

THEORETICAL STUDY ON THE MIGRATION PHENOMENA OF A CHELATED RADIONUCLIDE IN A POROUS MEDIUM

Min Hoon Baik and Kun Jai Lee
Dept. of Nuclear Engineering
Korea Advanced Institute of Science and Technology
373-1, GuSung-Dong, YuSung-Gu, TacJon, KOREA

ABSTRACT

A model was developed in order to investigate the effects of chelating agents on the migration of a radionuclide where it might be ionic or chelated forms. The migration behavior of the chelated radionuclide was analyzed by formulating an advective-dispersion transport equation which included a degradation of the chelating agent and chelated radionuclide. This mathematical model was solved by an analytic method and analyzed by examining retardation factor, numerical example, and sensitivity analysis of the important parameters. The calculated results from the model showed that the migration of the chelated radionuclide was much faster than the ionic radionuclide and this was due to the decreased retardation. The sensitivity analysis of the developed model for the major parameters (e.g., chelate formation constant and distribution coefficients of free radionuclide and chelated radionuclide) showed that all the parameters were important in the migration behavior of the chelated radionuclide. In particular, the adsorption of the chelated radionuclide was more important than the other parameters. Therefore, it was concluded that a new remedial action should be developed to reduce the generation and release of chelating agents from the nuclear power plant into the environmentals.

INTRODUCTION

A wide range of chemical and physico-chemical reactions can be considered to influence the migration phenomena of radionuclides of various forms in geological radioactive waste disposal sites. The possible reactions may be radioactive decay, sorption, precipitation, dissolution, filtration, degradations, hydrolysis, complexation, and colloid formation. However, an urgent need for information has led to research on relatively limited aspect of these complex problem and a tendency to oversimplify the simulation of natural conditions. It has been within only the past decade that the important effects of organic substances on the environmental geochemistry of trace metals have truly been recognized.

Also it has been stated (1) that complex formation of radionuclides with complexing agents found in ground water significantly influenced the migration behavior of the radionuclides. Because it forms extremely strong complexes with rare earths and actinides, ethylenediaminetetraacetic acid (EDTA) or similar chelating agents may also be contributing to the mobilization of these radionuclides from various terrestrial radioactive waste burial sites. The organic materials can be found in ground water in radioactive waste repository (specially in low level radioactive waste repository) such two categories as natural (e.g., humic or fulvic substances) and synthetic (e.g., decontamination agents such as EDTA, citric acid and picolinic acid) organics (2). The most abundant and important natural organic material is humic substances, which is consisted of humic acid and fulvic acid (3). Synthetic organic compounds such as EDTA, which is used in nuclear decontamination solutions increase radionuclide transport rate in at least two different low-level waste burial ground. Means et al. (1) identified the importance of synthetic chelating agents in the transport of Co-60 in low-level repositories. Cleveland and Rees (4) discovered similar migration Pu-chelate complexes in Maxey Flat trench leachates.

In order to analytically predict the transport of radionuclides in a porous medium which is affected by the presence of complexing agents, it is necessary to develop a complete

mathematical model. This means that the mechanisms must be described and the governing equation derived, along with their general solutions for the transport processes. In this study, the five mechanisms of advection, dispersion, adsorption, chelation, and degradation are described and mathematically modeled. A general advective-dispersion transport equation is used to predict the migration of radionuclides in the presence of chelating agents in a porous medium.

TRANSPORT MECHANISMS

Adsorption

If the isotherm is linear and reversible, the isotherm is uniquely defined by a distribution coefficient, K_d , which is constant and equal to the slope of the isotherm. Several investigators (6,7) have measured linear isotherms for adsorption of nonionic organic solutes onto soils, sediments, and aquifer materials. These isotherms may be described by:

$$S = K_d \cdot C \quad (\text{Eq. 1})$$

where S is contaminant concentration in the adsorbed solid phase (moles/Kg) C is contaminant concentration in the solution phase (moles/m³) and K_d is the distribution coefficient (m³/Kg).

The retardation factor, accompanied by the linear isotherm presented by distribution coefficient of Eq. (1), can be obtained as follows:

$$R = 1 + \frac{(1-\theta)\rho_b}{\theta} K_d \quad (\text{Eq. 2})$$

where θ is the porosity of the porous medium and ρ_b is the bulk density of the porous medium (Kg/m³).

Chelate Formation

For the expression of chelate formation, we introduce the conditional stability constant as an equilibrium constant for the chelate formation reaction. Ringbom (8) has used this to calculate the influence of a whole series of side reaction other than main complex formation reaction. He introduced the

term "conditional constant" in order to stress that the constant is not constant but depends on the experimental conditions. The general form of the overall conditional stability constant for a mononuclear complex (i.e., chelate) is given as follows (9):

$$\beta_n = \frac{[ML_n]}{[M'] [L']^n} \quad (\text{Eq. 3})$$

where $[M']$ is the apparent free metal ion concentration, i.e., the concentration of radionuclide ion that has not chelated. Similarly, $[L']$ is the apparent ligand concentration, i.e., the concentration of the ligand not bound to the central ion M, whether L is in protonated or non-protonated form, or in the form of complexes with other radionuclide ions. And n is the average number of ligands per radionuclide ion. Typically the ligand concentration will be significantly greater than the radionuclide ions. Hence the ligand concentration, $[L']$, can be approximated by the initial loading ligand concentration, $[L_0]$.

Using the conditional stability constant concept we can find the relationships between the concentrations of chelated and ionic radionuclides given as follows:

$$\frac{[ML_n]}{[M']} = \beta_n [L_0]^n = K_M \quad (\text{Eq. 4})$$

where K_M is the apparent stability constant of the chelate.

Degradation

Degradation of chelating agents are important factor in predicting the fate of a chelating agents in the environment. The degradation of chelating agents includes several types of degradation mechanisms such as biological, photolytic, radiolytic, chemical, and thermal degradations. Detailed explanation is presented by other studies (10, 11, 12).

To model the degradation of the chelating agent, a first-order kinetic model is also used.

$$\frac{dL}{dt} = -k_{dc} L \quad (\text{Eq. 5})$$

where, L is the concentration of the chelating agents (moles/m³) and k_{dc} is degradation rate constant of chelating agents (1/yr).

ANALYSIS

Governing Equation

Consider a radioactive solute as a free metal ion in pore water in porous soil medium. Also present in porous medium is chelating agent, on which an ionic radionuclide can form chelate with the chelating agent. We assume the one-dimensional convection-diffusive transport within the porous medium for the ionic radionuclide and chelated radionuclide. A number of assumptions are made as follows.

1. Initially, a radionuclides is dissolved as an ionic and a chelated form in the groundwater in a porous medium.
2. The groundwater flows through the medium at a constant rate, in one direction.
3. The groundwater and the medium are incompressible.

4. The medium is saturated, isotropic, and homogeneous. Hence interaction between the medium and the dissolved radionuclide is the same throughout the considered system, and the dispersivity is also constant.

The equation governing the transport of ionic radionuclide is given as follows:

$$\frac{\partial}{\partial x} \left(C_1 + \frac{(1-\theta)\rho_b}{\theta} S_1 \right) = D_1 \frac{\partial^2 C_1}{\partial x^2} - V_1 \frac{\partial C_1}{\partial x} - \lambda_1 \left(C_1 + \frac{(1-\theta)\rho_b}{\theta} S_1 \right) \quad (\text{Eq. 6})$$

$$x > 0, t > 0.$$

where C_1 is the concentration of an ionic radionuclide in the pore water solution phase (moles/m³), S_1 is the concentration of an ionic radionuclide in the solid phase (moles/Kg), D_1 is the dispersion coefficient of ionic radionuclide in porous medium (m²/yr), V_1 is the average pore water velocity in porous medium (m/yr), λ_1 is decay constant of ionic radionuclide (1/yr), x is distance (m), and t is time (year).

For the same species as a chelate, the governing equation is given as follows:

$$\frac{\partial}{\partial x} \left(C_2 + \frac{(1-\theta)\rho_b}{\theta} S_2 \right) = D_2 \frac{\partial^2 C_2}{\partial x^2} - V_2 \frac{\partial C_2}{\partial x} - (\lambda_2 + k_{dc}) \left(C_2 + \frac{(1-\theta)\rho_b}{\theta} S_2 \right) \quad (\text{Eq. 7})$$

$$x > 0, t > 0.$$

where k_{dc} is the degradation coefficient of the chelated radionuclides in pore water (1/yr) and all the subscripts except k_{dc} in Eq. (6) are replaced by 2 in this equation for the chelate. We assume linear adsorption equilibrium between the ionic radionuclide species in liquid and the same species adsorbed onto the solid.

Also, the chelates both in liquid and solid are assumed to undergo linear adsorption equilibrium and given as follows:

$$K_{d1} = \frac{S_1}{C_1}, K_{d2} = \frac{S_2}{C_2} \quad (\text{Eq. 8})$$

where K_{d1} is the distribution coefficient of the ionic radionuclide and K_{d2} is the distribution coefficient of the chelated radionuclide.

For the expression of the relationship between the concentration of the ionic radionuclide and chelated radionuclide in the solution (i.e., relationship of C_1 and C_2), Eq. (4) is used and K_M is assumed to be constant.

$$C_2 = \beta_n [L_0]^n C_1 = K_M C_1 \quad (\text{Eq. 9})$$

where K_M means the mole ratio of the ionic radionuclide to the chelated radionuclide in the solution.

Adding Eqs. (6) and (7), we can obtain the equation for in terms of the effective retardation factor R , effective dispersion coefficient D , effective velocity V , and effective total

degradation constant K_{dc} . Then overall governing equation can be given as follows:

$$R \frac{\partial C_2}{\partial t} = D \frac{\partial^2 C_2}{\partial x^2} - V' \frac{\partial C_2}{\partial x} - K_{dc} C_2 \tag{Eq. 10}$$

where

$$R = \frac{R_1}{K_M} + R_2 \tag{Eq. 11}$$

$$D = \frac{D_1}{K_M} + D_2 \tag{Eq. 12}$$

$$V' = \frac{(K_M + 1)}{K_M} V_1 \tag{Eq. 13}$$

since $V_1 = V_2$, and

$$K_{dc} = R\lambda_1 + R_2 k_{dc} \tag{Eq. 14}$$

since $\lambda_1 = \lambda_2$.

In the above equations, the effective retardation factor R , effective dispersion coefficient D , effective velocity V , and effective total degradation constant K_{dc} are given as complex forms incorporating the term for the ionic radionuclide and the term for the chelated radionuclide. K_M acts as a weighting factor controlling the relative importance of one of two terms in the complexed parameters.

Similarly, for C_1 , the major parameters are also given as follows:

$$R' = R_1 + K_M R_2 \tag{Eq. 15}$$

$$D' = D_1 + K_M D_2 \tag{Eq. 16}$$

$$V' = (1 + K_M) V_1 \tag{Eq. 17}$$

$$K_{dc}' = R'\lambda_1 + R_2 K_M k_{dc} \tag{Eq. 18}$$

Solution of the Equation

The initial condition at $t = 0$ is given as follows

$$C_1 = C_2 = 0 \text{ at } x \geq 0 \tag{Eq. 19}$$

The boundary conditions based upon the assumption of semi-infinite medium is given as follows:

$$\frac{\partial C_1}{\partial x} = \frac{\partial C_2}{\partial x} = 0 \text{ at } x \rightarrow \infty, t > 0 \tag{Eq. 20}$$

$$\left[-D \frac{\partial C_1}{\partial x} + VC_1 \right] = VC_{10} \text{ at } x = 0, t > 0 \tag{Eq. 21a}$$

$$\left[-D \frac{\partial C_2}{\partial x} + VC_2 \right] = VC_{20} \text{ at } x = 0, t > 0 \tag{Eq. 21b}$$

where C_{10} and C_{20} are the initial concentrations of ionic radionuclide and chelated radionuclide in the solution, respectively.

For a more detailed analysis of the source term conditions, two cases can be considered. In the absence of chelating agents, a dissolved radionuclide as only an ionic form are released at constant concentration C_s , i.e.,

$$C = C_s \text{ at } x = 0, t > 0 \tag{Eq. 22}$$

However, in the presence of chelating agents, the dissolved radionuclide is released as both of ionic and chelated forms at constant concentration C_0 , i.e.,

$$C_0 = C_{10} + C_{20} = \left(\frac{K_M + 1}{K_M} \right) C_{20} \tag{Eq. 23}$$

The governing equation for C_2 , Eq. (10), subject to the conditions Eqs. (20) and (21) is solved by the analytic method presented by van Genuchten et. al. (13) and given as follows:

$$\begin{aligned} \frac{C_2(x,t)}{C_0} = & \frac{V}{V + \beta} \exp\left[\frac{x(V - \beta)}{2D} \right] \operatorname{erfc}\left[\frac{Rx - \beta t}{2(DRt)^{1/2}} \right] \\ & + \frac{V}{V - \beta} \exp\left[\frac{Vx}{D} - K_{dc}t \right] \operatorname{erfc}\left[\frac{Rx - \beta t}{2(DRt)^{1/2}} \right] \\ & + \frac{V^2}{2DRt} \exp\left[\frac{Vx}{D} - K_{dc}t \right] \operatorname{erfc}\left[\frac{Rx + Vt}{2(DRt)^{1/2}} \right] \end{aligned} \tag{Eq. 24}$$

where

$$\beta = (V^2 + 4DRK_{dc})^{1/2} \tag{Eq. 25}$$

RESULTS AND DISCUSSION

Retardation Factor

The retardation factor is usually determined in the laboratory using a batch method based on the relationship between a retardation factor and a distribution coefficient presented in Eq. (2). A retardation factor has also been obtained by the column method using collected disturbed or undisturbed soil (14, 15). Since the retardation factor is the ratio of water velocity to the migration speed of a radionuclide, whether it is ion or not, the retardation factor is defined as follows:

$$R_D = \frac{V_w}{V_s} \tag{Eq. 26}$$

where V_w is an average groundwater velocity and V_s is the migration velocity of radionuclide.

In recent paper, Carlsen et al. (16) described a theoretical evaluation of the influence of complexation on radionuclide migration in environments containing an excess of complexing agents. They considered that the equilibrium between the free

and complexed metal ions could be regarded to follow pseudo-first order kinetics. They present an effective retention factor as a controlling factor, which is given as follows:

$$R_f^{eff} = \frac{R_f(M) + \beta' R_f(ML_i)}{1 + \beta'} \quad (\text{Eq. 27})$$

where β' is the apparent stability constant of the complex expressed as the ratio between the pseudo-first order rate constant for the formation of the complex and the first order rate constant for the dissociation of the complex, respectively; $R_f(M)$ is the retention factor for the metal ions in the absence of complexing agents, i.e., $\beta' = 0$; $R_f(ML_i)$ is the retention factor for the complex when the apparent stability constant β' approaches infinity, i.e., $\beta' \rightarrow \infty$; i is the average number of ligands per metal ion. However, this effective retention factor is thought to be not rigorous and do not includes detailed complexation mechanisms and related parameters.

In this study, retardation factor equivalent to the retention factor is expressed as follows:

$$R = \frac{R_1}{K_M} + R_2 \quad (\text{Eq. 28})$$

or

$$R = \left(\frac{K_M + 1}{K_M} \right) + \frac{(1 - \theta)\rho_b}{\theta} \left(\frac{K_{d1}}{K_M} + K_{d2} \right) \quad (\text{Eq. 29})$$

If $K_M > 1$, the first term of the right side of the Eq. (29) will be reduced to 1 and given as more sophisticated form:

$$R = 1 + \frac{(1 - \theta)\rho_b}{\theta} K_D \quad (\text{Eq. 30})$$

where

$$K_D = \frac{K_{d1}}{K_M} + K_{d2} \quad (\text{Eq. 31})$$

Then, the apparent migration speeds of ionic and chelated radionuclide can be evaluated by the following equations:

$$\frac{V}{R} = \frac{V'}{R'} = \frac{(1 + K_M)V_1}{(R_1 + K_MR_2)} \quad (\text{Eq. 32})$$

Depending upon the parameters, the apparent speed of ionic radionuclide in the presence of chelating agents can be greater or less than that of ionic radionuclide without chelating agents.

Since the apparent speed of the ionic radionuclide without chelating agents is given as V_1/R_1 , the relationship can be presented as follows:

$$\frac{V}{R} = \frac{V'}{R'} > \frac{V_1}{R_1} \quad \text{when} \quad \frac{R_2}{R_1} < 1, \quad (\text{Eq. 33})$$

and

$$\frac{V}{R} = \frac{V'}{R'} < \frac{V_1}{R_1} \quad \text{when} \quad \frac{R_2}{R_1} > 1. \quad (\text{Eq. 34})$$

In most cases, since the retardation factor of an ionic radionuclide is much greater than that of chelated radionuclide, Eq. (33) will prevail in actual geologic transport process and this phenomena may be due to the low capacity of the adsorption for the chelated radionuclide. In other words, the apparent speed of a radionuclide in the presence of chelating agents is greater than the case in the absence of the chelating agents. This is well consistent with the reported experimental results (1).

Numerical Calculation

The calculated results of the solution, Eq. (24), is shown in Fig. 1 for the numerical illustration of the results of calculation of the model with various times. Table I lists the values of parameters used for the calculation of the results. Also comparative results of calculation is showed in Fig. 2 between the case of presence of chelating agent (C1) which incorporating all the mechanisms developed in this study and the case of absence of chelating agents (C2) which is normally considered in previous studies. It is noticed that the presence of chelating agents accelerates the migration rate of radionuclide, i.e., the migration rate of the chelated radionuclide is faster than that of the ionic radionuclide in a porous medium. This may be due to the lower value of the retardation factor of the chelated radionuclide than that of ionic radionuclide.

Sensitivity Analysis

A sensitivity analysis is performed in order to investigate the effects of the parameters involved in the model on the model output (i.e., the concentration of the chelated radionuclide). In this study, as a example calculation, the parameters considered are chelate formation constant and distribution coefficients of the ionic and chelated radionuclides. Figure 3 shows the effects of the apparent chelate formation constant, K_M , on the C/C_0 . This figure shows that C/C_0 decreases with decreasing K_M . This is obvious from the fact that the

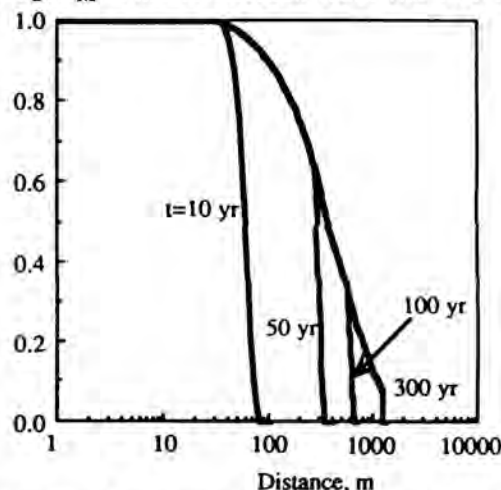


Fig. 1. The calculated results from the solution, Eq. (24), for the various time with distance from the source.

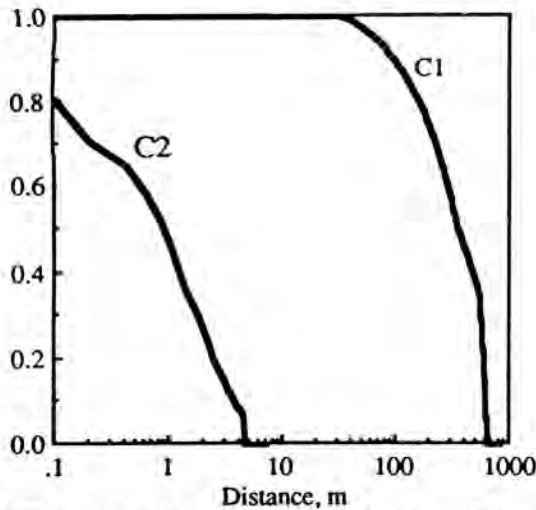


Fig. 2. The comparison of the calculated results from the solution, Eq. (24), in the presence of chelating agents (C1) and in the absence of chelating agents (C2), respectively.

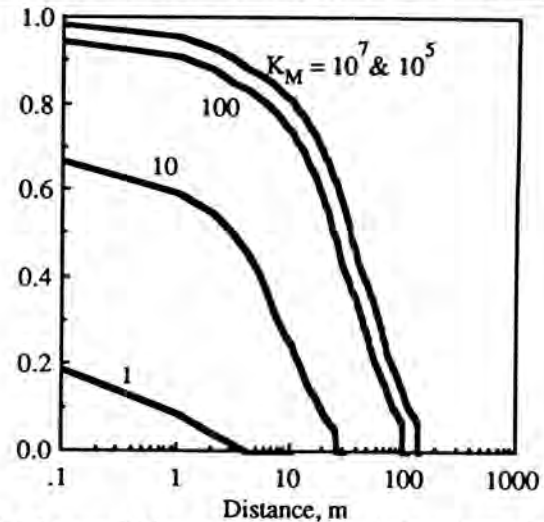


Fig. 3. The sensitivity analysis for the chelate formation constant (K_M) from the Eq. (24) using the values from Table I.

TABLE I
The Values and Notations of Parameters Used for the Numerical Calculations

Parameters	Notations	Values
θ	porosity of the porous medium	0.45
$\rho_b(\text{Kg/m}^3)$	bulk density of the porous medium	2600
$\gamma(1/\text{yr})$	decay constant of a radionuclide	0.05
$D_2(\text{m}^2/\text{yr})$	spersion coefficient of a free radionuclide	1.0
$D_2(\text{m}^2/\text{yr})$	spersion coefficient of a chelated radionuclide	1.0
K_M	groundwater velocity in a porous medium	100
K_M	parent chelate formation constant	10^7
$k_{dc}(1/\text{yr})$	radiation constant of a chelated radionuclide	10^{-4}
$K_{d1}(\text{m}^3/\text{Kg})$	distribution coefficient of a free radionuclide	10^5
$K_{d2}(\text{m}^3/\text{Kg})$	distribution coefficient of a chelated radionuclide	5×10^3

retardation factor will be increased with decreasing K_M as shown in Eq. (33) so that the increased retardation factor will decrease the releasing relative concentration of radionuclide, C/C_0 . In Fig. 4 the effects of the distribution coefficients of free and chelated radionuclides, K_{d1} and K_{d2} respectively, are shown. Although the distribution coefficient of the free radionuclide, K_{d1} , is increased, C/C_0 is little affected. However the effects of distribution coefficient of chelated radionuclide, K_{d2} , on the C/C_0 is much larger than K_{d1} . In particular, the result of calculation for $K_{d2} = 0$ shows that there is a negligible retardation so that the radionuclide migrate through the porous medium without adsorption on the geologic medium.

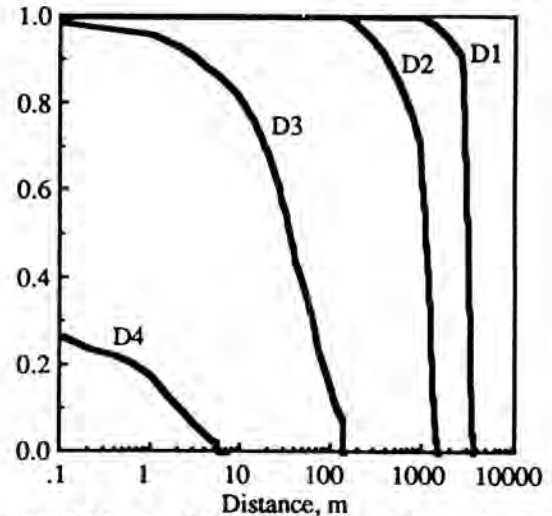


Fig. 4. The sensitivity analysis for the distribution coefficients of the ionic radionuclide (K_{d1}) and the chelated radionuclide (K_{d2}), respectively, using the values from Table I and D1 ($K_{d2} = 0$); D2 ($K_{d2} = 500$); D3 ($K_{d1} = 10^8$); D4 ($K_{d2} = 50000$).

CONCLUSIONS

This model study have demonstrated that the effects of chelating agents on the migration of a radionuclide is significant because the chelating agents increase the solubility of the radionuclide for the groundwater and decrease the adsorption capacity (i.e., distribution coefficient) of the sorbing geologic medium. The calculated results from the developed model show that the migration rate of the chelated radionuclide is much faster than that of the ionic radionuclide in spite of the degradation of the chelating agents and the chelated radionuclide.

Since the migration of the chelated radionuclide is much faster than the usual ionic radionuclide, a new remedial action should be developed to reduce the generation and release of chelating agents from the nuclear power plant into the environments. Also a performance assessment for the radioactive waste repository should include the migration of a chelated radionuclide.

ACKNOWLEDGEMENT

This work was supported by the Korea Science and Engineering Foundation.

REFERENCES

1. J.L. MEANS and D.A. CRERAR, "Migration of Radioactive Wastes Radionuclide Mobilization by Complexing Agents," *Science*, Vol. 200, pp 1477-1481 (1978).
2. J.L. MEANS, "The Importance of Organic Compounds in Ground Water Radionuclide Mobilizing Agents, Battelle's Columbus Laboratories," ONWI-348, Columbus (1982).
3. N. PAXEUS, B. ALLARD, U. OLOFSSON, and M. BENGTTSSON, "Humic Substances in Ground Waters," *Scientific Basis for Nuclear Waste Management*, Vol. IX, pp 525-532 (1985).
4. J.M. CLEVELAND and T.F. REES, "Characterization of Plutonium in Maxey Flats Radioactive Trench Leaches," *Science*, Vol. 212, pp 1506-1509 (1981).
5. R.A. FREEZE and J.A. CHERRY, *Groundwater*, Prentice-Hall, INC., Englewood Cliffs (1979).
6. J.C. MEANS, S.G. WOOD, J.J. HASSELT, and W.L. BANWART, "Sorption of Polynuclear Aromatic Hydrocarbons by Sediments and Soils," *Environ. Sci. & Technol.*, Vol. 14, pp 1524-1531 (1980).
7. C. T. CHIOU, P.E. PORTER, and D.W. SCHMEDDING, "Partition Equilibria of Nonionic Organic Compounds between Soil Organic Matter and Water," *Environ. Sci. & Technol.*, Vol. 17, pp 227-231 (1983).
8. A. RINGBOM, *Complexation in Analytical Chemistry*, Interscience Publishers, New York (1963).
9. J. INCZEDY, *Analytical Applications of Complex Equilibria*, John Wiley & Sons INC., London (1976).
10. J.L. MEANS and C.A. ALEXANDER, "The Environmental Biogeochemistry of Chelating Agents and Recommendations for the Disposal of Chelated Radioactive Wastes," *Nuclear and Chemical Waste Management*, Vol. 2, pp 183-196 (1981).
11. A.S. MAEST, D.A. CRERAR, E.C. DILLON, S.M. TREHU, and T.N. ROUNTREE, "Effect of Temperature on the Sorption of Chelated Radionuclides," *Scientific Basis for Nuclear Waste Management*, Vol. VIII, pp 377-384 (1985).
12. J.S. BOLES, K. RITCHIE, and D.A. CRERAR, "Reducing the Potential for Migration of Radioactive Waste: Aqueous Thermal Degradation of the Chelating Agent Disodium EDTA," *Nuclear and Chemical Waste Management*, Vol. 7, pp 89-93 (1987).
13. M. TH VAN GENUCHTE and W.J. ALVES, "Analytical Solutions of the One-Dimensional Convective-Dispersive Solute Transport Equation," *U. S. Dep. of Agric. Tech. Bull.*, Vol. 1661, pp 149 (1982).
14. J.F. RELYEA, "Theoretical and Experimental Considerations for the Use of the Column Method for Determining Retardation Factors," *Radioactive Waste Management and the Nuclear Fuel Cycle*, Vol. 3, pp 151-166 (1982).
15. T. OHNUKI, T. TANAKA, H. OGAWA, and T. YAMAMOTO, "Retardation Factor of a Sandy Soil," *Nuclear Technology*, Vol. 88, pp 55-63 (1989).
16. L. CARLSEN, O.J. NIELSEN, and P. BO, "The Influence of Complexation on Radionuclide Migration: A Theoretical Study," *Waste Management*, Vol. 9, pp 165-169 (1989).