LBL-25131 c.2

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

EARTH SCIENCES DIVISION

RECEIVED
LAWRENCE
BERKELEY LABORATORY

JUL 6 1988

LIBRARY AND
DOCUMENTS SECTION

To be published as Chapter 22 in **Coupled Processes Associated with Nuclear Waste Repositories**, C.F. Tsang, Ed., Academic Press, Inc., Orlando, FL, 1987

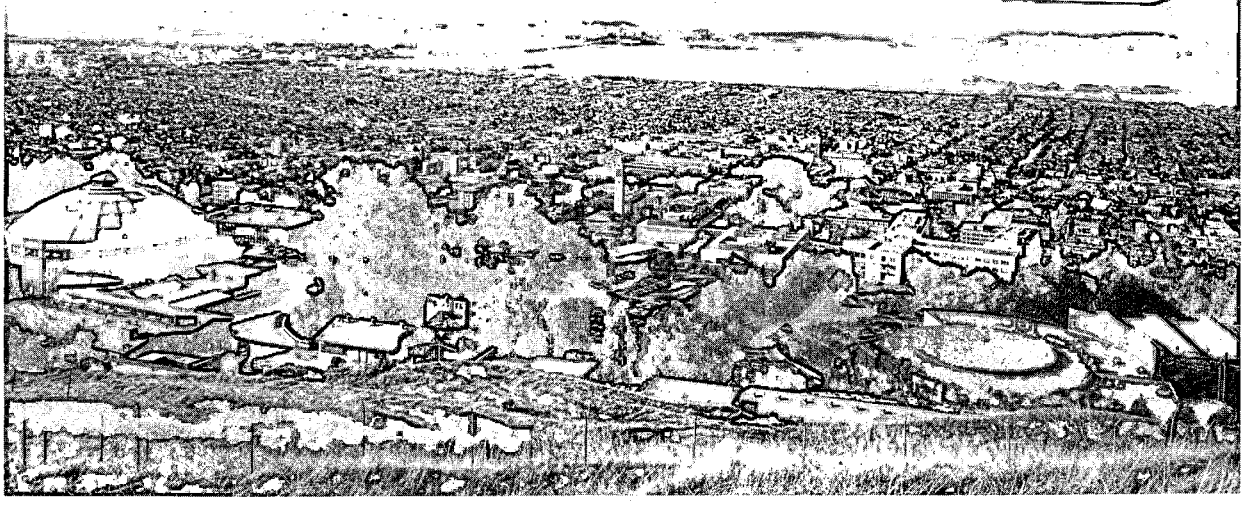
Electrolyte Diffusion in Compacted Montmorillonite Engineered Barriers

F.M. Jahnke and C.J. Radke

April 1986

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks.



LBL-25131 c.2

Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

LBL-25131

Electrolyte Diffusion in Compacted Montmorillonite Engineered Barriers

F.M. Jahnke and C.J. Radke

Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

April 1986

Supported by the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

Electrolyte Diffusion in Compacted Montmorillonite Engineered Barriers.

F. M. Jahnke and C. J. Radke

Chemical Engineering Department
University of California
Berkeley, CA 94720

Abstract

The bentonite-based engineered barrier or packing is a proposed component of several designs conceived to dispose of high-level nuclear waste in geologic repositories. Once radionulcides escape the waste package, they must first diffuse through the highly impermeable clay-rich barrier before they reach the host repository. To determine the effectiveness of the packing as a sorption barrier in the transient release period and as a mass-transfer barrier in the steady release period over the geologic time scales involved in nuclear waste disposal, a fundamental understanding of the diffusion of electrolytes in compacted clays is required. We present, and compare with laboratory data, a model quantifying the diffusion rates of cationic cesium and uncharged tritium in compacted montmorillonite clay. Neutral tritium characterizes the geometry (i.e., tortuosity) of the particulate gel. After accounting for cation exchange, we find that surface diffusion is the dominant mechanism of cation transport, with an approximate surface diffusion coefficient of 2×10^{-6} cm^2/s for cesium. This value increases slightly with increasing background ionic strength.

The implications of this work for the packing as a migration barrier are twofold. During the transient release period, K_d values are of little importance in retarding ion migration. This is because sorption also gives rise to a surface diffusion path, and it is surface diffusion which controls the diffusion rate of highly sorbing cations in compacted montmorillonite. During the steady release period, the presence of surface diffusion leads to a flux through the packing which is greatly enhanced. In either case, if surface diffusion is neglected, the appropriate diffusion coefficient of ions in compacted packing will be in considerable error relative to current design recommendations.

Introduction

High-level nuclear wastes will be stored in underground repositories. To aid the host formation in protecting the biosphere from the harmful, long-lived radioisotopes contained in the waste package, use of an engineered barrier or packing is being considered [6]. This barrier, based upon the clay mineral montmorillonite, is envisaged as an impermeable barrier surrounding the waste canisters which retards the migration of ions in the transient release period due to its high cation exchange capacity [3] and low hydraulic permeability [7]. As time passes and steady-state diffusion through the packing is established, it further serves as a mass-transfer resistance retarding the escape of ions from the canister to the fluid percolating around the waste package. To determine the steady-state plume of radionuclides eminating from the waste repository in the steady-state period and the protection an engineered barrier affords the waste disposal scheme in the transient release period, the diffusion rate of ions in compacted montmorillonite clay must be determined.

In this paper we summarize our findings on the diffusion of cesium chloride and tritium in compacted sodium-montmorillonite clays. Cesium is a representative radioisotope present in the waste form which is particularly toxic for the first few thousand years after the waste is stored. Tritium is used to characterize the geometric structure or tortousity of the swollen clay gel. Our approach is to determine independently the physico-chemical properties which parameterize the diffusion process within compacted packing, and then to compare experimental data with physically-based diffusion models. Only then is it possible to extrapolate with confidence laboratory data to the geologic time scales of nuclear waste disposal.

Theoretical

We visualize the diffusion process as follows. The local ion flux, N_x, is comprised of two parts, one due to pore diffusion and the other due to surface diffusion. These fluxes are additive, so

$$N_x = N_x^{\infty} + N_x^{\sigma} . \tag{1}$$

If the concentration of the diffusing ion is small relative to the background electrolyte concentration, the pore fluid and clay surface are in local equilibrium, and all ions are sorbed in the Stern layer, then each flux is described by Fick's first law. Thus,

$$N_x^{\infty} = -\frac{D_{\infty}}{\tau^2}\frac{\partial c}{\partial x} \tag{2}$$

and

$$N_x^{\sigma} = -\frac{1-\epsilon}{\epsilon}\frac{D_s}{\tau_s^2}\frac{\partial n}{\partial x} . \tag{3}$$

Here, ϵ is the porosity of the clay gel, D_{∞} and D_s are the molecular and surface diffusion coefficients, respectively, and n is the adsorption on the clay surface. τ^2 and τ_s^2 are the tortuosity of the pore and the surface paths. D_s has units identical to a bulk diffusion coefficient (cm^2/s), and n has units of a concentration (moles/solution volume). Invoking local equilibrium, we have

$$\frac{\partial n}{\partial x} = \frac{dn}{dc}\frac{\partial c}{\partial x} ,$$

where $\frac{dn}{dc}$ is the slope of the equilibrium ion-exchange isotherm. If we further assume that the pore and surface paths are identical, $\tau^2 = \tau_s^2$. Hence, by inserting the flux expressions (2) and (3) into Equation (1), we find

$$N_x = -D\frac{\partial c}{\partial x} , \tag{4}$$

where

$$D = \frac{D_{\infty}}{\tau^2}\left[1+\frac{1-\epsilon}{\epsilon}\frac{dn}{dc}\frac{D_s}{D_{\infty}}\right] . \tag{5}$$

For surface diffusion to be significant, we must have the far right term in the brackets of Equation (5) be of order unity, or

$$\frac{1-\epsilon}{\epsilon}\frac{dn}{dc}\frac{D_s}{D_{\infty}} = O(1) .$$

In the Henry's law region of the isotherm, the slope $\frac{dn}{dc}$ is typically large for cations contained in the waste package [10]. The validity of the assumptions listed above for ions and conditions expected in a nuclear waste repository is good. For details refer to Jahnke [4].

To relate the local flux to macroscopically measurable quantities, we write the mass balance as

$$\frac{\partial c}{\partial t}+\frac{1-\epsilon}{\epsilon}\frac{\partial n}{\partial t} = \left[1+\frac{1-\epsilon}{\epsilon}\frac{dn}{dc}\right]\frac{\partial c}{\partial t} = -\frac{\partial N_x}{\partial x} . \tag{6}$$

Here we have made the additional assumption that the gel is homogeneous and hence that diffusion is one-dimensional. That is, all structural information relevent to axial ion diffusion is contained in the tortuosity, which does not vary spacially in a macroscopic sense. Thus, inserting Equation (4) into Equation (6), we obtain Fick's second law of diffusion,

$$\frac{\partial c}{\partial t} = D_e\frac{\partial^2 c}{\partial x^2} . \tag{7}$$

This defines the effective diffusion coefficient D_e of ions in the swollen clay gel as

$$D_e = \frac{D_{\infty}}{\tau^2}\left[\frac{1+\frac{1-\epsilon}{\epsilon}K_d\rho_s\frac{D_s}{D_{\infty}}}{1+\frac{1-\epsilon}{\epsilon}K_d\rho_s}\right] \equiv \frac{D}{\alpha} \tag{8}$$

where we have replaced $\frac{dn}{dc}$ by the Henry's law slope, $K_d \rho_s$. K_d is the distribution coefficient used commonly in the nuclear waste disposal field [6], and ρ_s is the density of the clay. We further separate D_e into its components: D, from Equation (5) and α ($= 1+\frac{1-\epsilon}{\epsilon}K_d\rho_s$), the retardation coefficient [6] from the Equation (6). We see that ion adsorption on the clay surface, in the absence of surface diffusion, reduces the effective diffusion coefficient from its molecular value. Indeed, this is a primary motivation for the bentonite-based, engineered-barrier concept. If the surface diffusion coefficient is nonzero, the effective diffusion coefficient increases. We will return to this point below.

To determine if Equation (3) describes correctly the diffusion of ions in compacted clays, we must determine:

1. the ion-exchange isotherm,
2. the molecular diffusion coefficient,
3. the tortuosity of the medium, and
4. the surface diffusion coefficient.

The experimental determination of these parameters is described in the following section.

Experimental

Soudek [11] has measured the adsorption isotherm of uni- and divalent cations on disaggregated sodium montmorillonite clay in batch experiments. K_d values for cesium and strontium as a function of ionic strength are shown in Table 1 below. Observe that K_d varies by about one order of magnitude for each order of magnitude change in the background ionic strength.

Table 1: Measured K_d values for cesium and strontium on sodium montmorillonite at 22° C [11]. K_d in cm^3/g.

Ion	Background NaCl (M)		
	10^{-3}	10^{-2}	10^{-1}
Cs	6700	850	150
Sr	1.8×10^5	1.9×10^4	380

The ion-exchange equilibria were interpreted using an extension of the site-binding model of Davies, James and Leckie [1]. This model predicted correctly the effect of ionic strength on ion sorption, as well as multi-ion sorption. It shows further that the majority of the adsorbed cations are found in the Stern layer, as we assumed above.

The molecular diffusion coefficient was obtained by converting the limiting ionic mobility of cesium to a diffusion coefficient, using values from Robinson and Stokes [9]. We find $D_\infty=2\times10^{-5}$ cm^2/s. The tortuosity and dynamic concentration determinations were measured using a radially perfused diffusion cell developed in this laboratory. It is described here briefly; the interested reader is referred to Jahnke and Radke [5] for details.

The configuration of the diffusion cell is shown in Figure 1 (all figures are at the end of the paper). The clay gel G, initially devoid of solute, is confined below by a piston P and above by N, a Nuclepore membrane with pore size sufficiently small to confine the individual clay particles. The fragile Nuclepore membrane is supported by a sintered metal disk SD, which is in turn confined by the top of the apparatus. The ion whose diffusion behavior is being studied is initially contained in a well-stirred solute chamber, which is not shown in the figure. At $t=0$ the fluid is pumped from the solute chamber through the sintered metal disk and returned. As liquid flows through the sintered disk, ions diffuse from the convecting liquid through the Nuclepore membrane and into the clay gel. Special care is taken to assure that the mass transfer coefficient of the cell is sufficiently high that the diffusion data measured are not obfuscated by artifacts of the experimental design [5].

As the experiment proceeds, ions deplete from the solute chamber and a concentration profile develops in the gel. The solute chamber is sampled intermittantly to determine its concentration history. At the conclusion of an experiment, the diffusion cell is disassembled, and the gel is incrementally extruded, sectioned, and analyzed to determine the final concentration profile in the gel. It can be shown [4] that the effects of diffusion and sorption within the clay gel are decoupled by this experimental

procedure. This allows us to determine D and α uniquely, since we have equations describing the tank depletion and the gel profile, and two unknowns, D and α.

Since the tortuosity is governed by the geometry of the clay particles at a given compaction, we choose to measure τ^2 in the diffusion cell. To eliminate the effects of sorption (and hence surface diffusion), we measure the diffusion of neutral tritium [8]. Any deviation from its molecular diffusion coefficient is then due to the tortuosity of the clay gel. For a 16 w/o gel, we find the tortuosity to be about 4.

The surface diffusion coefficient can not be predicted *a priori*. It must be determined as a parameter fit to "anomolous" or enhanced diffusion or electrical conductivity data [2].

Results and Discussion

Typical experimental results are shown in Figures 2 and 3. Here, cesium is diffusing into a 16 w/o sodium-montmorillonite clay gel with a 10^{-2} M sodium chloride background electrolyte. Figure 2 plots the concentration in the solute chamber as a function of time. Data are indicated by the solid circles. Figure 3 shows the total concentration in the clay gel at the completion of the experiment against nondimensional distance. Data are denoted by the solid steps. Dashed lines in Figures 2 and 3 indicate the *a priori* prediction using the parameters determined above, neglecting surface diffusion. Notice that the uptake and the penetration of ions into the gel is severely underpredicted if surface diffusion is neglected. Solid lines are the best fit to the data. The value of α is predetermined from the measured isotherm and porosity. The best fit of the data gives $D = 2.8\times10^{-4}$ cm^2/s. Using Equation (5), we recover $D_s = 2\times10^{-6}$ cm^2/sec, or $D_s/D_\infty = 0.1$. Also observe that α scales the ordinate of Figure 3. That the data fit well with α predetermined is strong evidence that our physical picture of the diffusion process is correct.

As mentioned above, K_d depends strongly on the background ionic strength. Thus, varying the background ionic strength is a severe test of the surface diffusion model, since both the retardation coefficient α and the diffusion coefficient D change drastically. Figure 4 below shows the ionic strength dependence of the surface diffusion coefficient. Observe that D_s is nearly constant with ionic strength; the slight increase of D_s with ionic strength has been observed by others [2]. This evidence is conclusive: the existence of surface diffusion is real, and for cesium, is the major mode of ion migration in montmorillonite.

We note that in our experiments, the porosity of the clay gels studied is low ($\approx$0.92), and that waste repositories are expected to have much more highly compacted clays [7]. The impact of surface diffusion on the expected performance of a clay-based engineered barrier is discussed in the following section.

Ramifications

In the unsteady release period, the effective diffusion coefficient is given by Equation (7). If we note from Table 1 that at repository conditions, $K_d\rho_s$ values are large (>2000), that the porosity expected in the engineered barrier is about 0.50 [7], and that $\frac{D_s}{D_\infty}$ is typically 0.1 for cations [2], the effective diffusion coefficient takes the form

$$D_e = \frac{D_s}{\tau^2}.$$

No retardation coefficient appears in this expression. By providing a parallel path for cation migration, sorption does not reduce the effective diffusion coefficient within compacted packing much at all. This implies that K_d values are irrelevant during the transient release period. That is, we do not anticipate large reductions in transient ion migration rates due to sorption retardation on montmorillonite. Rather, as an approximation for the diffusion coefficient of ions in compacted packing, we use $\tau^2 = 10$ [8] and we calculate that

$$\frac{D_e}{D_\infty} \approx 10^{-2};$$

a fixed two order of magnitude reduction from the molecular diffusion coefficient.

In the steady release period, the effective cation diffusion D_e in Equation (8) coefficient no longer applies. The effect of packing as a mass-transfer barrier is now governed by the flux depicted in Equation (4). Hence, the packing resistance to migrating cations is proportional to D and not to D_e. Given a gel porosity of 0.5 and a tortuosity of 10, as above, and for highly sorbing cations, we find that

$$D \approx 0.1 K_d \rho_s D_s \ . \qquad (9)$$

Thus, K_d values are of extreme importance during the steady release period. Counter to what may have been anticipated, larger K_d values lead to higher release rates.

In both the unsteady and steady release periods, the deviation in currently predicted repository performance due to cation surface diffusion is identical and towards a diffusion coefficient that is dramatically in excess of accepted estimates. Surface diffusion of cations in a bentonite-based packing reduces its effectiveness. This does not imply that packing is ineffective in the waste disposal scheme. Montmorillonite clay is known to influence the oxidation potential, or Eh, near the canister and aid in radionuclide precipitation. Transport rates of precipitated colloidal material through bentonite should be nil. Smectite clay also can impede ground water imbibition up to the canister. Finally, and most importantly, the hydraulic impermeability of montmorillonite to bulk water flow can extend the integrity of the waste package.

If the surface mobility of cesium and other radionuclides found in the waste package is comparable, we caution that neglect of cation surface diffusion will result in a predicted packing performance which overestimates the actual protection such a barrier affords. As a corollary, we recommend that careful measurements of cation diffusion rates be made under realistic repository environments to assess the quantitative role of surface diffusion.

Acknowledgments: This work was supported by the United States Nuclear Regulatory Commission under interagency agreement DOE-50-80-97 through contract DE-AC03-76-SF00098 to the Lawrence Berkeley Laboratory.

References

1. Davies, J. A., James, R. O., and Leckie, J. O., "Surface Ionization at the Oxide/Water Interface," *J. Coll. Int. Sci.*, vol. 63, no. 3, p. 480, 1978.
2. Gast, R. G., "Applicablilty of Models to Predict Rates of Cation Movement in Clays," *Soil Sci. Soc. Amer. Proc.*, vol. 30, p. 48, 1966.
3. Grim, R. E., *Clay Mineralogy, Second Edition*, McGraw-Hill, New York, 1968.
4. Jahnke, F. M., "The Diffusion of Ion-Exchanging Electrolytes in Compacted Montmorillonite Clays," *Ph.D. Thesis*, University of California, Berkeley, 1986.
5. Jahnke, F. M. and Radke, C. J., "A Radially Perfused Cell for Diffusion in Compacted, Sorbing Systems," *submitted to Chem. Eng. Sci*, 1986.
6. Panel, Waste Isolation Systems, *A Study of the Isolation of Geologic Disposal of Radioactive Wastes*, Nat. Acad. Press, Washington, DC, 1983.
7. Pusch, R., "Highly Compacted Sodium Bentonite for Isolating Rock-Deposited Radioactive Waste," *Nuclear Tech.*, vol. 45, p. 153, 1979.
8. Relyea, J. F., Trott, D. P., McIntyre, C. V., and Rieger, C. G., "Diffusion of Tritium and Chloride in Basalt-Bentonite Mixtures.," RHO-BW-SA-431 P, Rockwell Hanford Operations, Richland, WA, 1985.
9. Robinson, R. A. and Stokes, R. H., *Electrolyte Solutions, Second Edition*, Academic Press, New York, 1959.
10. Serne, R. J., Rai, D., and Relyea, J. F., "Preliminary Results on Comparison of Adsorption-Desorption Methods and Statistical Techniques to Generate K_d Predictor Equations," U.S. DOE Report PNL-SA-7352, 1979.
11. Soudek, A., "Binary and Ternary Ion Exchange on Sodium Montmorillonite for Application to Backfill in Nuclear Waste Disposal," *M.S. Thesis*, University of California, Berkeley, 1984.

LAWRENCE BERKELEY LABORATORY
TECHNICAL INFORMATION DEPARTMENT
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720