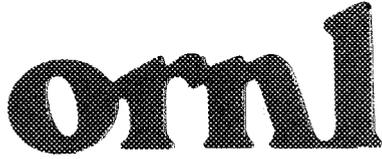




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**OAK RIDGE
NATIONAL
LABORATORY**

MARTIN MARIETTA

**A Multicomponent Ion-Exchange
Equilibrium Model for
Chabazite Columns Treating
ORNL Wastewaters**

J. J. Perona

OAK RIDGE NATIONAL LABORATORY

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Chemical Technology Division

**A MULTICOMPONENT ION-EXCHANGE EQUILIBRIUM MODEL
FOR CHABAZITE COLUMNS TREATING ORNL WASTEWATERS**

J. J. Perona

Date Published: June, 1993

NOTICE This document contains information of a preliminary nature.
It is subject to revision or correction and therefore does not represent a
final report.

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A MULTICOMPONENT ION-EXCHANGE EQUILIBRIUM MODEL FOR CHABAZITE COLUMNS TREATING ORNL WASTEWATERS

J. J. Perona

ABSTRACT

Planned near-term and long-term upgrades of the Oak Ridge National Laboratory (ORNL) Process Waste Treatment Plant (PWTP) will use chabazite columns to remove ^{90}Sr and ^{137}Cs from process wastewater. A valid equilibrium model is required for the design of these columns and for evaluating their performance when influent wastewater composition changes. The cations exchanged, in addition to strontium and cesium, are calcium, magnesium, and sodium. A model was developed using the Wilson equation for the calculation of the solid-phase activity coefficients. The model was tested against chabazite column runs on two different wastewaters and found to be valid. A sensitivity analysis was carried out for the projected wastewater compositions, in which the model was used to predict changes in relative separation factors for strontium and cesium subject to changes in calcium, magnesium, and sodium concentrations.

1. INTRODUCTION

The near-term upgrade of the PWTP will install zeolite columns downstream of the current plant to remove ^{137}Cs from the PWTP effluent stream.¹ The maximum flow capacity to be treated is 300 gal/min. This water, having gone through a water softening process, is relatively low in calcium and magnesium concentrations (around 10^{-5} to 10^{-6} equiv/L) and relatively high in sodium. The columns will be designed for a cesium concentration of 65 Bq/L (about 10^{-13} equiv/L).

In an upcoming FY 1995 line-item project, the current PWTP will be replaced by a zeolite system designed to remove both ^{90}Sr and ^{137}Cs . The water to be treated will be higher in calcium and magnesium and lower in sodium in comparison to the current PWTP effluent. Anticipated strontium and cesium levels in the feed water are 750 and 110 Bq/L, respectively. Treatment studies conducted during the last several years have shown chabazite to be the most economical ion exchange material tested. It is available in a natural form (TSM-300) and a synthetic form (Ionsiv IE-95).² Chabazite is a zeolite with a structure built from linkages of the double six-ring secondary building unit.³

Equilibrium data for the five cations with chabazite were published by Robinson et al.⁴ The concentration range covered by the equilibrium data was from about 10^{-3} to 10^{-6} equiv/L for each cation. This range covered the concentrations encountered in process waste treatment for calcium, magnesium, and sodium, but not for strontium and cesium. For the radioactive components, the concentration range of interest is lower by six or seven orders of magnitude. For this reason, it seems worthwhile to develop a model based on fundamental thermodynamic relationships. Distribution coefficients extracted from column breakthrough experiments with wastewaters were used as spot checks on model-predicted values at these low concentrations.

2. BACKGROUND

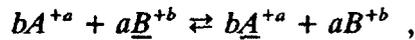
The problem of predicting multicomponent ion-exchange equilibria has attracted the interest of several researchers. Smith and Woodburn⁵ modeled the ternary system chloride-nitrate-sulfate on Amberlite IRA 400 using the Wilson equation. In their approach, an "equilibrium quotient" was defined as the selectivity coefficient (also called the relative separation factor) into which the liquid-phase activity coefficients have been factored. Thus,

the equilibrium quotient would be the true equilibrium constant for the ion-exchange reaction if the solid-phase activity coefficients were all unity. Smith and Woodburn⁵ found statistically best values for the binary interaction parameters of the Wilson equation by fitting equilibrium quotients calculated through the Wilson equation to experimentally based equilibrium quotient data.

Shallcross et al.⁶ followed essentially the same method as Smith and Woodburn⁵ in modeling the ternary system calcium-magnesium-sodium on Amberlite 252. The only variation was in the method of calculating liquid-phase activity coefficients. Smith and Woodburn⁵ used an extended Debye-Hückel equation, while Shallcross et al.⁶ used the Pitzer equation.⁷ Myers and Byington⁸ predicted multicomponent equilibria for the ternary system calcium-magnesium-potassium on KU-1 through an energetic heterogeneity approach, rather than using the Wilson equation. In the present study, the data of Robinson et al.⁴ on the strontium-cesium-calcium-magnesium-sodium system were modeled using the Wilson equation for solid-phase activity coefficients, but the Wilson binary interaction parameters were obtained in this study directly from isotherm data rather than fitting equilibrium quotients.

3. THEORY

For the binary exchange reaction



where the underline indicates the species in the solid phase, the equilibrium constant can be expressed in terms of activities:

$$K_{A-B} = \left(\frac{a_A}{a_A} \right)^b \left(\frac{a_B}{a_B} \right)^a = \frac{(\gamma_A^s \gamma_A)^b (\gamma_B^s C_B)^a}{(\gamma_A^l C_A)^b (\gamma_B^l \gamma_B)^a} , \quad (1)$$

where

y_i = equivalents fraction of i in the solid phase,

C_i = normality of i in the liquid phase,

γ_i = activity coefficient of i in the liquid phase,

γ_i^s = activity coefficient of i in the solid phase.

The activity coefficients for the cations in the liquid phase can be predicted with confidence using, for example, the Pitzer equations. From experiments, the selectivity coefficients (also called the relative separation factors) can be obtained:

$$S_{A-B} = \frac{y_A^b C_B^a}{C_A^b y_B^a} \quad (2)$$

Then, the problem is reduced to extracting solid-phase activity coefficients from the selectivity coefficients and the calculated liquid-phase activity coefficients. This must be done within a framework that will allow the prediction of multicomponent solid-phase activity coefficients that are thermodynamically consistent.

Smith and Woodburn⁵ calculated solid-phase activity coefficients with the Wilson equation, which satisfies the Gibbs-Duhem equation. The Wilson equation,

$$\ln \gamma_i^s = 1 - \ln \left(\sum_{j=1}^M y_j \Lambda_{ij} \right) - \sum_{k=1}^M \left(\frac{y_k \Lambda_{ki}}{\sum_{j=1}^M y_j \Lambda_{kj}} \right), \quad (3)$$

is applied to the binary experimental data to obtain values for the "interaction parameters," Λ_{ij} and Λ_{ji} , and then these parameters can be used in the Wilson equation for three, four, or more component systems.

To extract the values of the interaction parameters from the binary data, Smith and Woodburn⁵ defined an equilibrium quotient, λ_{A-B} :

$$\lambda_{A-B} = \frac{(\gamma_B C_B)^a y_A^b}{(\gamma_A C_A)^b y_B^a} \quad (4)$$

Values for the equilibrium quotient for each experimental point can be calculated from the selectivity coefficients and liquid-phase activity coefficients.

The equilibrium quotient can be expressed in terms of the equilibrium constant:

$$\lambda_{A-B} = K_{A-B} \frac{(\gamma_B^{s^a})}{(\gamma_A^{s^b})} \quad (5)$$

Substitution of the Wilson equation [Eq. (3)] into this expression for the equilibrium quotient yields:

$$\begin{aligned} \ln \lambda_{A-B} = & \ln K_{A-B} - b [1 - \ln(y_A + y_B \Lambda_{A-B}) \\ & - \left(\frac{y_A}{y_A + y_B \Lambda_{A-B}} + \frac{y_B \Lambda_{B-A}}{y_A \Lambda_{B-A} + y_B} \right)] + a [1 - \ln(y_A \Lambda_{B-A} + y_B) \\ & - \left(\frac{y_A \Lambda_{A-B}}{y_A + y_B \Lambda_{A-B}} + \frac{y_B}{y_A \Lambda_{B-A} + y_B} \right)] \quad (6) \end{aligned}$$

This equation contains three unknowns: K_{A-B} and the two interaction parameters. A minimum of three data points are needed to evaluate them. When more than three data points are available, a search procedure can be used to find the set of values of K_{A-B} , Λ_{A-B} , and Λ_{B-A} that minimize the sum of the squares of the deviations between experimental equilibrium quotients from Eq. (4) and theoretical equilibrium quotients from Eq. (6) for all points. This is the procedure that was followed by Smith and Woodburn⁵ and by Shallcross et al.⁶

The Wilson interaction parameters can be obtained more directly by fitting the isotherm data. For binary systems, the following procedure may be used, given experimental values for the total solution concentration C_t (normality), C_A , and y_A .

1. Assume trial values for K_{A-B} , Λ_{A-B} and Λ_{B-A} .
2. Select a value for y_A in the range of interest ($y_B = 1 - y_A$).
3. Calculate γ_A^s and γ_B^s from the Wilson equation.
4. Assume trial values for γ_A and γ_B . For the dilute solutions in this work, values ranged from about 0.7 to near unity.
5. Calculate C_A from the equilibrium constant and a mass balance:

$$C_A + C_B = C_t \quad , \quad (7)$$

$$C_A = \frac{y_A \gamma_A^s C_B \gamma_B}{K_{A-B} \gamma_A y_B \gamma_B^s} \quad , \quad (8)$$

eliminate C_A and solve for C_B .

6. Calculate the liquid-phase activity coefficients from the Pitzer equation using the calculated values of C_A and C_B and replace the assumed values in step 4.
7. Iterate steps 5 and 6 until liquid phase activity coefficients are in sufficient agreement.
8. Compare experimental values of C_A and C_B with those calculated using the assumed model parameters in step 1.

This procedure is easily extended to systems with more than two components.

4. RESULTS

The extent of the data published by Robinson et al.⁴ for the strontium-cesium-calcium-magnesium-sodium system is summarized in Table 1. Total solution concentrations including all components did not exceed 0.01 N for any of the data sets. Equilibrium quotients were

calculated for the binary data from Eq. (4). The Pitzer equation for cations was used to calculate liquid-phase activity coefficients. Because the solutions were so dilute, only the first term in the Pitzer equation was significant. The procedure used by previous investigators to obtain Wilson interaction parameters from equilibrium quotients [i.e., searching for values of K_{A-B} , Λ_{A-B} , and Λ_{B-A} that provide values of λ_{A-B} from Eq. (6) that most closely match experimental λ_{A-B} 's from Eq. (4)] was not successful for the present system. Experimental values for equilibrium quotients passed through a maximum when they were plotted against equivalents fractions in the solid phase, as illustrated for cesium-sodium in Fig. 1. Values for the interaction parameters that yielded a theoretical curve matching the data points on both sides of the maximum could not be found.

Table 1. Extent of experimental data^a

Number of components	Components	Number of solution/sorbent ratios
2	Strontium-sodium	8
	Cesium-sodium	6
	Calcium-sodium	6
	Magnesium-sodium	7
3	Strontium-cesium-sodium	7
	Calcium-magnesium-sodium	7
4	Strontium-calcium-magnesium-sodium	6
	Cesium-calcium-magnesium-sodium	6
5	Strontium-cesium-calcium-magnesium-sodium	13

^aRobinson et al.⁴

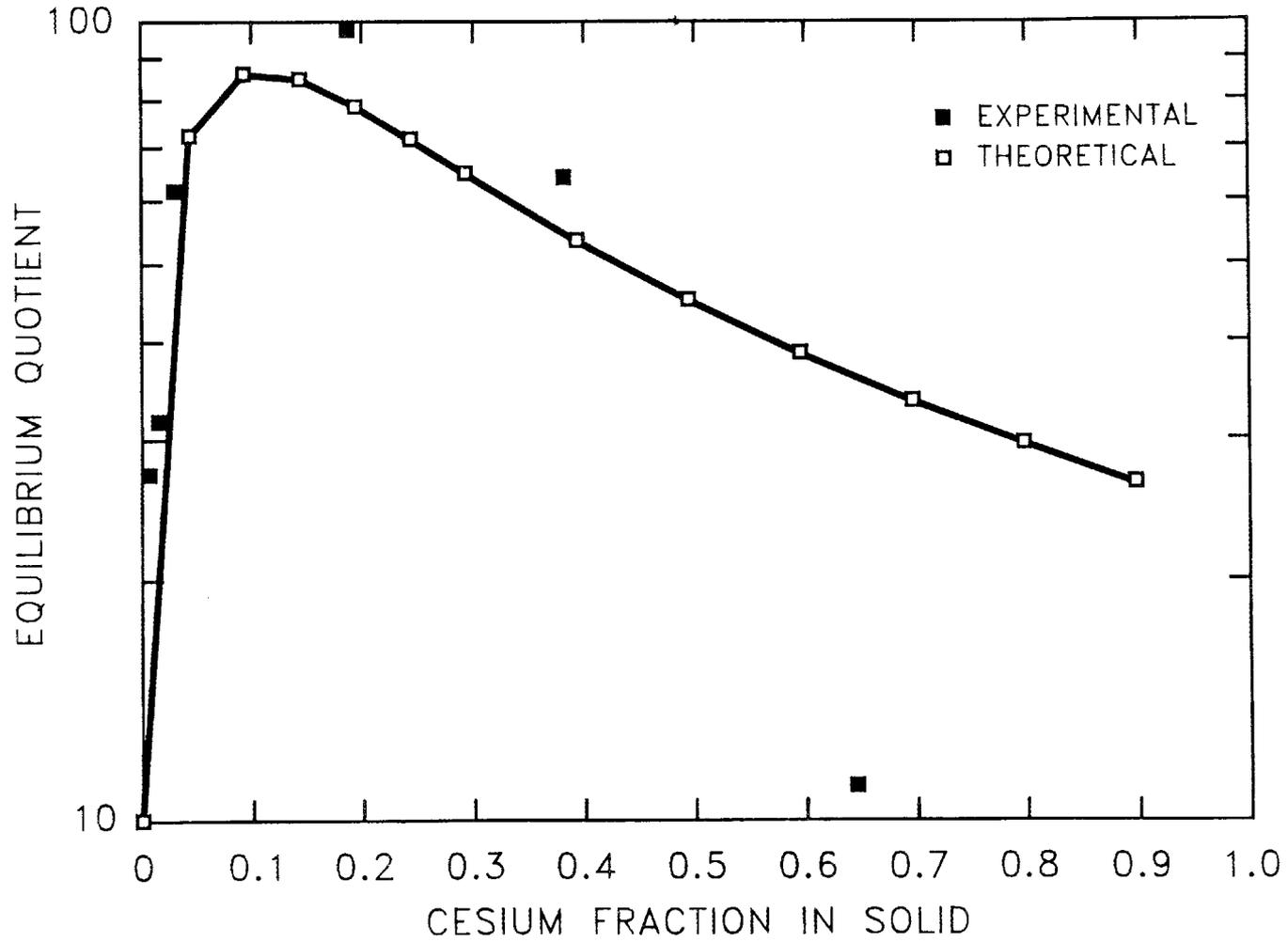


Fig. 1. Cesium-sodium equilibrium quotients, with theoretical points calculated using $K = 51$, $\Lambda_{\text{Cs-Na}} = 0.01$, $\Lambda_{\text{Na-Cs}} = 3.95$.

The data used by Smith and Woodburn⁵ contained no solid-phase equivalents fractions below 0.2. Equilibrium quotients from their data decreased monotonically as the solid-phase equivalents fractions increased. Similarly, the equilibrium quotients of Shallcross et al.⁶ did not exhibit a maximum.

Using the procedure of finding best values for the model parameters directly from the isotherm data, the researchers obtained the values for the binary data available. These values are given in Fig. 2 through 5. The sum of the squares of the deviations between experimental and theoretical points was used as a criterion for best fit:

$$R = \sum_{i=1}^N \left(\frac{\text{exp} - \text{theo}}{\text{exp}} \right)^2 . \quad (9)$$

For comparison of goodness of fit between data sets, the R value was divided by the number of data points, N , to obtain a measure related to the average deviation per data point.

Since binary data for strontium-cesium were not available, values for strontium-cesium interaction parameters were obtained by fitting the ternary system strontium-cesium-sodium, using the previously obtained parameter values for strontium-sodium and cesium-sodium. Similarly, values for calcium-magnesium interaction parameters were obtained by fitting the calcium-magnesium-sodium data. Interaction parameters for strontium-calcium, strontium-magnesium, cesium-calcium, and cesium-magnesium were obtained by fitting the four-component data using previously obtained parameter values. The results are summarized in Table 2.

The set of parameter values in Table 2 was used to predict the five-component equilibrium points for which experimental data were given by Robinson et al.⁴ The results are shown in Table 3. Equilibrium liquid-phase concentrations were calculated for strontium, cesium, calcium, and magnesium at 13 concentrations, each of which was at one or the other

of two different total solution concentrations. Strontium and cesium concentrations spanned three orders of magnitude. For these 52 predicted concentrations, the R/N was 0.30, which is comparable to or better than the R/N data sets including calcium or magnesium data.

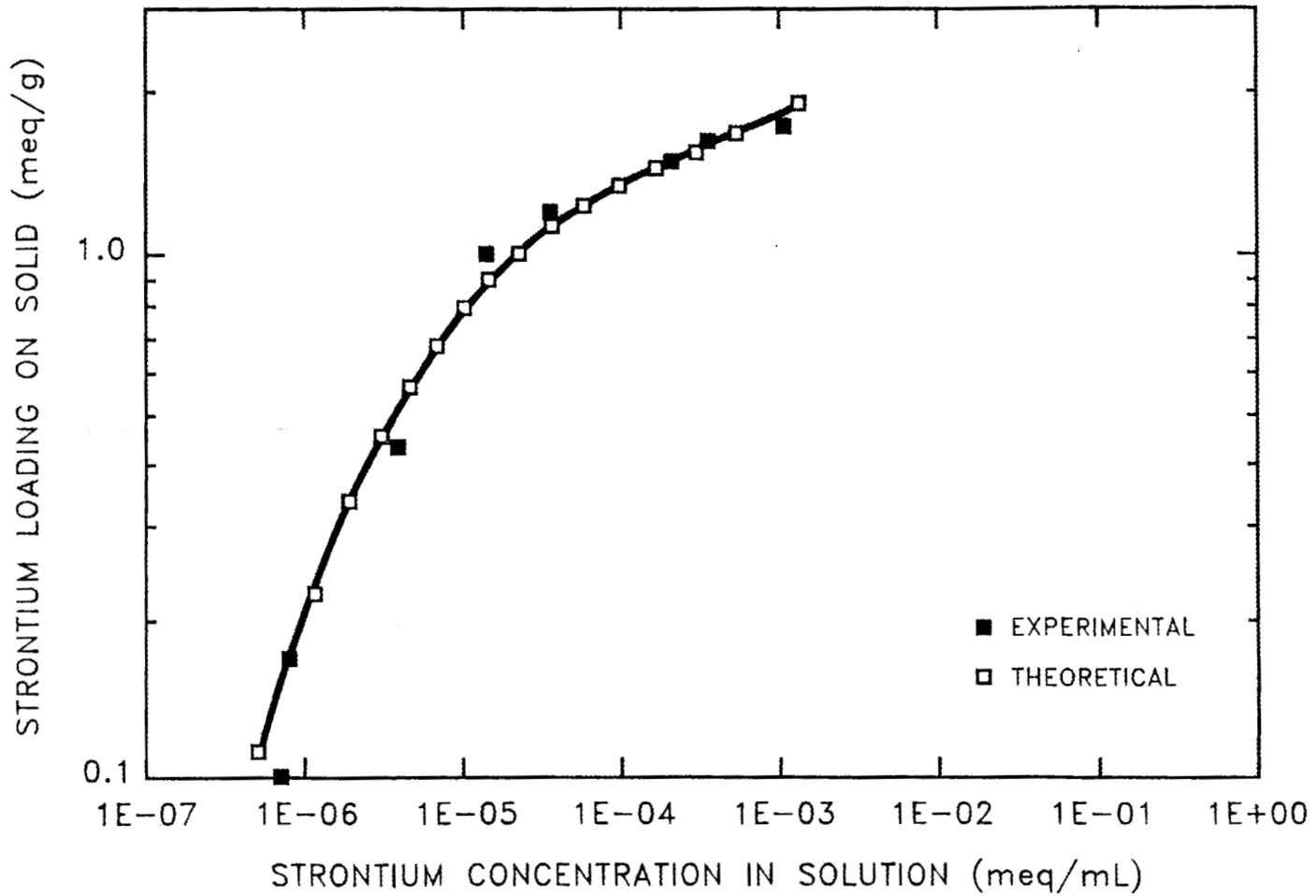


Fig. 2. Strontium-sodium isotherm, with theoretical points calculated using $K = 0.159$, $\Lambda_{Sr-Na} = 7.96$, $\Lambda_{Na-Sr} = 0.112$.

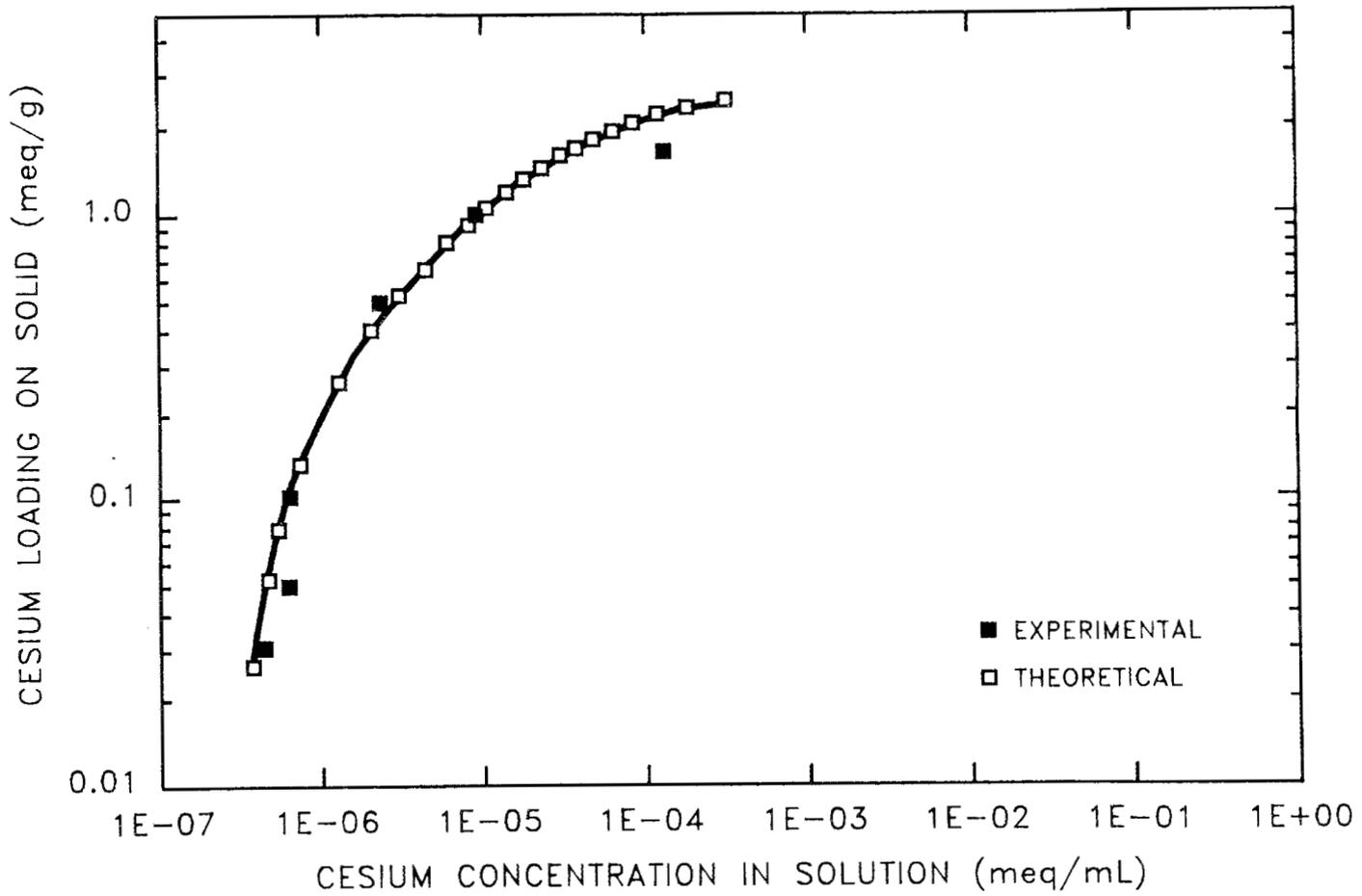


Fig. 3. Cesium-sodium isotherm, with theoretical points calculated using $K = 51$, $\Lambda_{Cs-Na} = 0.01$, $\Lambda_{Na-Cs} = 3.95$.

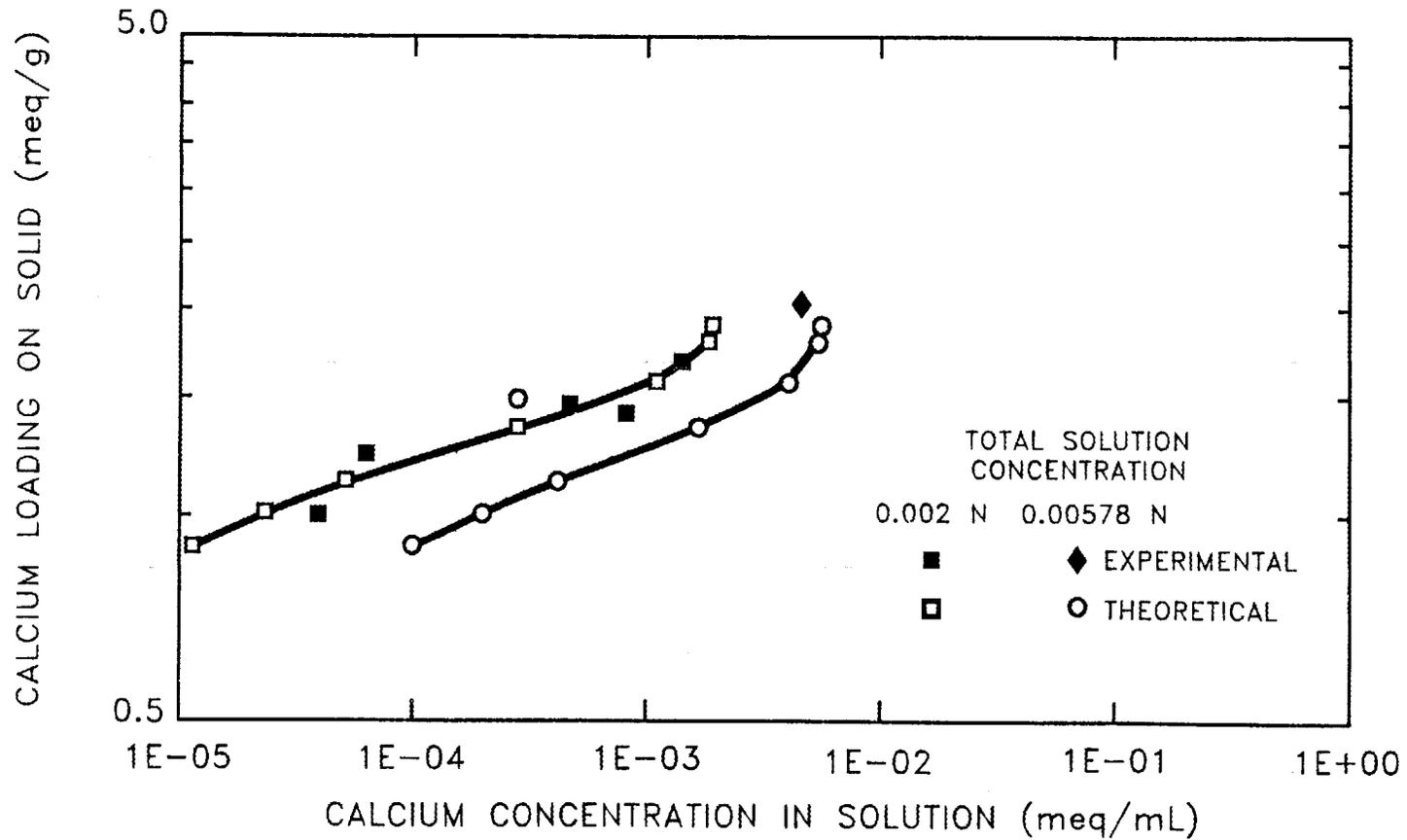


Fig. 4. Calcium-sodium isotherm, with theoretical points calculated using $K = 0.022$, $\Lambda_{Ca-Na} = 86$, $\Lambda_{Na-Ca} = 2.0$.

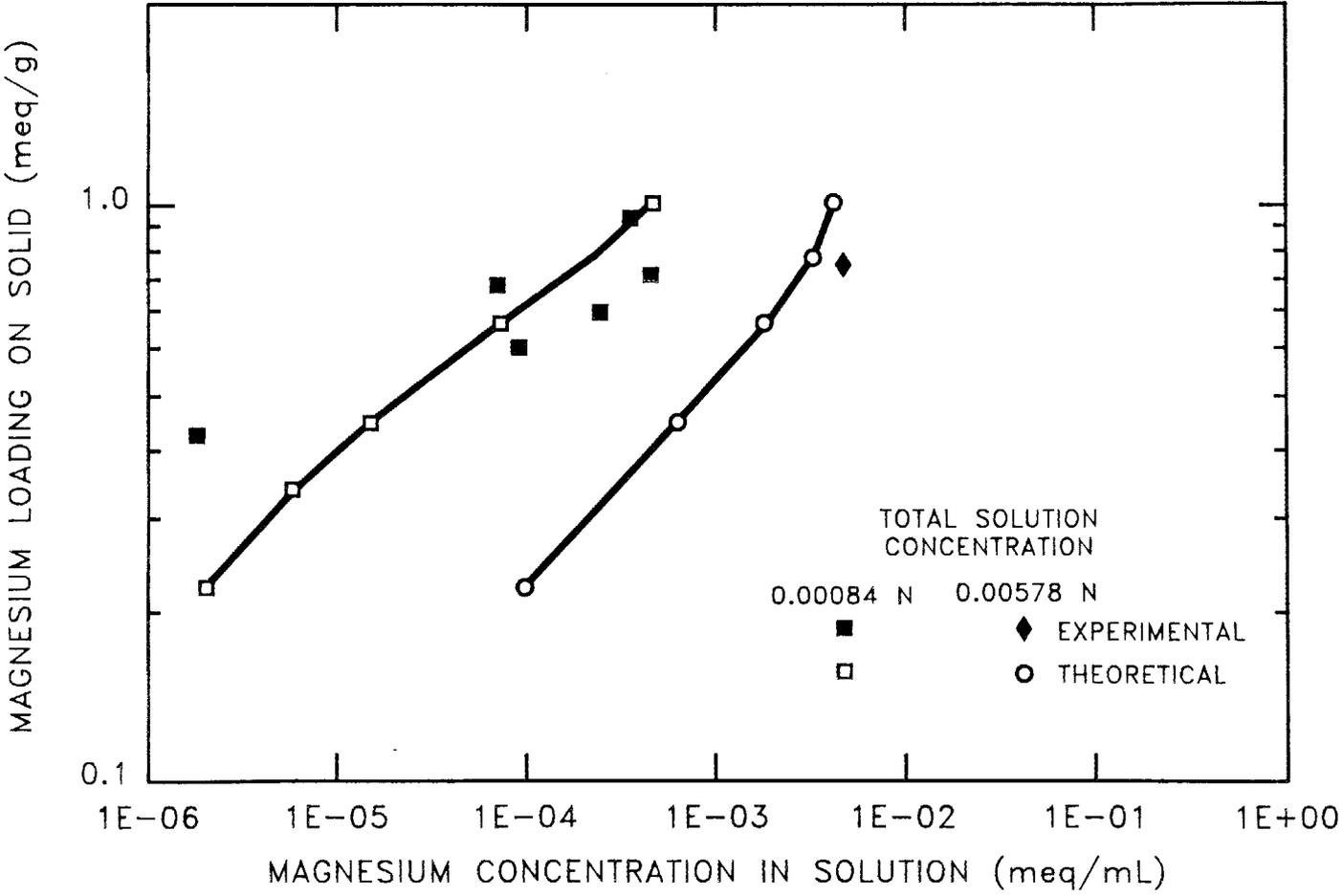


Fig. 5. Magnesium-sodium isotherm, with theoretical points calculated using $K = 0.0005$, $\Delta_{Mg-Na} = 86$, $\Delta_{Na-Mg} = 4.0$.

Table 2. Wilson interaction parameter values

Binary components		$K_{A,B}$	$\Lambda_{A,B}$	$\Lambda_{B,A}$	Number of experimental data points (N)	Goodness of fit R/N
A	B					
Strontium	Sodium	0.159	7.96	0.112	8	0.13
Cesium	Sodium	51	0.01	3.95	6	0.10
Calcium	Sodium	0.022	86	2.0	6	0.25
Magnesium	Sodium	0.0005	20	4.0	7	5.10
Strontium	Calcium	-	0.001	2.0	14	0.11
Calcium	Magnesium	-	52	92	14	0.40
Strontium	Calcium	-	25	4.0	18	0.65
Strontium	Magnesium	-	0.03	42	18	0.65
Cesium	Calcium	-	4.8	0.2	18	0.22
Cesium	Magnesium	-	2.0	100	18	0.22

Table 3. Predicted liquid-phase concentrations for the five-component data

liq/sol (mL/g)	Strontium conc.		Cesium conc.		Calcium conc.		Magnesium conc.	
	exp.	predict.	exp.	predict.	exp.	predict.	exp.	predict.
<i>Total dissolved solids: 5.76E-03 meq/mL</i>								
25	1.16E-06	1.39E-06	4.87E-07	4.87E-07	4.99E-07	1.35E-07	4.49E-06	2.35E-06
50	2.39E-06	3.10E-06	8.78E-07	7.51E-07	4.99E-07	3.39E-07	6.34E-06	6.41E-06
99	6.24E-06	8.31E-06	1.82E-06	1.62E-06	4.99E-07	12.3E-07	2.04E-05	2.73E-05
504	6.26E-04	4.60E-04	4.66E-05	7.01E-05	5.75E-04	2.72E-04	7.83E-04	8.69E-04
1012	1.34E-03	0.80E-03	2.35E-04	1.89E-04	1.31E-03	0.37E-03	8.88E-04	10.4E-04
1955	1.63E-03	2.28E-03	4.02E-04	5.46E-04	1.58E-03	1.81E-03	9.16E-04	9.93E-04
<i>Total dissolved solids: 1.45E-03 meq/mL</i>								
50	1.69E-07	0.34E-07	1.07E-07	0.83E-07	3.24E-06	0.38E-08	1.05E-06	0.55E-07
100	2.05E-07	0.83E-07	1.70E-07	1.08E-07	3.24E-06	0.86E-08	8.54E-07	1.35E-07
201	2.58E-07	1.87E-07	2.60E-07	1.69E-07	3.24E-06	0.23E-07	5.38E-07	4.00E-07
506	6.46E-07	7.74E-07	5.98E-07	5.40E-07	3.24E-06	1.48E-07	2.05E-06	3.23E-06
830	2.20E-06	2.74E-06	1.46E-06	1.66E-06	3.24E-06	0.81E-06	1.13E-05	1.79E-05
1240	1.69E-05	1.22E-05	4.68E-06	5.63E-06	1.94E-05	0.59E-05	9.10E-05	6.37E-05
2370	1.86E-04	0.60E-04	2.89E-05	2.53E-05	2.11E-04	0.40E-04	2.02E-04	0.83E-04

$$R = \sum \left(\frac{\text{exp} - \text{predict}}{\text{exp}} \right)^2 = 15.5 \quad (10)$$

$N = 52$ points
 $R/N = 0.30$

5. APPLICATION TO ORNL LOW-LEVEL WASTEWATER

Two spot checks were made on model-predicted equilibria at the low process waste concentrations of strontium and cesium. Breakthrough curves for small chabazite test columns operating on ORNL wastewaters were presented by Kent.¹ A breakthrough curve for strontium was obtained with the following water composition representative of the PWTP influent:

strontium	750 Bq/L or 3.2×10^{-12} equiv/L
cesium	110 Bq/L or 2.3×10^{-13} equiv/L
calcium	75 mg/L or 3.75×10^{-3} equiv/L
magnesium	12 mg/L or 1.0×10^{-3} equiv/L
sodium	64 mg/L or 2.8×10^{-3} equiv/L

For this liquid-phase composition, the model predicts the following solid-phase loading:

strontium	4.65×10^{-9} meq/g
cesium	1.86×10^{-9} meq/g
calcium	1.67 meq/g
magnesium	0.0897 meq/g
sodium	0.840 meq/g

That is, near the bed inlet, which is in equilibrium with the feed water, about 2/3 of the ion exchange capacity is occupied by calcium and 1/3 by sodium. The radioactive components occupy only a trace. The value for strontium can be compared to one extracted from the breakthrough curve of Kent.¹ The curve indicates a mass transfer zone (MTZ) length of

about 7 in. and a velocity of about 0.005 ft/h. The MTZ is the part of the column where the solid loading changes from saturation to zero. The velocity of the MTZ is related to the saturation loading by the following equation:

$$U = \frac{L (C_{Af} - C_{Ab})}{2.60 \rho y_A}, \quad (11)$$

where

L = liquid flowrate = 605 L/(h)(ft²),

C_{Af} = strontium concentration in feed water,

C_{Ab} = strontium concentration at breakthrough (negligible),

ρ = chabazite density (dry) = 45 lb/ft³,

y_A = fractional strontium loading on solid.

Equation (11) yields a value for y_A of 7.3×10^{-9} , or a loading of 19.0×10^{-9} meq/g, a factor of 4 larger than the model-predicted value. Considering the extension to the extremely small concentrations involved, this result appears to confirm the validity of the model.

A similar check was made for cesium. In this case, the wastewater composition representative of the PWTP effluent is:

strontium	<10 Bq/L	< 4×10^{-14} equiv/L
cesium	65 Bq/L	1.36×10^{-13} equiv/L
calcium	0.22 mg/L	1.1×10^{-5} equiv/L
magnesium	0.054 mg/L	4.5×10^{-6} equiv/L
sodium	160 mg/L	7.0×10^{-3} equiv/L

For this liquid-phase composition, the model predicts the following equilibrium loading:

strontium	< 6.6×10^{-10} mequiv/g
cesium	9.3×10^{-9} mequiv/g
calcium	0.523 mequiv/g

magnesium 0.010 mequiv/g

sodium 2.067 mequiv/g

The breakthrough curve used was reported by Kent.¹ The velocity of travel of the MTZ was estimated at 6.3×10^{-4} ft/h. Applying again Eq. (11) (with the same values for L and ρ), a value for the equilibrium loading of cesium is found of 6.4×10^{-9} mequiv/g. The agreement is within a factor of 1.5, which again verifies the validity of the model.

Finally, the model was used to investigate the sensitivity of strontium and cesium distribution coefficients to changes in process water composition. Figures 6, 7, and 8 show the results of starting with the PWTP influent and increasing the concentration of one of the components up to a factor of ten while holding all other concentrations constant. The distribution coefficient is the solid loading divided by the liquid-phase concentration for a particular component. Increases in calcium concentration affected the distribution coefficient for cesium more strongly than increases in sodium concentration did. Strontium was affected by calcium to about the same degree as by sodium. The effect of magnesium was slight. Curves are not shown for increases in strontium or cesium concentration because these gave no effect, even for increases of five orders of magnitude.

Curves based on the PWTP effluent composition are shown in Figs. 9, 10, and 11. Here the sodium concentration affected both the strontium and the cesium distribution coefficients more strongly than the calcium concentration did because the calcium concentration was much lower.

6. CONCLUSIONS

A multicomponent ion-exchange equilibrium model for five cations (strontium, cesium, calcium, magnesium, and sodium) on chabazite was developed from the equilibrium data of Robinson et al.⁴ The model was tested against chabazite column runs with two different

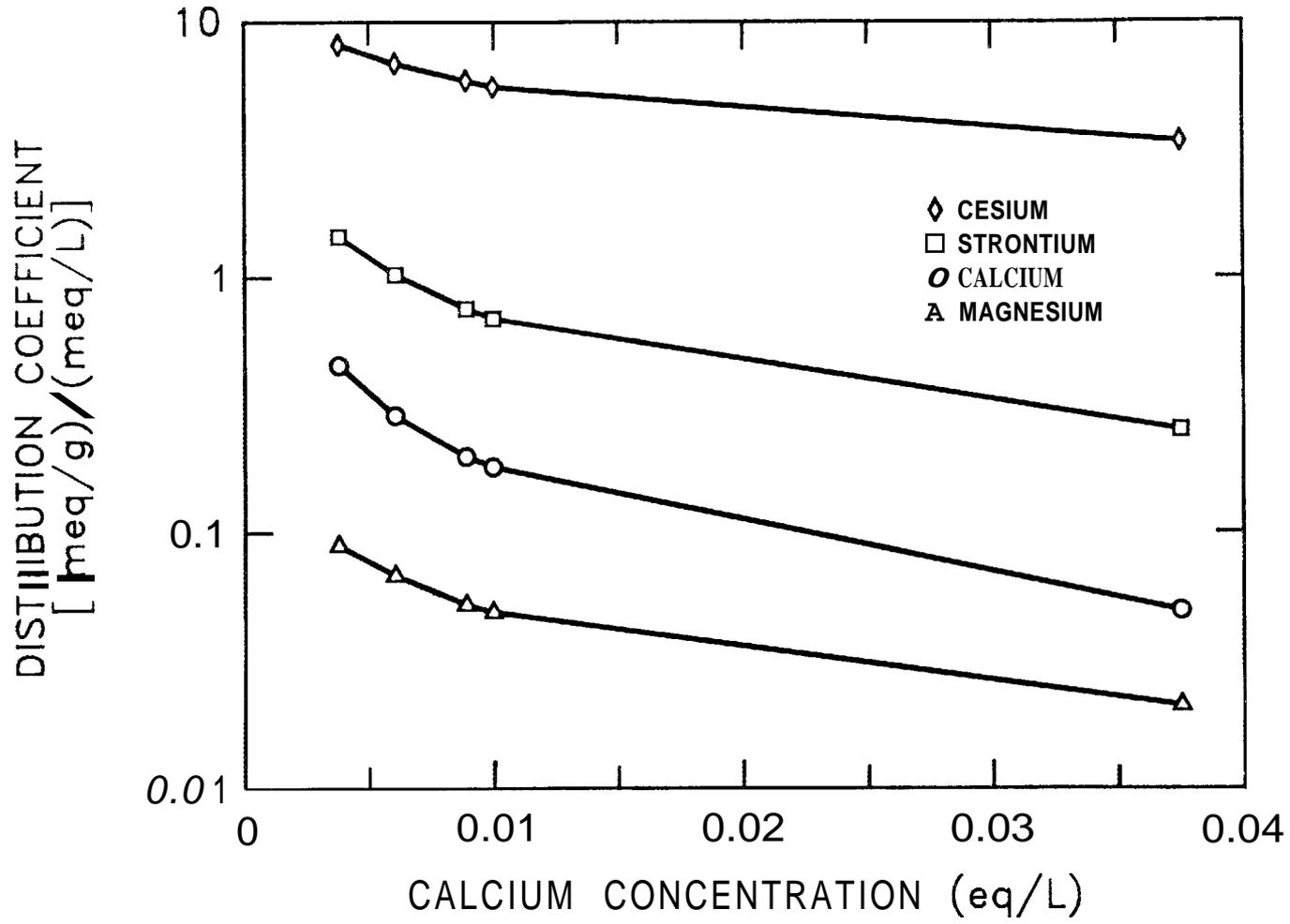


Fig. 6. Distribution coefficients for Process Waste Treatment Plant influent with increases in calcium concentration.

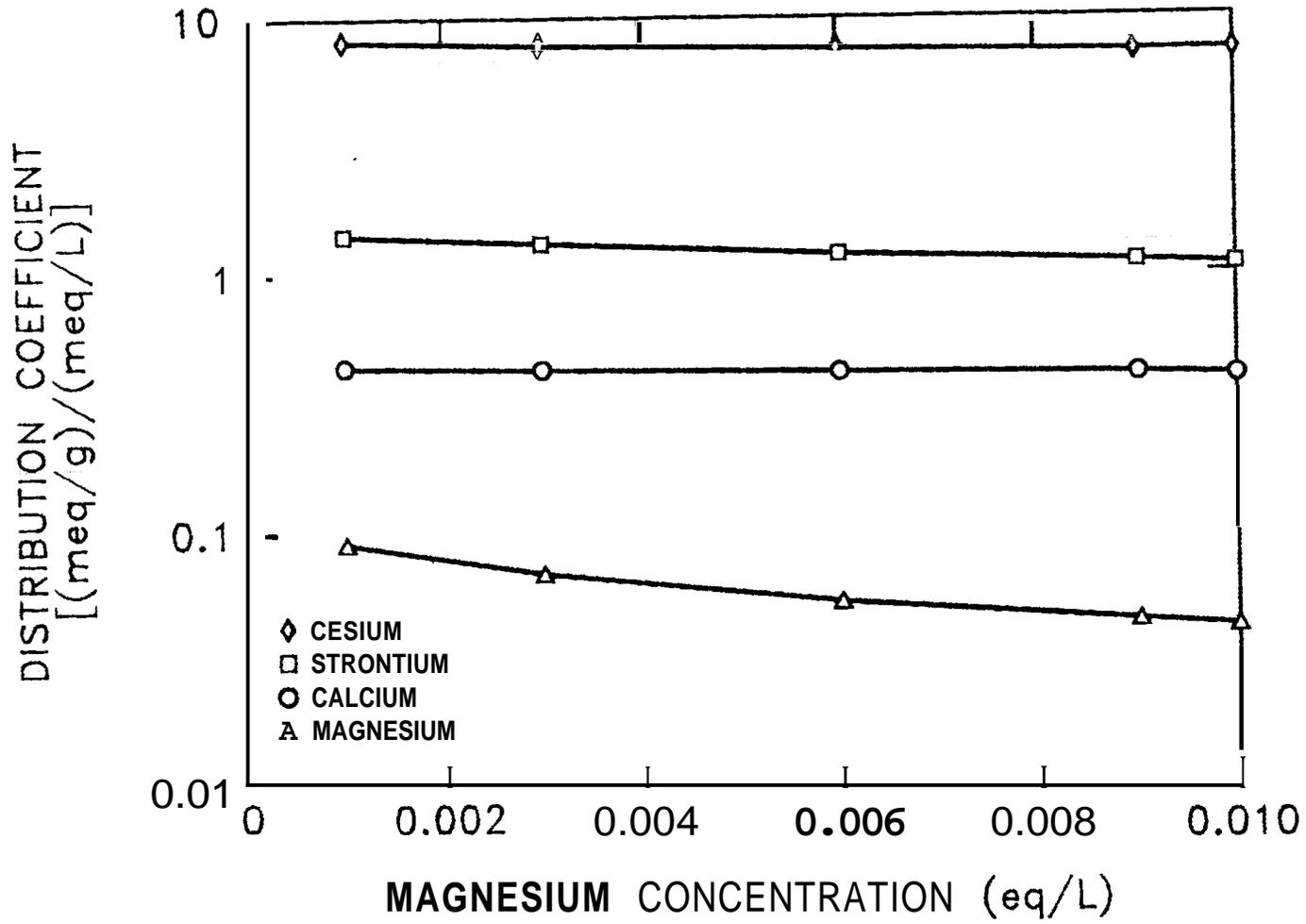


Fig. 7. Distribution coefficients for Process Waste Treatment Plant influent with increases in magnesium concentration.

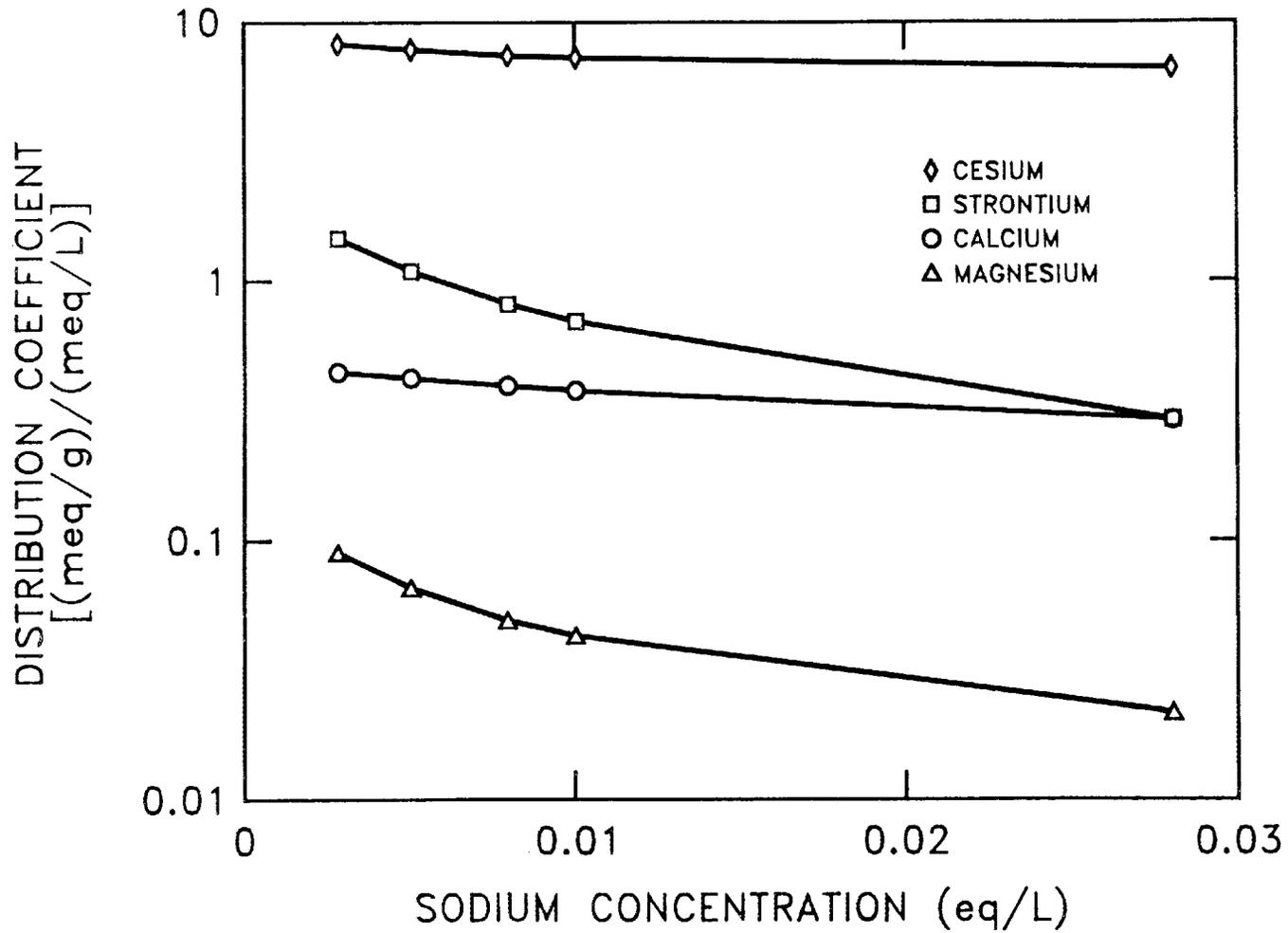


Fig. 8. Distribution coefficients for Process Waste Treatment Plant influent with increases in sodium concentration.

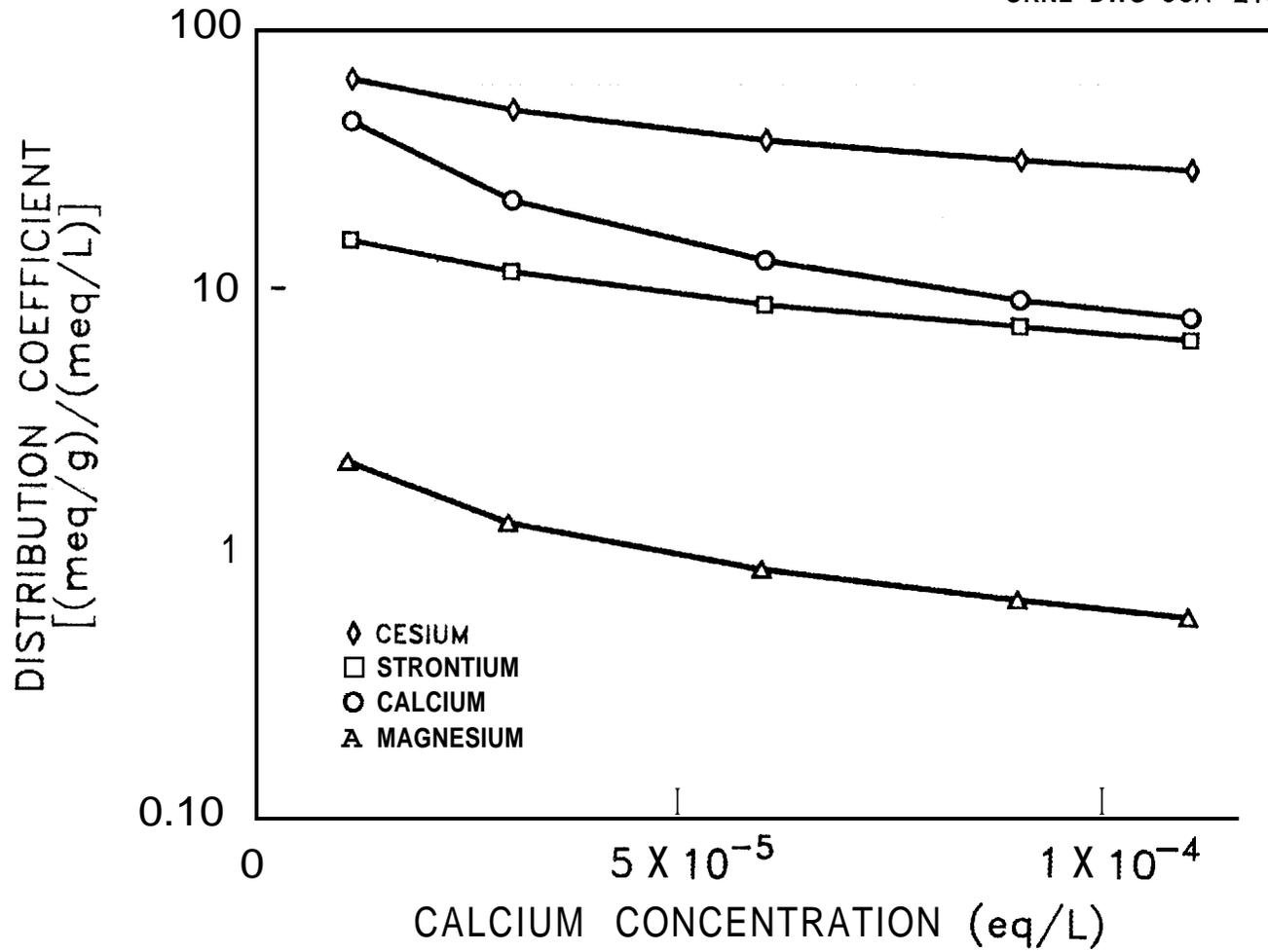


Fig. 9. Distribution coefficients for Process Waste Treatment Plant effluent with increases in calcium concentration.

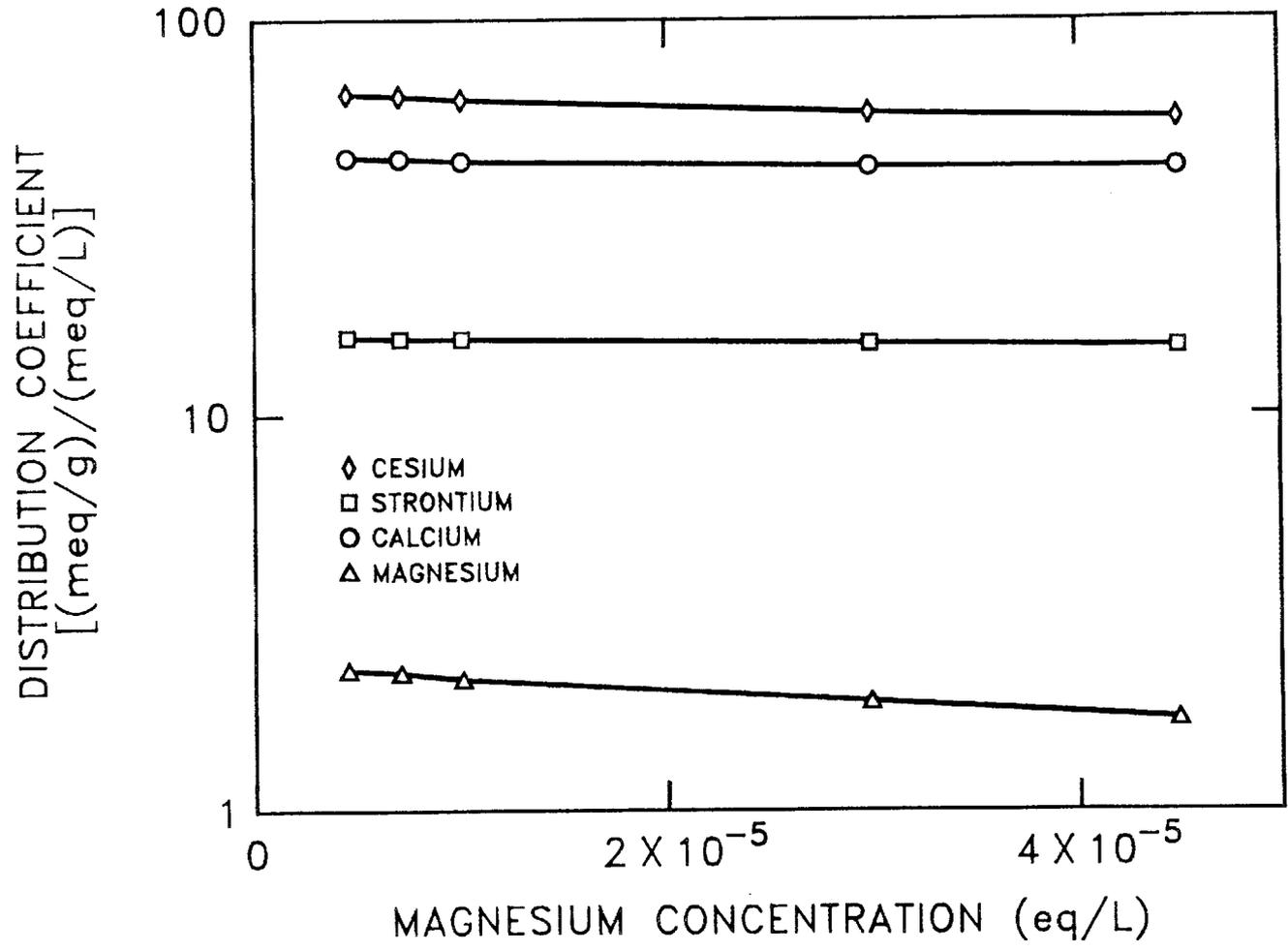


Fig. 10. Distribution coefficients for Process Waste Treatment Plant effluent with increases in magnesium concentration.

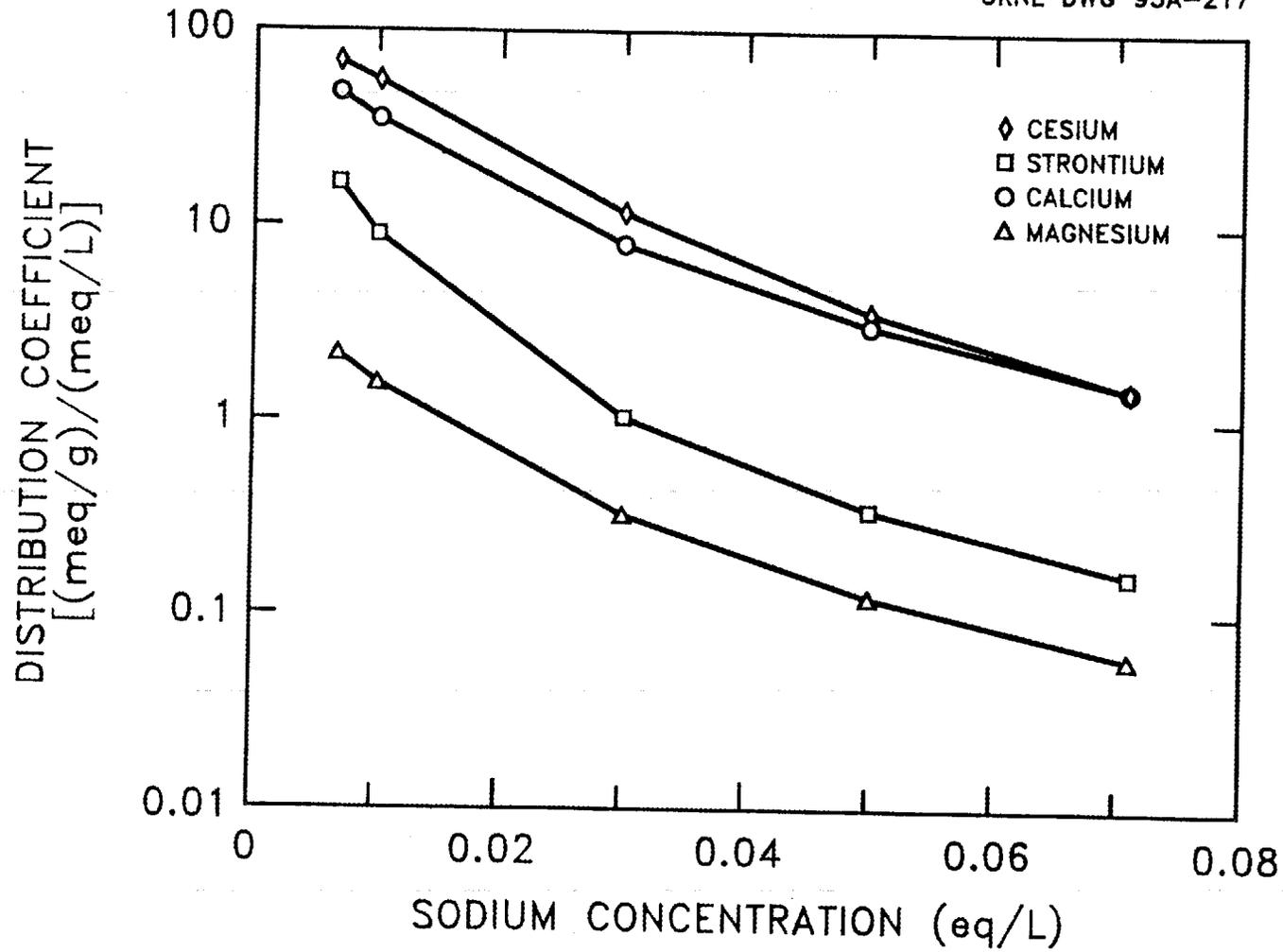


Fig. 11. Distribution coefficients for Process Waste Treatment Plant effluent with increases in magnesium concentration.

wastewaters and found to be valid. The effects of changes in feedwater composition on distribution coefficients for strontium and cesium were investigated with the model. For the PWTP influent, an increase in calcium concentration most affected the cesium distribution coefficient, while strontium was affected by calcium to about the same degree as by sodium. For the PWTP effluent, which has much lower calcium concentration and higher sodium concentration, an increase in sodium concentration has the strongest effect on both strontium and cesium.

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