

Lawrence Berkeley National Laboratory

Recent Work

Title

TOWARDS A COMPREHENSIVE MODEL OF CHEMICAL TRANSPORT IN POROUS MEDIA

Permalink

<https://escholarship.org/uc/item/1sq2z9bv>

Author

Miller, C.W.

Publication Date

1982-06-01

c.2



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

RECEIVED
LAWRENCE
BERKELEY LABORATORY

EARTH SCIENCES DIVISION

JUN 15 1982

LIBRARY AND
DOCUMENTS SECTION

Submitted for Oral Presentation at Materials
Research Society 1982 Annual Meeting, Symposium D:
Scientific Basis for Nuclear Waste Management,
Boston, MA, November 1-4, 1982

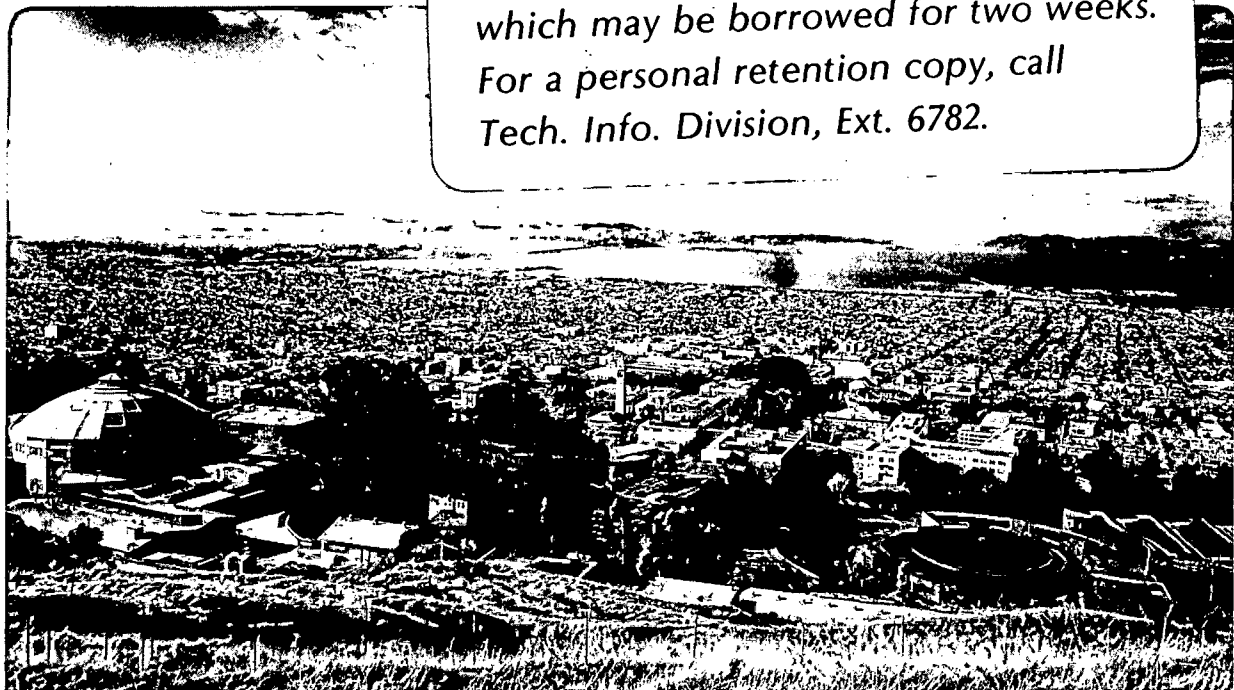
TOWARDS A COMPREHENSIVE MODEL OF CHEMICAL
TRANSPORT IN POROUS MEDIA

Constance W. Miller

June 1982

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 6782.*



LBL-14604
c.2

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.

ABSTRACT

TOWARDS A COMPREHENSIVE MODEL OF CHEMICAL TRANSPORT IN POROUS MEDIA.

Constance W. Miller, Earth Sciences Division, Lawrence Berkeley Laboratory,
University of California, Berkeley, California 94720.

A chemical transport model that includes dispersion/diffusion, convection, complexation, sorption, and precipitation has been written. The sorption process is modelled by an ion exchange mechanism except it is possible to consider the electric double layer in this process when it is important. Chemical equilibrium is assumed so mass action equations are written for each reaction. In addition a mass conservation equation is written for each species as well as a site constraint on the number of sorption sites. This set of equations are expressed in a Differential/Algebraic form and the equations are solved simultaneously. The solution procedure described is flexible enough that time dependent boundary conditions can be considered and that different chemical mechanisms as non-equilibrium kinetics can be included. The model is used to investigate the applicability of a K_D model to describe sorption, to determine the importance of precipitation when a waste form as $SrCO_3$ comes in contact with the groundwater, the effect of including the electric double layer concept in sorption, and the sensitivity of the parameters as equilibrium coefficients and dispersion coefficients needed in chemical transport calculations of radionuclide transport through engineered barriers.

Constance W. Miller
Bldg. 50A Rm. 1136
Lawrence Berkeley Laboratory
1 Cyclotron Rd.
Berkeley, CA 94720

TOWARDS A COMPREHENSIVE MODEL OF
CHEMICAL TRANSPORT IN POROUS MEDIA

Constance W. Miller
Earth Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

To simulate the migration of chemical species in porous media, a numerical model CHEMTRN has been developed. The model includes convection, dispersion/diffusion, formation of complexes in the aqueous phase, sorption of bare ions and complexes on the solid matrix, and precipitation of solids. The sorption process is modelled by an ion exchange mechanism, but an option of including the electric double layer concept in this process has been provided. At present, chemical equilibrium is assumed to exist at every point in the porous medium. Therefore, given an equilibrium coefficient for each reaction or sorption process, a mass action equation can be written. In addition to these mass action equations, a mass conservation equation of the form

$$\frac{\partial W_j}{\partial t} + \frac{\partial \bar{m}_j}{\partial t} + \frac{\partial p_j}{\partial t} \left(\frac{D \partial^2}{\partial x^2} - \frac{v \partial}{\partial x} \right) W_j \quad (1)$$

can be written for each species j , where W_j is the total concentration of species j in the aqueous phase (both in the bare ion and complex state), \bar{m}_j is the concentration of sorbed species j , p_j is the amount of precipitate with species j , D is the dispersion/diffusion coefficient, and v is the fluid velocity. All concentrations are written as moles/liter solution. To complete the set of equations, the total number of sorption sites is kept constant. Most existing chemical models do not include all of the above chemical effects and even these models tend to solve the set of equations in a two step procedure as Grove and Wood (1979) or Walsh, et al (1982). First the transport equations are solved assuming either an approximation for the chemical reactions, such as a K_D model for the sorption process, or no reactions at all, then the species are allowed to re-equilibriate. Existing chemical equilibrium packages can be adapted in this manner to solve transport problems. However, CHEMTRN solves the transport and mass action equations simultaneously, although the precipitation is still handled in a two step fashion at present. Rubin and James, (1973) and Valocchi (1981) do solve the mass transport and mass action equations simultaneously. However, they both neglect complexation, and have simple ion exchange models for sorption. Rubin and James do consider a simple precipitation problem but the precipitate exists throughout the porous medium.

If the mass action equations are finite differenced in space then a set of ordinary differential equations results. When these equations are combined with mass action equations and the sorption site constraint equation, we now have a set of differential algebraic equations (DAE's).

These equations fit the form

$$A(m,t) \frac{dm}{dt} + F(m,t) = 0 \quad (2)$$

where m is the set of unknowns, i.e. bare ions, complexes, sorbed bare ions, and sorbed complexes. The important point as shown by Kee and Miller, 1981, who used this approach to solve chemically reacting boundary layers, the matrix A can be non singular which will be the case when the mass action equations are written in this form. The system of equations are solved using a Newton-Raphson iteration technique where dm/dt is approximated as $(m^{l+1} - m^l)/\Delta t$. More elaborate DAE solvers that use several time steps are available but it would be difficult for them to handle precipitation since the number of equations change every time a new precipitate forms. By only using two time levels, a precipitation model can be included either by re-equilibrating at every node point when the solubility constraint is exceeded (done at present) or by solving the increased number of equations at node points where precipitates form. The Newton-Raphson method solves the set of equations by first guessing the new values of the unknowns, calculating the residue, R_j , of the equations for the guess, and then obtaining a new guess by using the Jacobian, $\partial R/\partial m$, to predict it. As the matrix A is never inverted, it can be singular. New chemical mechanisms can be handled by simply calculating the residue of these new equations. The calculation of the Jacobian is done numerically so no change is necessary here. Boundary conditions can also be expressed in the form of equation (2) allowing the solution of time dependent boundary conditions.

The model can be used to investigate transport of radionuclides through engineered barriers. A less comprehensive model was used to study the transport of strontium through a porous medium (Miller and Benson, 1982). From these calculations, it was shown that the method of using a constant K_D model to express the sorption of a species as $K_D m_j$ is not always appropriate as the competition for sites on the solid matrix makes the sorption of a bare ion or complex a function of the other sorbing ions. Also the addition of the chemical waste reacts with the ground water altering its pH and changing the transport of chemical species.

The attached figure shows the calculation for the precipitate (CaCO_3) when strontium carbonate is placed at $x=0$. Only the Ca^{2+} and CO_3^{2-} bare ion concentrations are included in the figure but species Na, Sr, H with various complexes were included in the calculation. As the Ca^{2+} ion is displaced from the solid, it reacts with the increased CO_3^{2-} concentration resulting in the precipitation of CaCO_3 . The concentration of CaCO_3 plotted is the number of moles/liter solution of Ca^{2+} and CO_3^{2-} that were used to form this precipitate. Plots of these concentrations are given for 2, 7, and 15 years. (The change in Ca^{2+} is small over this time on the plot so only 1 line is drawn). Additional calculations of the effect of precipitation will be shown as well as the effect of considering the electric double layer concept in sorption, and the sensitivity of the data i.e. equilibrium constants, dispersion coefficients, etc. needed to study the chemical transport away from waste canisters.

References

Grove, D.B. and Wood, W.W., Groundwater 17 (13), p.250-257, 1979

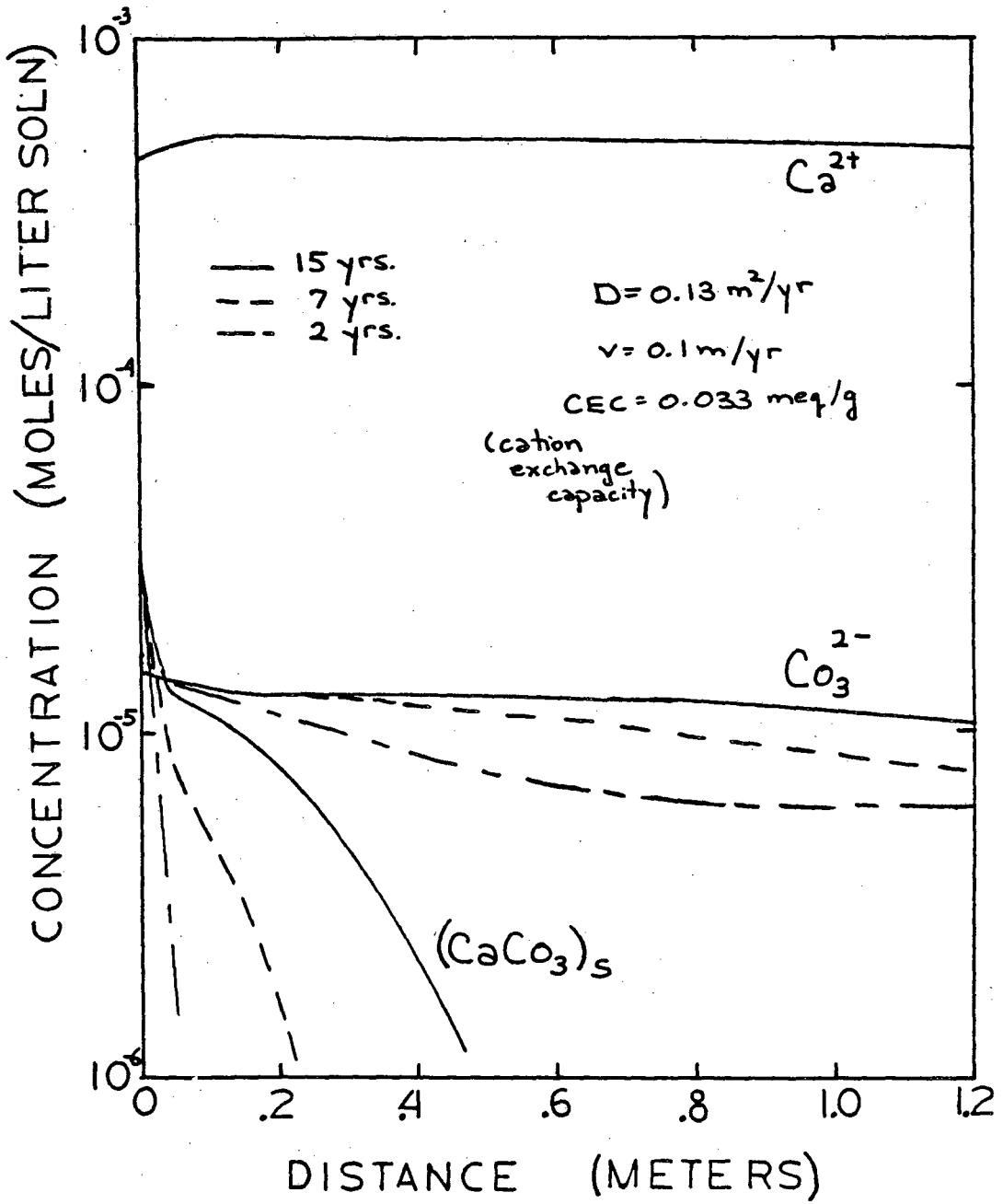
Kee, R.J. and Miller, J.A., Sandia Report #SAND81-8241, Sandia National Laboratories, Livermore, CA

Miller, C.W. and Benson, L.V., LBL report #13828, Lawrence Berkeley Laboratory, submitted for publication to Water Resources Res.

Rubin, J. and James, P. V., Water Resources Res. 9, p. 1332-1356, 1973

Valocchi, A.J., Street, R.L. and Roberts, P.V., Water Resources Res., 17, p. 1517-1527, 1981

Walsh, M.P., Lake, L.W. and Schechter, R.S., SPE #10625, presented at the 1982 SPE International Symposium on Oilfield and Geothermal Chemistry, Dallas, Tx



This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

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