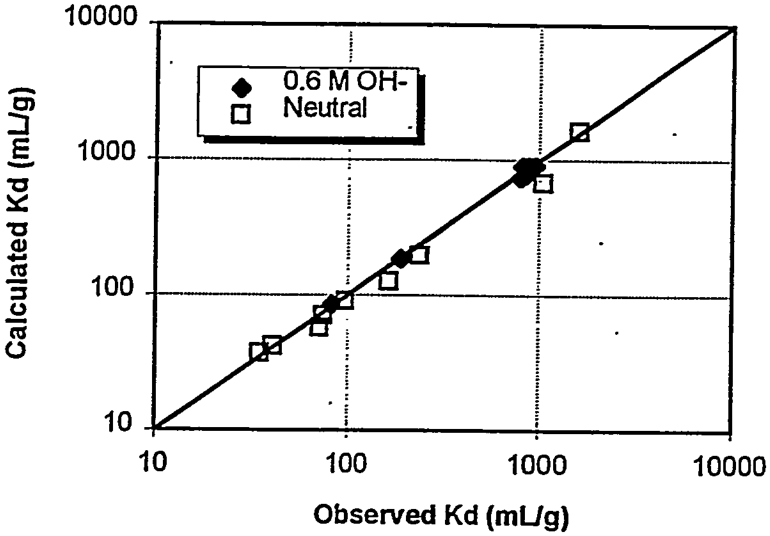

Figure 4. Comparison of fitted cesium distribution coefficients with experimental data.

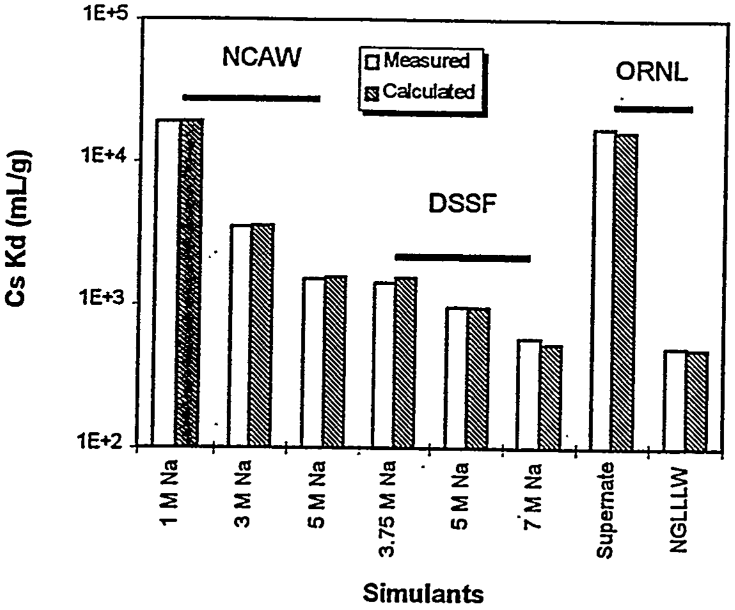

Figure 5. Comparison of experimental data with model calculation for cesium distribution coefficients in different simulants.