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Summary

The two tasks of the project were to modify the equilibrium model for IONSIV IE 911, and to estimate new values of the effective diffusivity for IE-911. The modification of the equilibrium model was successful and Figure 1 illustrates the current predictive capability for the average SR waste. For the effective diffusivity we proposed two new methods for measuring effective diffusivities, but because of major damage to our atomic absorption system and our XRD unit we were unable to perform any new experiments. However, column experiments conducted at ORNL, WSR, SNL and Hanford-PNNL were reviewed. We also review the effect of viscosity and structure on the effective diffusivities. Based on these review values of effective diffusivities in the range of 0.5×10^{-10} to 1.0×10^{-10} m²/s are reasonable for the Savannah River Wastes. We will attempt to have new data prior to the end of the project for the effective diffusivities.

Effective Diffusivity for Cesium in IE-911

One task of the project was to obtain a better estimate of the effective diffusivity for cesium. We had intended to measure new values of effective diffusivities for different solutions in an attempt to gain better estimates of the values. We had also proposed a couple of new methods for measuring the effective diffusivity for cesium. In addition, we wanted to correlate the effective diffusivities with the viscosity of the solutions. Three methods were considered for conducting this task, but because of analytical equipment failures we were unable to measure new values for the effective diffusivities. In the case of our AA unit, we concluded we would have to buy a new unit, which has been ordered using another account, to complete the project. However, considering the range of values that we have determined by using our data, data collected at ORNL, Hanford-PNNL, WSRL and the molecular diffusivity of cesium in solution, the following discussion presents a review of values of effective diffusivities and the issues associated with the measurement of effective diffusivities.

As we examine the methods of measuring effective diffusivities, we need to realize and remember that the literature is replete with examples and discussions of the inability to measure effective diffusivities within 30% of the true values. Huckman (1999) chapter III of his dissertation extensively discusses the sensitivity of effective diffusivities to errors in measurements. We also must seriously consider the structure of the IE-911 granules, and the effect of this structure on the measured effective diffusivities.

The IE-911 granules are composed of micropores and macropores. The micropores are the pores within the crystalline CST. The diameter of the crystalline particles produced in commercial batches is approximately 0.4 microns, i.e., 400 nanometers. When the CST powder is prepared in the laboratory smaller crystallites with a diameter of 0.2 micron, i.e. 200 nm are produced. The openings into the crystallites are on the order of 0.34 nm. Since a crystallite is composed of an exceedingly large number of unit cells, most of the ion exchange at low cesium concentrations will occur in the outer layers of the crystallites.

Since the IE-911 granules are composed of macropores and the micropores within the crystallites, the question arises. Is a complex macro-micro pore model required to adequately model the ion

exchange process, or is a simpler macropore model sufficient to adequately predict the performance of a column packed with IE-911.

Huckman et al. (1996), Gu et al. (1997), Huckman (1999), Latheef et al. (2000) and Huckman et al. (1999, 2000) have indicated that the two-phase homogeneous model is sufficient for predicting the behavior of the IE-911 granules for most cases. Furthermore, dimensionless parameters developed by Ruckenstein et al. (1971), Ruthven and Loughlin (1972), Helfferich (1962), and Huckman (1999) provide criteria for considering micropore or crystal phase diffusional resistance to be negligible. The parameter presented by Huckman (1999) is shown in the following Equation, which applies for nonlinear isotherms.

$$N_{Cr} = \frac{\mathbf{e}_p}{3(1-\mathbf{e}_p)} \frac{D_e R_c^2}{D_s R_p^2} \frac{C^0}{F(C^0)}$$

where D_s is the crystal-phase diffusivity and $F(C^0)$ is the evaluation of the equilibrium isotherm function $F(C)$ at the initial concentration, $C = C^0$. When the crystal resistance parameter, N_{Cr} , is much greater than one, micropore resistance to diffusion controls. However, if N_{Cr} is much, much less than one (i.e., $N_{Cr} < 0.001$), the macropore resistance to diffusion controls. This equation shows that the waste with a cesium concentration of 20 mg/L was in the intermediate zone of using the macropore model instead of the micro-macro pore model. The intermediate zone is determined based on the work of Helfferich (1962) and Huckman et al. Helfferich (1962) showed that the critical constant needed to be much less than 1 to satisfactorily model a system of particles with macro-micro pores as a particle with only macropores. Huckman et al. showed that this parameter had to be less than 0.001 for the resistance to micropore diffusion to have a negligible effect on the experiments as well as in the model. For a linear isotherm N_{Cr} is not a function of the concentrations, and is only a function of the geometrical characteristics of the granules. We have found that the void fraction of the particles is about 0.24. Utilizing the effective diffusivities previously measured for the particles and the powder, the value of N_{Cr} is equal to approximately 0.01. Huckman (1999) discusses this parameter extensively in his dissertation, Chapter 5.

The next factor to consider is the molecular diffusivity of cesium, which is $2.05 \times 10^{-9} \text{ m}^2/\text{s}$ in dilute solutions. The effective diffusivity is a function of geometry and molecular properties. The most rigorous approach to estimate values of effective diffusivities is to determine the geometry and integrate over this geometry. The next best approach is to assume that the molecular diffusivity can be multiplied by some geometric factor to account for the effect of the particle structure on the effective diffusivity. This approach usually results in multiplication of the void fraction divided by the tortuosity times the molecular diffusivity.

Since the molecular diffusivity given above is for dilute solutions, then it needs to be corrected for the viscosity and non-ideality of the solution. The equation for the correction is given below:

For solutions other than infinite dilution Gordon (1937) presents the following equation, which was taken from Perry's Handbook, 4th Edition.

$$D_L = D_0 \left(1 + \frac{m \partial \ln \mathbf{g}_{\pm}}{\partial m} \right) \frac{l}{c_B \underline{V}_B} \left(\frac{\mathbf{m}_B}{\mathbf{m}} \right)$$

m = molality;

\tilde{a}_{\pm} = mean ion activity coefficient based on molality

c_B = g.-moles water/cc of solution;

\underline{V}_B = partial molal volume of water, cc/mole

$\dot{\eta}_B$ = viscosity of water

$\dot{\eta}$ = viscosity of solution.

This equation as well as Stokes equation illustrates that the molecular diffusivity is a function of solution composition, temperature and viscosity. As temperature increases the molecular diffusivity increases. As the viscosity of a solution increases the molecular diffusivity decreases. We have measured the viscosities of a 1M sodium solution with 0.6 M OH⁻ and 0.4 M NO₃⁻, a solution of 5.7 M Na⁺, 0.6 M OH⁻ and 5.1 M NO₃⁻, and a solution with 5.2 M Na⁺, 0.5 M K⁺, 0.6 M OH⁻ and 5.1 M NO₃⁻ are 1.01 cp, 1.59 cp, and 1.83 cp respectively. The Stokes-Einstein relationship is

$$D_m^2 = D_m^1 \frac{\mathbf{m}_1}{\mathbf{m}_2}$$

Superscripts refer to solutions 1 and 2 and are not exponents.

Since we have addressed the effect of solutions on molecular diffusivities we can now look at the effect of structure. By using the simpler approach effective diffusivity is estimated by three models, the random pore model, the parallel cross-linked pore model, and Beeckman and Froment's pore network model.

$$D_e = \frac{\mathbf{e}_p}{\mathbf{t}} * D_m = 0.24/3 * 2.0 \times 10^{-9} = \mathbf{1.6 \times 10^{-10} \text{ m}^2}$$

$$D_e = \mathbf{e}^2 * D_m = \mathbf{1.52 \times 10^{-10} \text{ m}^2/\text{s}}$$
 where epsilon is 0.24, and molecular diffusivity equals 2.0 x 10⁻⁹ m²/s

p.

$$D_e = \frac{\mathbf{e}_p}{\mathbf{t}} * D_m = 0.24/4 * 2.0 \times 10^{-9} = \mathbf{1.2 \times 10^{-10} \text{ m}^2}$$

These three models are discussed in Froment and Bischoff beginning on page 148, i.e., second edition, Chemical Reactor Analysis and Design (1990) by G. F. Froment and K. B. Bischoff.

In each case above the molecular diffusivity for cesium has been for a dilute solution of cesium nitrate, which should have a viscosity of approximately 1 cp. Therefore, the molecular diffusivity needs to be corrected for viscosity. Huckman (1999) reported viscosity 1.89 cp for a solution of 5.7 molar sodium cation, 0.6 molar hydroxide anion and 5.1 molar nitrate anion. The average of the above effective diffusivities divided by the solution viscosity yields an effective diffusivity of $0.76 \times 10^{-10} \text{ m}^2/\text{s}$.

In a review of the data taken at Savannah River in 1998 using the average waste and a slow flowrate, the value that we reported was $0.6 \times 10^{-10} \text{ m}^2/\text{s}$. In a review of these data, the effective diffusivity could have been estimated at about $0.8 \times 10^{-10} \text{ m}^2/\text{s}$, even though we reported a value of $0.6 \text{ m}^2/\text{s}$. These values are within 30% of each other, which is well within the range of expected error range.

Based on the review of past simulations, the effect of viscosities, compositions and the fact that effective diffusivities can be estimated to only within 30%, the values of effectivity for cesium in the CST must be in a range of 0.4 to $1.0 \times 10^{-10} \text{ m}^2/\text{s}$. Also, in the review of experiments conducted at ORNL and Hanford, there are a number of column experiments that have not been modelled. Modeling of these experiments would add substantially to the data base in the estimation of effective diffusivities for different solutions. However, viscosities and densities must also be measured and reported with the data.

ZAM model modification

1. Added the Kd value of sodium in the output data

Zheng (1996) and Zheng et al. (1997) have successfully evaluated ion exchange of cesium ion, potassium ion, rubidium ion and sodium ion by TAM 5, the hydrous crystalline silicotitanate, by using data obtained from ion exchange experiments in simple solutions and data obtained from knowledge of the structure of TAM 5. A set of model reactions were also proposed for multicomponent ion exchange of group I metal by TAM 5. Furthermore, these model equations produced good predictions for the equilibrium compositions and the cesium distribution coefficients in highly complex solutions by using Bromley's model for activity coefficients of multicomponent electrolytic solutions.

However, there has been no output data of sodium equilibrium in the program. The Kd value of sodium, which is calculated from the equilibrium model, was added in the output data of the modified ZAM program.

2. The solubility product of KNO_3 as an input data

Zheng² found that the solid phase loadings greater than the total ion exchange capacity of TAM 5 in 1.6 M NaNO_3 step change experiment, which indicates some of the potassium precipitated as a salt. The salt was determined to be a KNO_3 based on the solubility data. The crystallization was

observed only in the solution that contains TAM 5, which was concluded that crystallization of KNO_3 is induced by TAM 5. The solubility product of KNO_3 with TAM 5 was estimated from the potassium isotherm in 1.6 M NaNO_3 . The value was fixed as 0.19 mol/L in the program. This value can be changed with the other factor such as ionic strength, therefore the solubility product of KNO_3 was added in the input file to change the value easily.

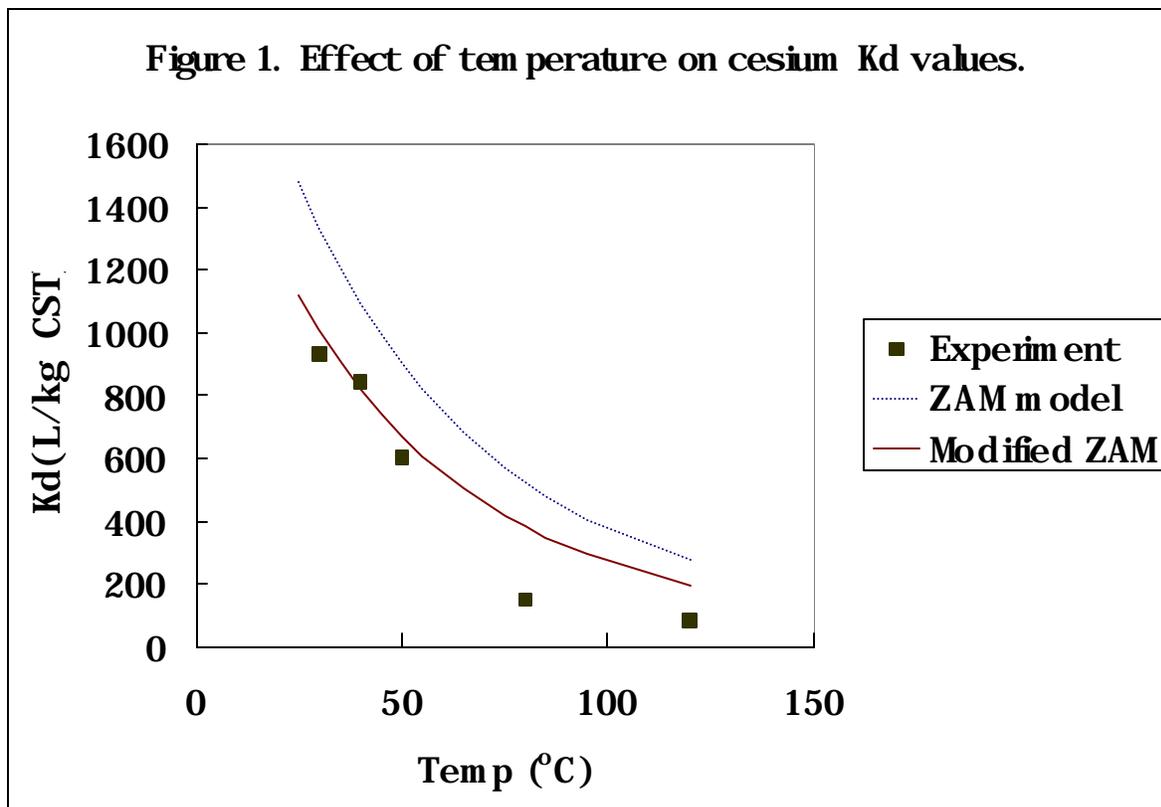
Figure 1. Illustration of the improvement in the ZAM equilibrium model for IE-911 granules.

3. Modification for Cesium Distribution Coefficient to IE-911

The data from Latheef (1999) and Huckman (1999) on IE 911 were used to modify the ion exchange model for the effect of binder. No adjustments were made to the activation energies to modify the effect of temperatures. Data were also taken from Zheng (1996) as needed. After the modification of the parameters in the model, the modified model was used to estimate the data in Table 9, ORNL/TM-1999/233, "Thermal and Chemical Stability of Crystalline Silicotitanate Sorbent," by R. A. Taylor and C. H. Mattus. Figure 1 illustrates the improvement in the predictability of the model. The predictions for distribution coefficients for potassium, rubidium and strontium have not been modified in the revised model.

The model does an excellent job of predicting the distribution coefficients for the average waste simulate as illustrated in Figure 1.

References



- Anthony, R.G., C.V. Philip and R.G. Dosch, "Selective Adsorption and Ion Exchange of Metal Cations and Anions with Silico-Titanates and Layered Titanates," *Waste Management*, **13** (1993) 503-512.
- Anthony, R.G., R.G. Dosch, D. Gu and C.V. Philip, "Use of Silicotitanates for Removing Cesium and Strontium from Defense Waste," *Ind. Eng. Chem. Res.* **33** (1994) 2702-2705.
- Froment, G. F.; Bischoff, K. B. *Chemical Reactor Analysis and Design*, John Wiley & Sons: New York, 1990.
- Gu, D., "Synthesis, Kinetics and Scale-up of TAM-5 and Modified TAM-5 for Use in Radioactive Waste Treatment," Dec. 1994. (This dissertation was released for public access in Dec. 1999).
- Gu, D., L. Nguyen, C. V. Philip, M. E. Huckman, and R. G. Anthony, J.E. Miller and D.E. Trudell, "Cs⁺ Ion Exchange Kinetics in Complex Electrolyte Solutions Using Hydrous Crystalline Silico-Titanates," *Ind. Eng. Chem. Res.* **36**, 5377-5383 (1997).
- Helfferich, F. *Ion Exchange*, McGraw-Hill: New York, 1962.
- Huckman, M.E., "Ion Exchange kinetics of Cs⁺, SrOH⁺ and Rb⁺ for the hydrous crystalline silico-titanates, UOP IONSIV[®] IE911" May, 1999.
- Huckman, M.E., Latheef, I.M., Anthony, R.G., "Ion Exchange of Several Radionuclides on the Hydrous Crystalline Silicotitanates, UOP IONSIV IE-911," *Separation Science and Technology*, 34: (6-7) 1145-1166 (1999)
- Huckman, M.E., Latheef, I.M., and R.G. Anthony, "Designing a Commercial Ion-Exchange Carousel to *AICHE J.*, **47**, #6 (2001) 1425-1431.
- Latheef, Iqbal, "Ion Exchange Column Studies for the Selective Separation of Radionuclides using the Hydrous Crystalline Silicotitanate, UOP IONSIV IE-911," May, 1999.
- Latheef, I.M., M.E. Huckman, R.G. Anthony, "Modeling Cesium Ion Exchange on Fixed-Bed Columns of Crystalline Silicotitanate (CST) Granules," *Industrial and Engineering Chemistry Research*, **39**, 1356-1363 (2000).
- Ruckenstein, E., Vaidyanathan, A. S.; Youngquist, G. R. Sorption by Solids with Bidisperse Pore Structures. *Chem. Eng. Sci.* **1971**, 26, 1305.
- Ruthven, D. M. *Principles of Adsorption and Adsorption Processes*, John Wiley & Sons: New York 1984.
- Ruthven, D. M. and Loughlin, K. F. The Diffusional Resistance of Molecular Sieve Pellets. *Can. J. of*

Chem. Eng. **1972**, *50*, 550.

Zheng, Z., D. Gu and R.G. Anthony, "Estimation of Cesium Ion Exchange Distribution Coefficients for Concentrated Electrolytic Solutions When Using Crystalline Silicotitanates," *Ind. & Eng. Chem. Res.*, **34**, (1995) 2142-2147.

Zheng, Z., C. V. Philip, And R. G. Anthony, "Ion Exchange of Group I Metals by Hydrous Crystalline
Ind. Eng. Chem. Res. **35** (1996) 4246-4256.

Zheng Z., R. G. Anthony and J. E. Miller, "Modeling Multicomponent Ion Exchange Equilibrium Utilizing Hydrous Crystalline Silicotitanates by a Multiple Interactive Ion Exchange Site Model," *Ind. Eng. Chem. Res.* **36**,(1997) 2427-2434.

Zheng, Zhixin (Frank), "Development of Ion Exchange Theory for Predicting the Performance of TAM-5 and Modified TAM-5 for Radioactive Waste Treatment," May 1996.