

An Analysis on Remediation of Soil Contaminated with Cobalt by Solvent Flushing

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(Received January 5, 2000)

Abstract

A soil whose texture is silt loam was collected for the study from an area around a nuclear facility in Korea. The equilibrium sorption coefficient between Co^{2+} in water and the soil was 1.5 l/kg, on the other hand, that between Co^{2+} in EDTA and the soil was 0.2 l/kg. The values calculated by the developed nonequilibrium sorption code corresponded to the experimental values better than those calculated by the existing equilibrium sorption code. When an EDTA solution was used as a solvent to decontaminate Co^{2+} in the soil column, the relative Co^{2+} concentrations of the effluent were higher at 2~10 pore volumes than those of the case using water. The soil in the column was decontaminated by 95.5% of the total amount of Co^{2+} after being flushed with EDTA solution of 20 pore volumes.

Key Words : solvent flushing, nonequilibrium sorption code, hydrodynamic dispersion coefficient, water, EDTA

1. Introduction

The soil around nuclear facilities are being contaminated with radionuclides during the operation and decommissioning of those facilities, especially during a nuclear accident such as the one at Chernobyl in the Ukraine. Also, soil excavation may not be possible when the source is located under permanent structures, and especially when a large volume of soil is contaminated. In such cases, solvent flushing may be considered as an more plausible alternative.

In this paper, a study on decontaminating the soil contaminated with Co^{2+} was carried out by a solvent flushing method. Co^{2+} was found to exhibit a two-stage approach to equilibrium by experimental results: a short initial phase of fast uptake or release, where roughly 10-50% of the total sorption occurs within minutes to hours, followed by an extended period of a much slower uptake/release occurring over a period of hours or days.

The sorption-related nonequilibrium may result from chemical nonequilibrium or from rate-limited diffusive mass transfer. Chemical nonequilibrium

occurs when the sorption process at the fluid and the sorbent surface is rate-limited [1]. Three different processes involving rate-limited diffusive mass transfer can cause sorption-related nonequilibrium: film diffusion, retarded intraparticle diffusion, and intrasorbent diffusion. Film diffusion is generally insignificant in comparison to other mechanisms. Retarded intraparticle diffusion involves a solution-phase diffusion of solute within pores of microporous particles mediated by retardation resulting from instantaneous sorption to pore walls. Intrasorbent diffusion involves the diffusive mass transfer of sorbate within the matrix of the sorbent [2]. Intrasorbent diffusion is an important factor involving rate-limited diffusive mass transfer. This type of behavior is readily approximated by use of a nonequilibrium theory. The nonequilibrium theory has been used successfully to describe diffusion-limited sorption of hydrophobic organic chemicals during transport in soil [3,4]. Meanwhile, a computationally efficient algorithm was applied to solve the governing equations for the nonequilibrium case [5], and aspects of effects of mixed solvents on contaminant sorption and transport were studied [6].

In this study, the soil sample contains some organic chemicals and was decontaminated using a pump to increase remediation velocity. Accordingly, in order to analyze Co^{2+} transport within the soil sample, a new governing equation and a numerical code on the basis of nonequilibrium theory were developed. Meanwhile, the remediation characteristics of soil contaminated with Co^{2+} was analyzed by the solvent flushing method. An apparatus for soil remediation was designed and used for the remediation experiment. Also, in order to predict Co^{2+} concentration in the effluent from the apparatus, the developed numerical model was used. It was verified by experimental results.

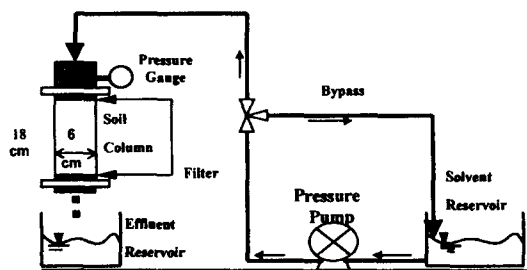


Fig. 1. Apparatus for Solvent Flushing

2. Remediation Experiment

2.1. Design of Apparatus for Decontaminating Soil

The soil remediation apparatus of laboratory size in Fig. 1 was designed to decontaminate the soil by the solvent flushing method. The soil sampled from the area around a nuclear facility in Korea was firstly mixed with a 0.01 M Co^{2+} solution in a large bowl. And it was packed on the same porosity as field situation, and then was attached the soil apparatus. The soil column has a 6 cm diameter and an 18 cm length. The solvent is put into the solvent reservoir and pressurized by a pressure pump. The pressure gauge measured the solvent pressure at the top of the soil column. The pressed solvent decontaminated Co^{2+} on the soil. In order to avoid the loss of fine soil particles, a glass fiber filter was placed at the bottom of the soil column. After the injected solvent decontaminated Co^{2+} in the soil column, it gathered at the effluent reservoir. Then, the Co^{2+} concentration of the effluent was analyzed by atomic absorption spectroscopy.

2.2. Experiment 1 : Water as a Solvent

A 0.01 M Co^{2+} solution was prepared to contaminate the soil sampled from the area around a nuclear facility in Korea. First, it was

mixed with the soil in a large bowl. And it was packed into the soil column on the same porosity as field situation by tapping the soil column on the bottom. Second, in order to mix the soil and Co^{2+} solution more effectively, a 0.01 M Co^{2+} solution was put in a solvent reservoir of the solvent flushing apparatus and the mixed soil into the soil column. Co^{2+} solution was pressurized by the pressure pump, and then sent into the column and sorbed by the soil in the column. It took 134 minutes to inject Co^{2+} solution of 1 pore volume into the column. The Co^{2+} solution was injected into the column for 12 hours, interrupted for 12 hours for a sufficient sorption, then injected again for more than 3 hours. In the next step, the water as a solvent was pressurized by the pressure pump according to the same method mentioned above and decontaminate the soil in the column. The Co^{2+} concentration of the effluent gathered in the reservoir was analyzed by atomic absorption spectroscopy.

2.3. Experiment 2 : EDTA Solution as a Solvent

The sequence of sorbing Co^{2+} artificially was the same as mentioned above. In the following step, the EDTA solution, as a solvent, was pressurized by the same method as above to decontaminate the soil contaminated with Co^{2+} in the column. The Co^{2+} concentration of the effluent gathered in the reservoir was analyzed by atomic absorption spectroscopy. The predominant chemical reaction occurring in the soil column is as follows:
 $\text{Soil-Co}^{+2} + \text{H}_2\text{EDTA}^{2-} \rightarrow \text{CoEDTA}^{2-} + 2\text{H}^+$ (around pH 4.3),
 where Soil- Co^{2+} is the Co sorbed within soil.

3. Modeling

The objective of modeling a soil remediation

experiment is for use in designing large-size solvent-flushing remediation equipment and optimizing its efficiency

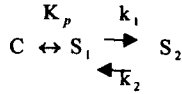
3.1. One-Dimensional Nonequilibrium Sorption Solute Transport Model Development

When the contaminated soil is decontaminated using a pump, the solutes in the solution released from the contaminated soil transfer very fast. Accordingly, the solutes in pore the solution usually migrate to another position before being obtained to an equilibrium with solutes in soil at one position. Therefore, the solutes migrate in the nonequilibrium state due to their fast velocity. The outward solutes of the soil are instantaneously decontaminated with the solvent, while the inward solutes are slowly decontaminated. The existing equilibrium sorption code analyzes the solute transport with the assumption that the solutes in the pore solution migrate in the equilibrium state with those in the soil. Therefore, the development of a code to analyze the solute transport in a nonequilibrium sorption state is needed.

In this paper, a numerical model for the analysis of a nonequilibrium theory was developed. This nonequilibrium model can analyze one-dimensional saturated Solute Transport with Non-Equilibrium Sorption (named as STNES). In the STNES code, a fraction of sorption is assumed to occur in an instantaneous manner, while the remainder of sorption is assumed to occur by a first-order mass transfer. Ratio-limited sorption has been attributed to solute diffusion constraints within the soil or retarded intraparticle diffusion.

The developed STNES code can analyze the transport of solutes during one-dimensional, steady water flow within a saturated domain. The nonequilibrium model was based on the first-order mass transfer [7]. The model system is

conceptualized as follows:



where C is the solute concentration in the water phase [M/L^3], S is the sorbed-phase concentration in the equilibrium domain [M/M], S_2 is the sorbed-phase concentration in the mass-transfer-constrained domain [M/M], and k_1 and k_2 are the forward and backward first-order mass-transfer rate constants [T^{-1}], K_p is the equilibrium sorption coefficient [L^3/M].

With the first-order model, sorption is conceptualized to occur in two domains:

$$S_1 = F K_p C$$

$$dS_2/dt = k_1 S_1 - k_2 S_2$$

where F is a fraction of the instantaneous sorption domains [8]. In an equilibrium state, the above equation reduces to:

$$k_1 S_1 = k_2 S_2, \quad S_2 = (1-F) K_p C$$

Thus, for the ratio of rate constants, we obtain:

$$k_1/k_2 = (1-F)/F$$

The governing equation of the one-dimensional nonequilibrium sorption solute transport model is obtained as follows :

$$\begin{aligned} \frac{\partial C}{\partial t} + \frac{\rho}{\theta} \frac{\partial S_1}{\partial t} + \frac{\rho}{\theta} \frac{\partial S_2}{\partial t} &= D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - \lambda \left(C + \frac{\rho}{\theta} S \right) \\ S_1 &= F K_p C \\ \frac{\partial S_2}{\partial t} &= k_2 ((1-F) K_p C - S_2) \end{aligned} \quad (1)$$

The above equation can be rearranged as follows :

$$\begin{aligned} \frac{\partial R \theta C}{\partial t} &= \theta D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - \theta V C + W \\ R &= 1 + \frac{\rho}{\theta} K_p F \\ V &= \frac{\rho}{\theta} K_p (k_2 (1-F) + \lambda F) + \lambda \\ W &= \rho (k_2 - \lambda) S_2 \end{aligned} \quad (2)$$

where t is time [T], v is pore water velocity [L/T], D is the hydrodynamic dispersion coefficient [L^2/T], λ is the radioactive decay constant [T^{-1}], x is the

distance from the top of the column [L], ρ is the dry bulk density, θ is the volumetric water content, and R is the retardation factor.

Also, the initial and boundary conditions of the governing equation (2) are as follows :

$$C(0, x) = C_0 \quad 0 < x < \ell$$

$$C(t, 0) = 0$$

$$\frac{\partial C}{\partial x}(t, \ell) = 0$$

The STNES code developed on the basis of the governing equation (2) was written in FORTRAN 77 language, and used the Galerkin finite element method with a linear basis function, an implicit difference scheme for the space derivative, a backward difference scheme for the time derivative, and the Thomas algorithm for the matrix calculation. Also, in order to avoid numerical oscillation, the space step (Δx) should be selected such that P_e (Pecret number), and the time step (Δt) such that Cu_e (Courant number) ≤ 1 .

3.2. Measurement of Input Parameter for Modeling

3.2.1. Soil Components

The soil was sampled at the area around a nuclear facility site in Korea. The compositions of inorganic components of the soil sample were analyzed by X-ray fluorescence and are shown in Table 1. Like

Table 1. Principal Components of Soil Sample

Element	Content(%)
Si	31.8
Al	8.8
K	6.9
Na	1.9
Fe	0.9
O	46.1
Others	3.6

other common soils, about one third of the soil consisted of silica. Aluminum was the next abundant mineral. Organic matter content of the soil was 2.4%. Meanwhile, the soil consists of 38% sand, 55% silt, and 7% clay and is classified as a silt loam.

3.2.2. Dry Bulk Density, Porosity, Water Content, and pH

The soil was dried off in an oven at 110°C for about 12 hours. The soil sample was then sieved with a 1.18 mm sieve (No. 16), and the soil passing through it was used for the remediation experiment. The physical characteristics of the soil, such as dry bulk density, porosity, and water content of the soil are listed in Table 2. Experiment methods are as follows: dry bulk density (ρ_b) is the oven-dried mass of sample divided by its field volume. Porosity (n) is obtained by $1-(\rho_b/\rho_s)$. Particle mass density, ρ_s , is the oven-dried mass divided by the volume of the soil particles. Water content (θ) is the volume of the water (V_w) divided by the total volume (V_T).

3.2.3. Hydraulic Conductivity and Pore Velocity

Hydraulic conductivity and pore velocity were calculated on the basis of the flux of the solution passing through the column of the apparatus at 1atm. The pore velocity of the soil passing through a 2.00 mm sieve (No.10) was 0.327 cm/min, while that of the soil passing through a 1.18 mm sieve (No.16) was 0.133 cm/min. The hydraulic conductivity was 2.31×10^{-3} cm/min and

8.46×10^{-4} cm/min, respectively.

3.2.4. Hydrodynamic Dispersion Coefficient

In order to obtain a hydrodynamic dispersion coefficient, a nonreactive uranyl (UO_2) solution was injected continuously into the soil column and dispersed in the soil column depending on the arrangement and structure of soil particles. Uranyl effluent was collected in the reservoir, and its concentration versus time was measured by atomic absorption spectroscopy. Then, the hydrodynamic dispersion coefficient calculated using Ogata's (1970) analytic solution [9] with uranyl effluent concentration data was 0.2cm²/min.

3.2.5. Equilibrium Sorption Coefficient

In order to obtain an equilibrium sorption coefficient, 5 sets of Co^{2+} solutions of different concentrations were prepared and put into individual plastic bottles with 10g of soil. Temperature was 25°C, and 100ml of 0.01 M EDTA for 10g soil was used as soil extractant ration, and shaking time was 24 hours.

After 24 hours, the Co^{2+} concentration remaining in each solution was measured by

Table 2. Properties of Soil

Dry bulk density(g/cm ³)	1.55
Porosity(%)	36.27
Water content(%)	12.00
pH	4.30

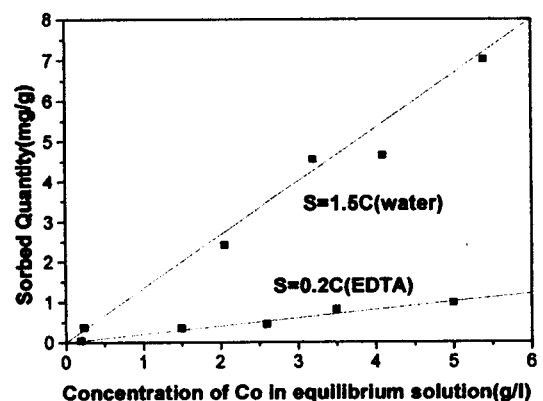


Fig. 2. Equilibrium Sorption Coefficient of Co^{2+} Solution with the Soil Sample

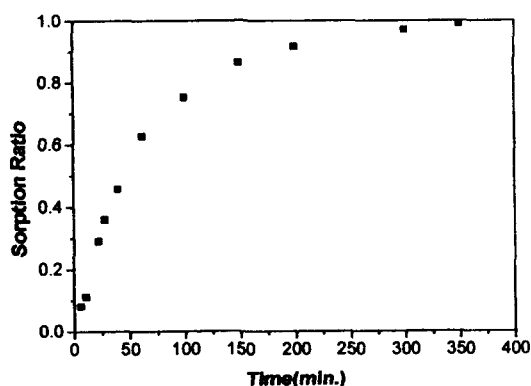


Fig. 3. Co^{2+} Sorption Ratio into the Soil Versus Time

atomic absorption spectroscopy. The Co^{2+} rates sorbed in the soil were calculated. Under above experiment conditions, the equilibrium sorption coefficient between Co^{2+} in water and soil was 1.5 l/kg, while that between Co^{2+} in EDTA and soil was 0.2 l/kg, as shown in Fig. 2.

3.2.6. Fraction of Instantaneous Domains and Backward First-order Mass-transfer Rate Constant

The sorption ratio of Co^{2+} versus time is shown in Fig. 3. Since it took 134 minutes for water to

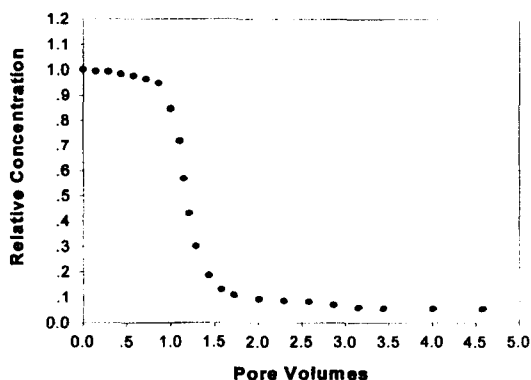


Fig. 4. Experimental Results from Flushing the Soil with a Higher Hydraulic Conductivity with Water

pass through the soil column, the time of instantaneous sorption in the soil column was assumed to be below 30 minutes. Accordingly, the ratio of sorption ratio of Co^{2+} at 10~20 minutes was about 0.15. Therefore, the fraction of instantaneous domains (F) was assumed to be 0.15.

The range of k_2 was decided on the basis of the experimental data from Nkedi-Kizza and Bouchard [10,11]. Data from remediation experiment with soil columns were analyzed using numerical values from STNES code to obtain K_p and k_2 .

4. Results

4.1. Experiment 1 : Water as a Solvent

When water was used as a solvent, the relative Co^{2+} concentration of the effluent from flushing the soil with a hydraulic conductivity of 2.31×10^{-3} cm/min with water of 5 pore volumes was reduced by 95% (Fig. 4), whereas that from flushing the soil with a hydraulic conductivity of 8.46×10^{-4} cm/min was reduced by 87% (Fig. 5).

It was revealed that the higher the hydraulic

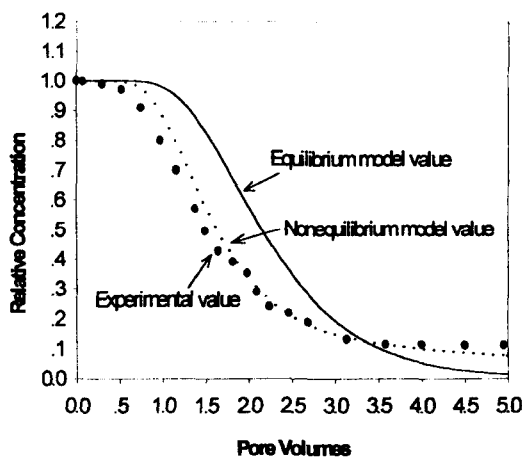


Fig. 5. Experimental and Simulated Results from Flushing the Soil with a Lower Hydraulic Conductivity with Water

conductivity is, the higher the efficiency of soil remediation is. Meanwhile, the developed nonequilibrium model and the existing equilibrium model were compared with the results of the remediation experiment, namely, the measured Co^{2+} concentration of the effluent. The input parameters of the nonequilibrium and the equilibrium models were pore velocity, porosity, bulk density, the hydrodynamic dispersion coefficient, the equilibrium sorption coefficient, Co^{2+} concentration in the solution, and so on, as mentioned above. But the nonequilibrium model requires a fraction of the instantaneous sorption domains(F) and the backward first-order mass transfer rate constant (k) with the described parameters. The values calculated by the nonequilibrium model were more in accordance with the experimental values than those by the equilibrium model, as shown in Fig. 5. Also, the soil in the column was decontaminated by 43.5% of the total amount of Co^{2+} after being flushed with 20 pore volumes with water.

4.1.2. Experiment 2 : EDTA Solution as a Solvent

The relative Co^{2+} concentrations of the effluent from flushing the soil with a hydraulic conductivity of 8.46×10^{-4} cm/min with EDTA solution were higher at 2~10 pore volumes than those with water. The relative Co^{2+} concentrations of the the effluent was reduced by 96% at a 20 pore volume. When EDTA solution was used as a solvent, the soil remediation efficiency by EDTA solution was greater than that by water(Fig. 6). Namely, the soil in column was decontaminated by 95.5% of the total amount of Co^{2+} after being flushed with EDTA solution of 20 pore volumes. The values calculated by the nonequilibrium model corresponded to the experimental values fairly, as shown in Fig. 6. However, in more than 10 pore

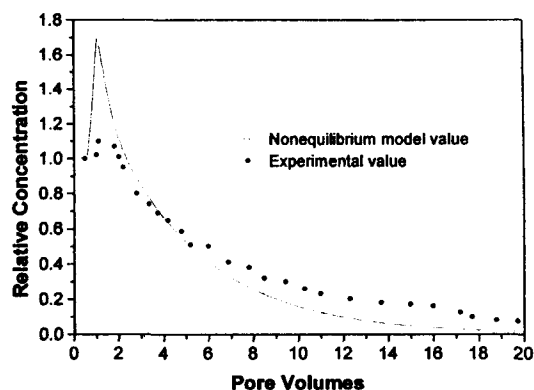


Fig. 6. Experimental Results from Flushing the Soil with a Lower Hydraulic Conductivity with EDTA Solution

volumes, the experimental values were higher than those of nonequilibrium model. It is assumed to be due to the generation of some channelling phenomenon in the soil column. Also, in order to obtain such high remediation efficiency, a period longer than 20 pore volumes was required.

5. Conclusions

A soil whose texture is silt loam was collected for the study from an area around a nuclear facility in Korea. Its hydraulic conductivity was higher than 8.46×10^{-4} cm/min, and its hydrodynamic dispersion coefficient was $0.2 \text{ cm}^2/\text{min}$. The equilibrium sorption coefficient Co^{2+} between water and silt loam was 1.5 l/kg, whereas that between EDTA and silt loam was 0.2 l/kg. The relative Co^{2+} concentration of the effluent from flushing the soil with a hydraulic conductivity of 2.31×10^{-3} cm/min with water of 5 pore volumes was reduced by 95%, whereas that from flushing the soil with a hydraulic conductivity of 8.46×10^{-4} cm/min was reduced by 87%. The soil in column was decontaminated by 43.5% of the total amount of Co^{2+} after being flushed with water of 20 pore volumes.

The relative Co^{2+} concentrations of the effluent from flushing the soil with a hydraulic conductivity of 8.46×10^{-4} cm/min with EDTA solution were higher at 2~10 pore volumes than those from flushing the soil with water. And the soil in the column was decontaminated by 95.5% of the total amount of Co^{2+} after being flushed with EDTA solution of 20 pore volumes. In addition, the values calculated by the developed nonequilibrium model(STNES) were more in accordance with the experimental values than those by the existing equilibrium model.

Acknowledgements

This project has been carried out under the Nuclear R&D Program by MOST in KOREA

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