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IN CHABAZITE ZEOLITE**

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# MULTICOMPONENT ION-EXCHANGE EQUILIBRIA IN CHABAZITE ZEOLITE

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## ABSTRACT

Efficient design ion-exchange columns, using Ionsiv IE-96 chabazite zeolite, for the decontamination of process wastewater that contains ppb levels of Sr-90 and Cs-137 requires a detailed study of binary and multicomponent ion-exchange equilibria. Experimental isotherms were acquired for Ca-Na, Mg-Na, Sr-Na, Cs-Na, Sr-Cs-Na, Ca-Mg-Na, Sr-Ca-Mg-Na, Cs-Ca-Mg-Na, and Sr-Cs-Ca-Mg-Na comparing batch and column experimental approaches. Binary isotherms obtained by the batch technique were most successfully fitted with a modification of the Dubinin-Polyani equilibrium model. Prediction of the multicomponent equilibria from binary data will require more sophisticated modeling.

## INTRODUCTION

Fixed bed ion exchange in which resins serve as the granular medium has been established for many years as an important technique for water purification and for the recovery of ionic components from mixtures. However, inorganic media, such as porous crystalline aluminosilicates zeolites, have had limited application as ion exchangers. As the field of applications for ion exchange broadens, a class of applications has developed where economic considerations, a high thermal and/or radiation flux, or the molecular sieve properties of zeolites make them more attractive than ion-exchange resins. Their molecular sieve properties give zeolites the advantage of selectivity sometimes not obtainable with adsorbers and resins. Because of their unique properties,

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growing interest has focused on molecular sieve zeolites for use in ion-exchange separations in water softening, pollution abatement, energy production, agriculture, animal husbandry, aquaculture, metals processing, and biomedical areas (Sherman, 1978).

Some of the considerations discussed have led Oak Ridge National Laboratory plans the use of chabazite zeolites for decontamination of process wastewater containing ppb levels of Sr-90 and Cs-137. A typical characterization of the ORNL process waste stream is shown in Tables 1 and 2. Treatability studies (Robinson and Parrott, 1989; Robinson, et al, 1990) indicate that chabazite zeolites are highly selective for Cesium and Strontium while admitting high loadings of there metals. Thus it is suited to the removal of trace amounts of Cs-137 and Sr-90 from wastewater that contains relatively high concentrations of calcium and magnesium. These studies also indicate that the efficiency of the zeolite system depends strongly on the column design and operating conditions and that through optimization of the design of full-scale columns one could halve the generation rate of loaded zeolite requiring disposal.

The objective of fixed-bed column design is to predict the characteristics of the breakthrough curve for a particular column operating under a given set of conditions. Two approaches to the prediction of column response were considered: (1) the interpretation and subsequent extrapolation of pilot-scale data and (2) solution the convective diffusion equation as a function of time and column position for each component in the waste stream. The logistics, time, expense, and uncertainties associated with the establishment of an adequate pilot program often makes the use of models very attractive. Numerical models usually involve simultaneous integration of the following equations: (a) fluid phase and solid phase mass balances, (b) equations for each mechanism affecting mass transfer, and (c) the equilibrium equation.

Models of multicomponent liquid ion-exchange systems were virtually nonexistent before the 1980s. Although a considerable effort has been made in this area, multicomponent models have not been developed to the point where they can be used in general industrial applications without using laboratory- or pilot-scale data to predict the equilibrium and mass transfer relationships. A knowledge of multicomponent equilibrium is essential for modeling ion-exchange separation processes. (Need a reference or two – Otherwise statements are too sweeping).

The objective of this paper is to present experimental binary and multicomponent equilibrium data for synthetic mixtures which simulate ORNL's process wastewater. Binary equilibrium models are compared with experimental data to assess the most appropriate model for the ion exchange systems relevant to the problem at hand. The applicability of simple multicomponent relationships, based strictly on binary data, to the prediction of multicomponent data is examined. Longer term, we will use these relationships in a comprehensive transport theory for the ion exchange in chabazite zeolite columns.

## THEORY

The complexity and diversity of the mechanisms of single- and multicomponent ion exchange equilibrium behavior has led to the development of a large number of equations, both theoretical and empirical in nature. Useful reviews of area by Soldatov and Bichkova (1980), Myers and Byington (1986), and Shallcross et al (1988) are available. The most frequently used models are the following: The binary Langmuir model,

$$q = \frac{q_s bc}{1 + b} = \frac{ac}{1 + bc} \quad (1)$$

The binary Freundlich model,

$$q = kc^n, \quad (2)$$

and the Dubinin-Polyani model,

$$q = q_s \exp \left\{ -kR^2T^2 \left[ \ln \left( \frac{c_m}{c} \right) \right]^2 \right\}. \quad (2)$$

In these equations,  $q$  and  $c$  are the equilibrium concentrations in the solid and liquid phases, respectively,  $q_s$  is the saturation concentration in the solid, and  $b$ ,  $n$ , and  $K$  are coefficients fitted to the experimental data.

These models may be extended in a logical manner to describe multicomponent equilibrium. For instance the multicomponent Langmuir model is

$$\frac{q_i}{q_{si}} = \frac{b_i c_i}{1 + b_1 c_1 + b_2 c_2 + \cdots b_n c_n}. \quad (4)$$

The multicomponent Freundlich equation is

$$\frac{q_i}{q_{si}} = \frac{b_i c_i^{n_i}}{b_1 c_1^{n_1} + b_2 c_2^{n_2} + \cdots b_n c_n^{n_m}}, \quad (5)$$

and the Langmuir-Freundlich equation (Ruthven, 1984), which combines the form of the Langmuir equation with the parameters of the Freundlich Equation for multicomponent mixtures is

$$\frac{q_i}{q_{si}} = \frac{b_i c_i^{n_i}}{1 + b_1 c_1^{n_1} + b_2 c_2^{n_2} + \cdots b_n c_n^{n_m}}. \quad (6)$$

The coefficients,  $b_i$  and  $n_i$ , are obtained from binary isotherm data.

The multicomponent form of the Dubinin-Polyani equation (Ruthven, 1984) for liquids is

$$\frac{V_m(q_1 + q_2 + \cdots)}{W_0} = \exp(k\varepsilon^2), \quad (7)$$

where

$$V_m = X_1 V_1 + X_2 V_2 + \dots, \quad (8)$$

$$\frac{1}{k} = \frac{x_1}{k_1} + \frac{x_2}{k_2} + \dots, \quad (9)$$

$$\text{and} \quad \varepsilon = -RT \ln \left( \frac{c_1 + c_2 + \dots}{c_m} \right). \quad (10)$$

The Ideal Adsorbed Solution Theory Model (IAST) is based on the Gibbs adsorption equation and only requires single-solute data to predict multicomponent equilibrium (Weber and Smith, 1987):

$$\frac{1}{q_1 + q_2 + \dots} = \frac{X_1}{q_1^0} + \frac{X_2}{q_2^0} + \dots \quad (11)$$

When the binary Freundlich adsorption isotherm equation is substituted into Eq. 8, the following equation can be obtained for modeling purposes (Crittenden, et al., 1985):

$$c_i = \frac{q_i}{\sum_{j=1}^m q_j} \left( \frac{\sum_{j=1}^m q_j n_j}{\frac{k_j}{n_j}} \right)^{\frac{1}{n_i}} \quad \text{for } i = 1 \text{ to } m. \quad (12)$$

Predictions of liquid phase equilibrium have been successful in a limited number of cases using the more rigorous classical thermodynamic approach and the generalized statistical model (Ruthven, 1984; Myers and Byington, 1986). The thermodynamic approach has received much attention in recent years, but these rigorous models require refinement before they can be applied to systems containing several highly interactive components.

Several references have reported that the experimental method used in the study affects the isotherm for multicomponent systems. Crittenden and Weber (1978) have

indicated that the equilibrium dynamics of multicomponent adsorption in fixed beds cannot be adequately predicted from batch tests. Several other researchers indicate that complex equilibrium behavior will occur if multicomponent feed solutions, multivalent cations, or high solution concentrations are used (Sherman, 1978; Ausikaitis, 1984; Loizidou and Townsend, 1987; Barri and Rees, 1980; Cremers, 1977). In these cases the equilibrium isotherm will depend on the initial solution concentration, and the isotherm should be determined by varying the ion exchanger dosage.

## EXPERIMENTAL

Chabazite zeolite is available both in natural (eg. Tenneco Specialty Minerals, TSM-300) and synthetic form (eg. Union Carbide Ionsiv IE-90 or IE-96). Ionsiv IE-96, a pelletized form of Ionsiv IE-90 crystals in a clay binder, was used as the sorbent in these studies. Structurally chabazite consists of stacked double six-membered ring prisms, interconnected through four rings, in a cubic close-packed array (Ruthven, 1984; Breck, 1974). Repetition of the stacking of prisms produces  $11 \times 6.6 \text{ \AA}$ , joined to adjacent cavities through six eight-membered rings with  $4.1 \times 3.7 \text{ \AA}$  free diameters, and six-membered rings with  $2.6 \text{ \AA}$  diameters. The neutralizing cation mainly coordinates to water molecules in the eight-membered rings. It is coordinated only to the oxygen in the double six-membered ring and is not usually active in ion exchange. The Ionsiv IE-96 was obtained from Union Carbide in the hydrated sodium form as 20 to 50 mesh (840 to  $297 \mu\text{m}$ ) irregularly shaped particles. Most of the material is 30 to 35 mesh (590 to  $500 \mu\text{m}$ ) and the laboratory measurements were made with this size fraction.

Simulated wastewater solutions were used in the experimental tests to avoid variability in feed composition. The solutions were prepared by dissolving various amounts



of  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CsCl}$ ,  $\text{CaCl}_2$ , and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  in demineralized water. The solutions containing strontium and cesium were also spiked with Sr-85 and Cs-137 tracers, respectively. The calcium and magnesium concentrations in the simulated wastewaters were the same as the concentrations listed in Tables 1 and 2, but the strontium and cesium concentrations were increased to 0.002 and 0.001 N, respectively, so that residual concentrations in the equilibrated solutions could be accurately measured with available analytical equipment.

The concentrations of cations in the solution phase were measured using the atomic absorption or gamma counting analytical equipment. The concentrations of cations in the zeolite were calculated from mass balances using the initial and final solution concentrations. All tests were performed in triplicate at room temperature (23° C). The total ion-exchange capacity of Ionsiv IE-96 was measured with  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{CsCl}$ ,  $\text{SrCl}_2$ , and  $\text{CsCl-SrCl}_2$  solutions. Samples of the zeolite were contacted overnight three times with 2 N  $\text{NaCl}$  to assure that it was in the sodium form and then washed with deionized water. After each contact with  $\text{NaCl}$  solution or with water, the samples were centrifuged for 30 min at 5000 relative centrifugal force. The washed zeolite was dried overnight at 110°C. Samples of the dried zeolite were contacted overnight with 200 mL of 0.2 N exchange solution per gram of exchanger. The samples were weighed, centrifuged for 30 minutes at 5000 rcf, and the supernate was analyzed by atomic absorption for sodium. The results indicated that Ionsiv IE-96 has a cation exchange capacity of 2.24 meq/g when the solution phase does not contain cesium and 2.60 meq/g when cesium is present.

Because of the problems described in the literature, three different experimental methods were compared for use in this study: (a) batch tests where the volume and

concentration of the solution phase was held constant and solids dosage was varied, (b) batch tests where the solution concentration was varied and the solids dosage was held constant, and (c) column tests where the amount of solids was held constant and the solution concentration was varied. Binary Sr-Na and Cs-Na and ternary Sr-Cs-Na isotherms were obtained by each method. Some tests were repeated using the first experimental method at different initial solution concentrations (the relative concentration of cations was held constant) for several binary and multicomponent systems. The isotherms obtained by each experimental method for the Sr-Na system are shown in Fig. 1. The strontium isotherms for the Sr-Na and Sr-Cs-Na systems obtained by experimental method (a) are shown in Fig. 2, and the strontium isotherms for the Sr-Cs-Ca-Mg-Na system obtained by method (a) for two initial solution concentrations are shown in Fig. 3.

Based on the results from these tests (discussed in detail the Results and Discussion section), a standard method was adopted for obtaining isotherms for modeling purposes. A batch process was used in which the solution phase volume was held constant at 10 mL and the solids dosage was varied between 0.002 and 0.4 g. The solution and solids were contacted for 24 hr to obtain each isotherm point. The initial concentrations of the exchanging cations in the solution phase were  $2.0 \times 10^{-3}$  N Sr,  $1.0 \times 10^{-3}$  N Cs,  $2.0 \times 10^{-3}$  N Ca, and/or  $8.0 \times 10^{-4}$  N Mg. The initial sodium concentration was zero in the solution phase. The resulting isotherms for the binary systems and a typical multicomponent system are given in Figs. 4 and 5 respectively.

The zeolite reached greater than 90% equilibrium in less than 1 hr and at least 99.7% equilibrium after 5 hrs. Maximum zeolite loadings of 96% were obtained in the equilibrium tests. Stoichiometry of exchange was established in several cases within

the limits of experimental error, so that the possibility of complications due to non-exchange adsorption was eliminated.

## RESULTS AND DISCUSSION

### Impact of Experimental Conditions.

Figure 1 is a typical example of how the experimental method affected the binary isotherms. There was no statistical difference between the isotherms obtained by the batch and column methods when the initial solution concentration was varied. However, there were differences between isotherms obtained by these two methods and those obtained by the batch method when the solids dosage was varied and the solution concentration was held constant. This held true for both monovalent-monovalent and divalent-monovalent ion exchange. The data for the binary and ternary systems showed similar trends.

For two very strongly held cations, such as cesium and strontium, there was no significant difference between the binary and ternary isotherms as long as the same experimental method was used (See Fig. 2). This held true when the total solution concentration was changed. However, the total solution concentration had a significant effect on the isotherms obtained for cations with different selectivities. In these cases, the multicomponent isotherms (such as Fig. 3) followed the concentration valence theory which says that the exchanger will have a higher selectivity for higher valence cations when the total normality of the solution phase decreases. The isotherms for the different solution concentrations converged at the upper end of all graphs where the solution and solids phase concentrations were highest. This held for all cations regardless of whether they were strongly or weakly held.

These results indicated that column equilibrium can be accurately predicted from

batch data. They also indicate that the initial concentration of cation, the total solution concentration, and the solid to liquid ratio will affect the equilibrium results for multicomponent systems.

### Binary and Multicomponent Isotherms.

The binary isotherms shown in Fig. 4 are "favorable" for uptake of the sorbates. The isotherms for multicomponent Sr-Cs-Ca-Mg-Na system (Fig. 5) are typical of all multicomponent systems tested. The isotherm data indicate that Ionsiv IE-96 has the selectivity order  $Cs > Sr > Ca > Mg$  and that the zeolite is selective for the entering cations over sodium for the solution composition range tested.

In the multicomponent systems, the shapes of the isotherms for the cation with the highest selectivity were similar to those of the corresponding binary isotherms. However, cation interactions affected the isotherms for the cations with lower selectivities, and these cations were displaced when the solution concentration increased relative to the available exchange sites. This was more pronounced with decreasing selectivity and resulted in a magnesium isotherm with a convex shape. Slight displacement of strontium and calcium occurred at the highest loadings tested.

### Isotherm Models.

Standard isotherm equations were used to model the data. The binary data were modelled using Eqs. 1 - 3. The Dubinin-Polyani equation was solved for  $k$  by substituting values for  $R$ ,  $T$ , and  $c_m$  into Eq. 3. Values for  $c_m$ , the solubility of the salt in water, were obtained from the literature (Nemeth, 1975): 195,000 meq/mL for calcium, 322,000 meq/mL for cesium, 103,000 for magnesium, and 176,000 for strontium.

A modified version of the Dubinin-Polyani equation was also tested:

$$q = \exp \{ b_0 + b_1 \cdot \ln(c) + b_2 \cdot [\ln(c)]^2 \}. \quad (13)$$

The Dubinin-Polyani equation was solved for  $b_0$ ,  $b_1$ , and  $b_2$ . This form of the equation is referred to as the modified Dubinin-Polyani in the remainder of this report. If the systems are ideal, Eqs. 3 and 10 should be equal, Resulting in the following relationships:

$$\begin{aligned} b_0 &= \ln(q_s) - kR^2T^2 [\ln(c_m)]^2 \\ b_1 &= kR^2T^2 \ln(c_m), \\ \text{and} \quad b_2 &= -kR^2T^2. \end{aligned} \quad (14)$$

The constants for the binary isotherm equations were determined from the isotherm data by regression analyses of the linearized equations. The results indicate that all of the models except the Dubinin-Polyani equation are reasonable fits for the data. The modified Dubinin-Polyani model is the best equation for fitting the data for all four systems. The fact that Eqs. 3 and 10 are not equal for any of the four binary isotherms indicates that the solubility of salts in the liquid phase is not adequate to account for the nonidealities which occur during liquid ion exchange. This is not surprising since the Dubinin-Polyani equation was developed from the theory of pore filling for gases in microporous carbon adsorbents.

Turning to the multicomponent systems, predictions were made of the isotherms which had been evaluated experimentally. Predictions were based on binary data using the multicomponent Langmuir, Freundlich, Langmuir-Freundlich, and the IAST models. When the coefficients for the binary isotherms were substituted into Eqs. 4,

5, 6, and 12, the results did not accurately predict the experimental multicomponent data. These results indicate that the multicomponent data in this study cannot be predicted from binary data, and rigorous thermodynamic or empirical equations will be required to model the multicomponent data. Since thermodynamic models are not well developed for highly interactive multicomponent systems, empirical equations having the basic forms of Eqs. 4, 5, 6 and 13 were fit to the equilibrium data. Equation 13 fit the data most accurately. The resulting equation parameters are listed in Table 3 and the modelling results are shown in Figs. 4 and 5.

## SUMMARY

This study has generated isotherm data for binary and multicomponent systems containing Ca, Mg, Na, Sr and Cs. The results indicate that the isotherms are dependent on experimental method and the total solution concentration. All data obtained in this study were accurately predicted by the modified Dubinin-Polyani model, but multicomponent data could not be predicted from binary data.

The optimization of ion-exchange columns becomes increasingly important in applications requiring high efficiency to meet low discharge requirements where the disposal costs for the secondary waste are extremely high. This is the case for zeolite columns used to remove trace quantities of radionuclides from ORNL process wastewater. Since the optimal operation of the ion-exchange columns is the key to the economic operation of this system, a predictive mathematical model is being developed for this purpose. This model will incorporate the effects of equilibrium and mass transfer mechanisms on the column dynamics for multicomponent liquid ion exchange with zeolites. The model will be based on the equilibrium parameters determined in this

study and transport parameters to be determined in future studies.

After verification in pilot tests, this model can be used to examine design parameters other than those directly measured and project column response and sensitivity to many variables. This approach should reduce the need for future pilot-scale tests and the uncertainty involved in the design of full-scale zeolite columns.

## NOMENCLATURE.

$a$	isotherm constant
$b$	isotherm constant
$c$	sorbate concentration, meq/mL
$c_m$	solubility, meq/mL
$k$	isotherm constant
$m$	number of solutes
$n_i$	exponent of the $i$ component, Freundlich Isotherm
$q$	sorbent concentration, meq/g
$q_o$	for the pure components, meq/g
$q_s$	saturation limit, meq/g
$R$	gas constant
$T$	temperature
$V_i$	partial molar volume of component
$V_m$	molar volume of sorbate
$W_o$	specific micropore volume of adsorbent
$X$	mole fraction in adsorbed phase

## REFERENCES

- Ausikaitis, J. P., Fundamentals of Adsorption, AIChE, New York, 1984, 49-63.  
Barri, S. A. I., and Rees, L. V. C., J. Chromatogr., **201** (1980), 21.

- Breck, D. W., Zeolite Molecular Sieves, Wiley and Sons, New York, (1974).
- Cremers, A., Molecular Sieves-II, J. R. Katzer, ed., ACS Symp. Series, 40, Washington, DC, 1977, 179-93.
- Crittenden, J. C. et al., Environ. Sci. Technol., **19**(11), (1985), 1037-43.
- Crittenden, J. C. and Weber, Jr., W. J., ASCE Env. Eng. Div., **104**(EE6), 1978, 1175-1195.
- Loizidou, M., and Townsend, R. P., Zeolites, **7**(2), 1987.
- Myers, A. L., and Byington, S., "Thermodynamics of ion exchange: prediction of multicomponent equilibria from binary data.", in Ion Exchange: Science and Technology edited by A. E. Rodrigues, NATO ASI Series E 107, Martinus Nijhoff Publishers, Boston, 1986, 119-145.
- Nemeth, B. A., Chemical Tables, John Wiley and Sons, New York, 1975. Robinson, S. M., and Parrott, Jr., J. R., Pilot-Scale Demonstration of Process Wastewater Decontamination Using Chabazite Zeolites," ORNL/TM-10836, Oak Ridge National Laboratory, Oak Ridge, TN, December 1989.
- Robinson, S. M., et al., "The Development of a Zeolite System for Upgrade of the ORNL Process Waste Treatment Plant," ORNL/TM-10836, Oak Ridge National Laboratory, Oak Ridge, TN, in publication.
- Ruthven, D. M., Principles of Adsorption and Adsorption Processes, John Wiley & Sons, New York, 1984.
- Sherman, J. D., AICHE Symposium Series, **74**(179), 1978.
- Smallcross, D. C., Hermann C. C., and McCoy, B. J., Chem. Eng. Sci., **43**, 1988, 279-288.
- Soldatov, V. S., and Bichkova, V. A., Separ. Sci., **15**, 1980, 89-110.
- Weber, Jr., W. J. and Smith, E. H., Environ. Sci. Technol., **21**(11), 1987, 1040-50.



**Table 1. Radiochemical composition of ORNL process wastewater**

Radionuclide	Concentration, Bq/L	Concentration, <u>N</u>
Gross alpha	5	—
Gross beta	6000	—
Co-60	25	$2.0 \times 10^{-14}$
Sr-90	4000	$1.7 \times 10^{-11}$
Cs-137	400	$9.1 \times 10^{-13}$
Ru-106	10	$2.3 \times 10^{-15}$

Table 2. Chemical composition of ORNL process wastewater

Component	Concentration, mg/L	Concentration, <u>N</u>
$\text{Ca}^{2+}$	40	$2.0 \times 10^{-03}$
$\text{Mg}^{2+}$	8	$6.6 \times 10^{-04}$
$\text{Na}^+$	5	$2.2 \times 10^{-04}$
$\text{K}^+$	2	$5.1 \times 10^{-05}$
$\text{Si}^{3+}$	2	$2.1 \times 10^{-04}$
$\text{Sr}^{2+}$	0.1	$2.3 \times 10^{-06}$
$\text{Al}^{3+}$	0.1	$1.1 \times 10^{-05}$
$\text{Fe}^{2+}$	0.1	$3.6 \times 10^{-06}$
$\text{Zn}^{2+}$	0.1	$3.1 \times 10^{-06}$
$\text{HCO}_3^-$	93	$1.5 \times 10^{-03}$
$\text{SO}_4^{2-}$	23	$4.8 \times 10^{-04}$
$\text{Cl}^-$	10	$2.8 \times 10^{-04}$
$\text{NO}_3^-$	11	$1.8 \times 10^{-04}$
$\text{CO}_3^{2-}$	7	$2.3 \times 10^{-04}$
$\text{F}^-$	1	$5.3 \times 10^{-05}$

Table 3. Parameters for the Modified Dubinin-Polyani Model<sup>1</sup>

Isotherm	Coefficients			$R^2$
	$b_0$	$b_1$	$b_2$	
<u>Binary Systems</u>				
Sr Isotherm	-1.637	-0.6839	-0.05015	0.97
Cs Isotherm	-2.165	-0.6839	-0.06261	0.95
Ca Isotherm	1.833	0.2655	0.00961	0.96
Mg Isotherm	-0.4651	-0.1279	-0.01202	0.74
<u>Sr-Cs-Na System</u>				
Sr Isotherm	-4.952	-1.262	-0.0781	0.97
Cs Isotherm	-4.315	-1.134	-0.0733	0.99
<u>Ca-Mg-Na System</u>				
Ca Isotherm	-5.326	-1.506	-0.09814	0.99
Mg Isotherm	-15.81	-3.312	-0.1877	1.00
<u>Sr-Ca-Mg-Na System</u>				
Sr Isotherm	-1.592	-0.5100	-0.04096	0.99
Ca Isotherm	-0.6791	-0.1495	-0.01558	0.99
Mg Isotherm	-18.06	-3.674	-0.2017	0.91
<u>Cs-Ca-Mg-Na System</u>				
Cs Isotherm	-5.073	-1.287	-0.08128	0.97
Ca Isotherm	-3.219	-0.7620	-0.04545	0.99
Mg Isotherm	-29.40	-6.105	-0.3213	0.91
<u>Sr-Cs-Ca-Mg-Na System</u>				
Sr Isotherm	-4.742	-1.157	-0.07507	0.99
Cs Isotherm	-1.532	-0.5890	-0.05002	0.99
Ca Isotherm	-4.212	-0.8560	-0.04703	1.00
Mg Isotherm	-17.28	-3.345	-0.1818	0.93

<sup>1</sup> See Equation 10.

## FIGURE CAPTIONS

**Figure 1.** Effect of experimental method on the strontium isotherm for the Sr-Na system. (+ 0.5 g solids, 2.1 mL solution,  $2 \times 10^{-06}$  to 0.4 N Sr in feed; 40 g solids, 166 mL solution,  $2 \times 10^{-06}$  to 0.4 N Sr in feed; \* 0.005 to 0.4 g solids, 10 mL solution,  $2 \times 10^{-03}$  N Sr in feed).

**Figure 2.** Strontium isotherms for Binary and Ternary Systems (0.005 to 0.4 g solids, 10 mL solution; X  $2 \times 10^{-03}$  N Sr; +  $2 \times 10^{-03}$  N Sr, 1 y  $\times 10^{-03}$  N Cs).

**Figure 3.** Effect of feed concentration on the strontium isotherm for the Sr-Cs-Ca-Mg-Na system (0.005 to 0.4 g solids, 10mL solution, 2/2/1/0.8 Sr/Ca/Cs/Mg ratio in feed).

**Figure 4.** Isotherms for Binary Ion Exchange. (a) Sr-Na; (b) Cs-Na; (c) Ca-Na; (d) Mg- Na.

**Figure 5.** Isotherms for Sr-Cs-Ca-Mg-Na ion exchange. (a) Sr, (b) Cs, (c) Ca, (d) Mg.

Figure 1

ORNL DWG 90A-339

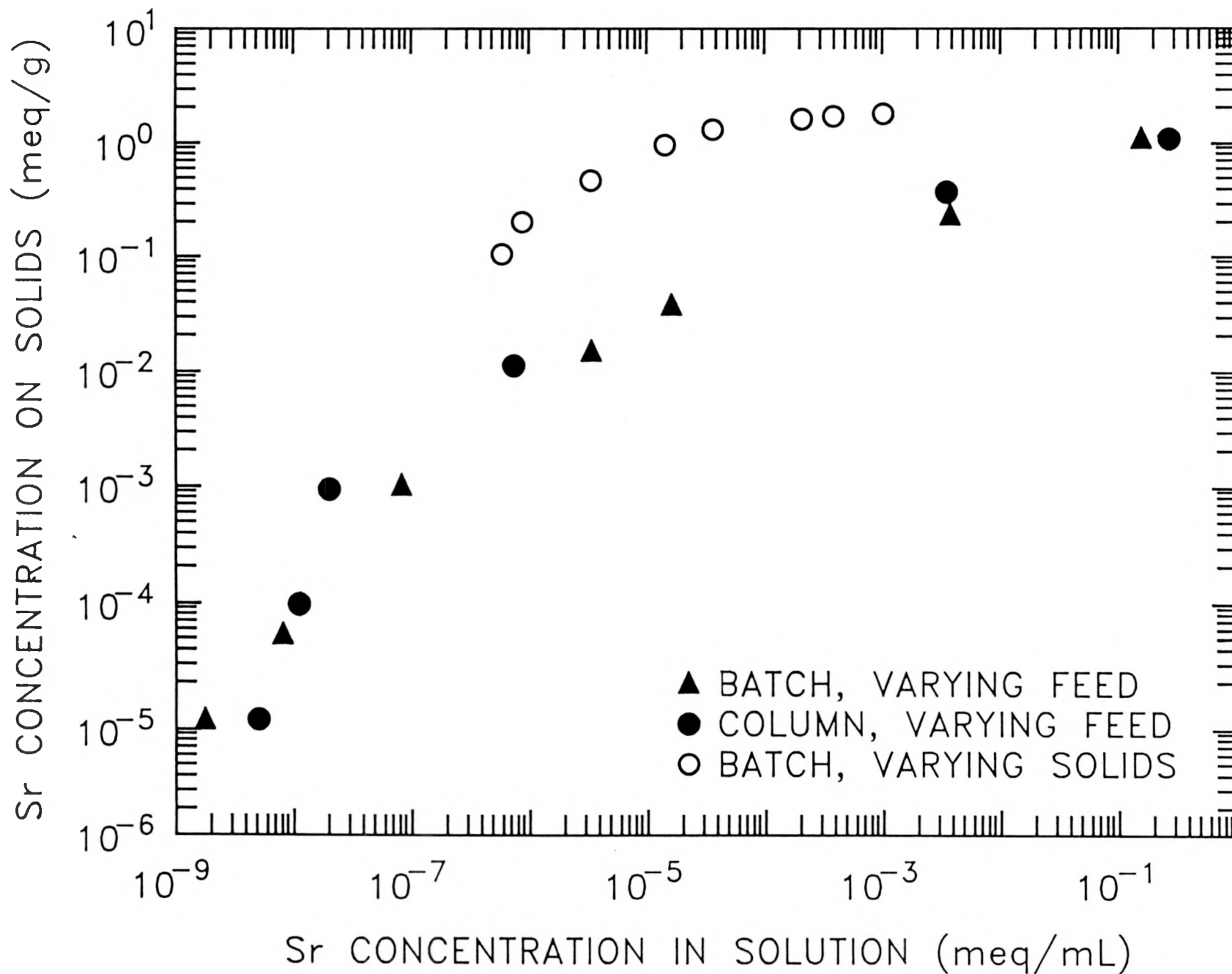


Figure 2

ORNL DWG 90A-341

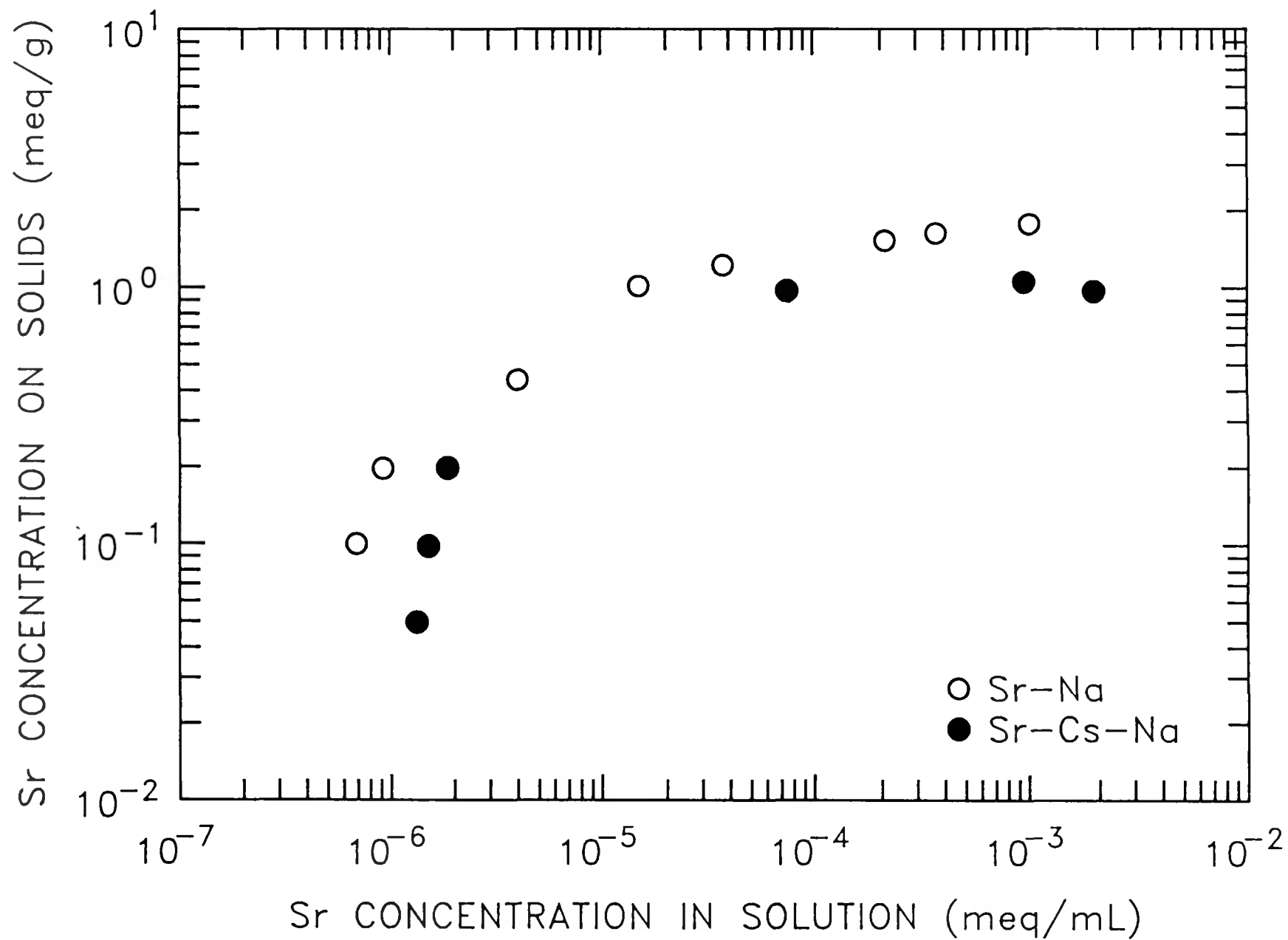


Figure 3

ORNL DWG 90A-342

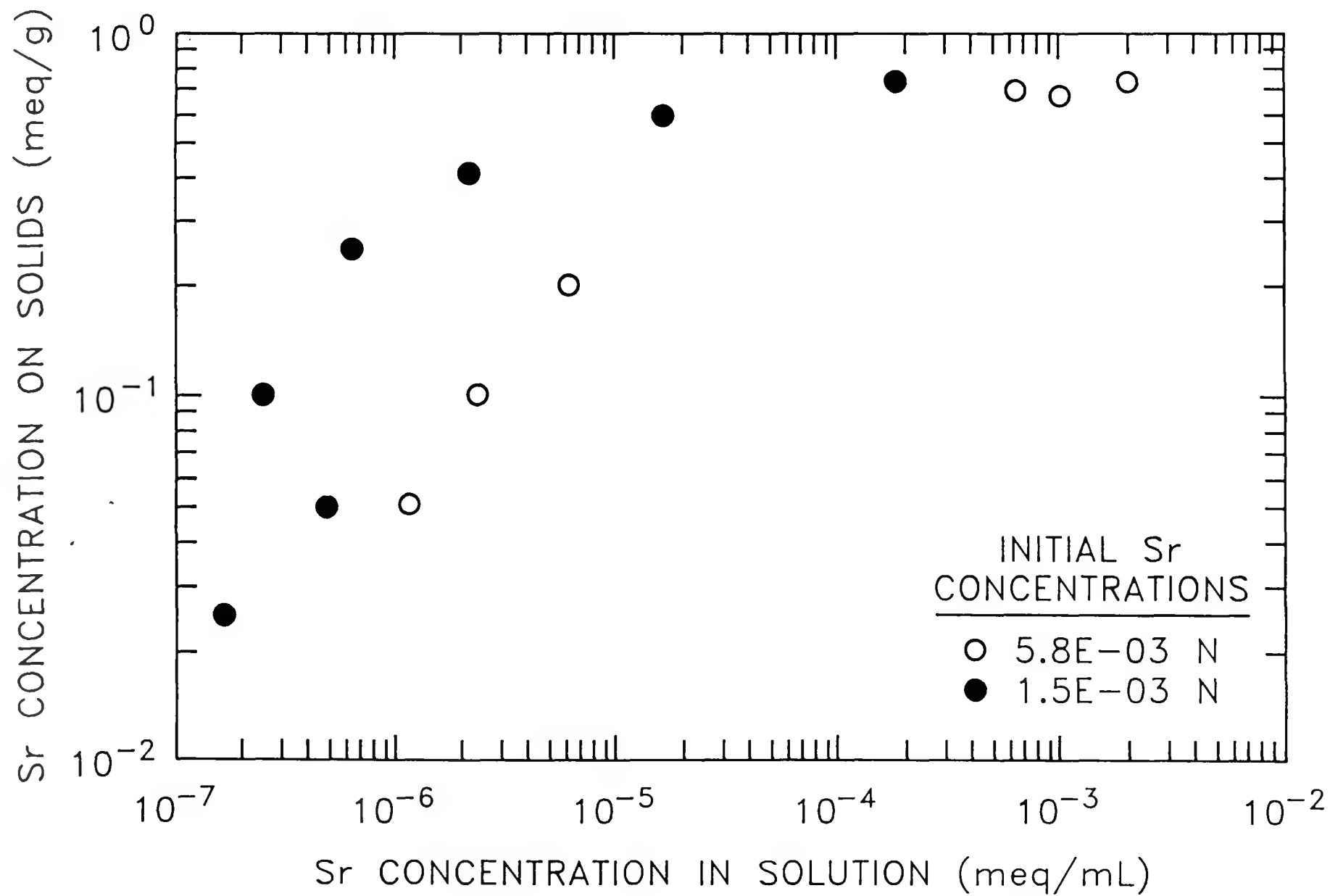
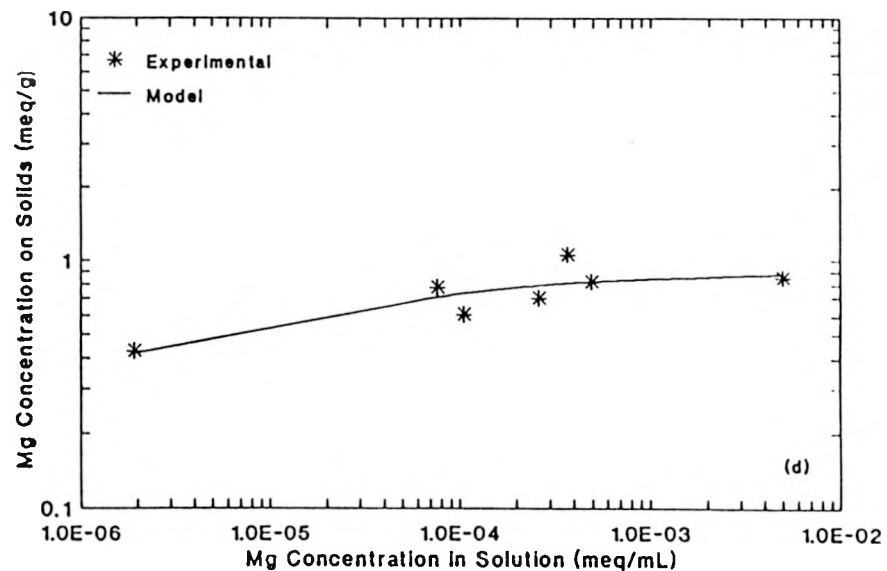
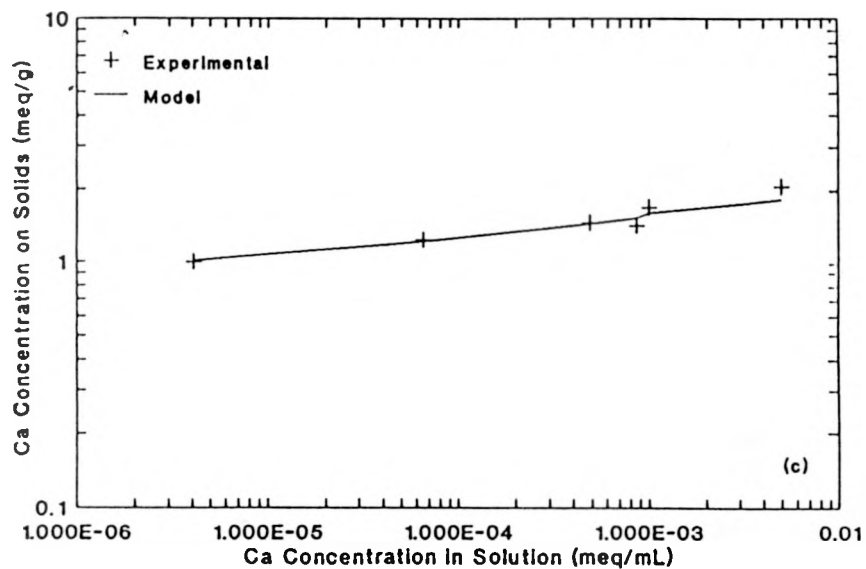
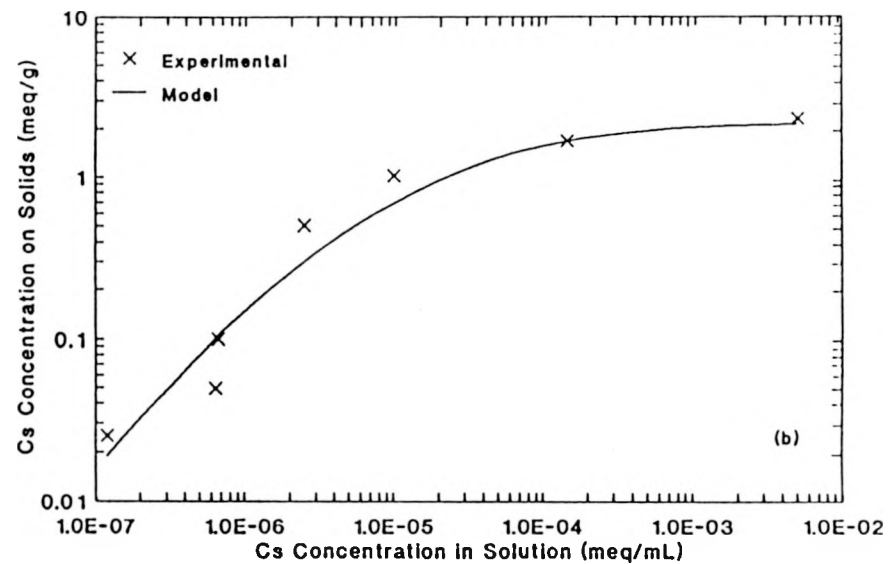
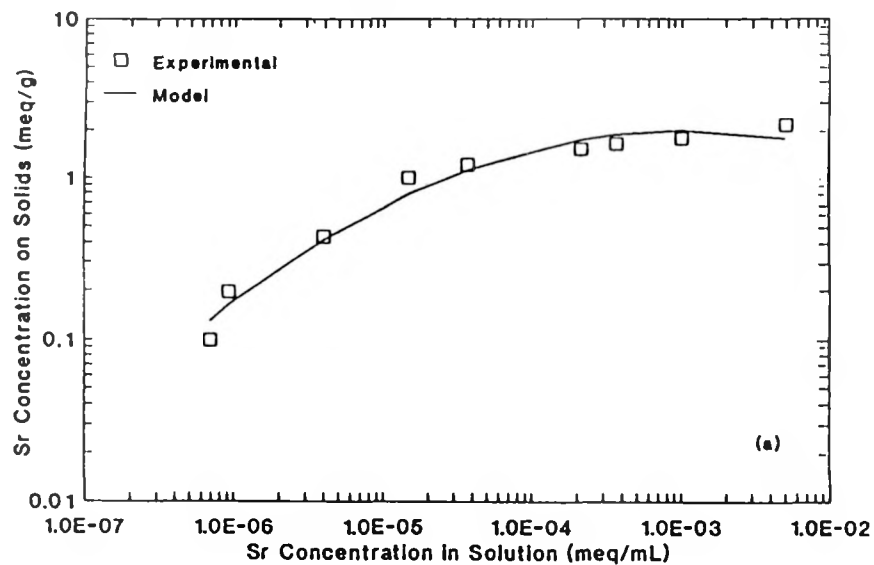


Figure 4

ORNL DWG 90-129





# Figure 5

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