

Electrokinetic Remediation of Cobalt Contaminated Soil Using Ethanoic Buffer

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Abstract

After kaolin clay was artificially contaminated with Co^{2+} ion, the remediation characteristics were analyzed by the electrokinetic method. Ethanoic buffer was injected in the soil column and CH_3COOH was continuously inputted to the cathode reservoir to restrain the pH increase. Since the pH of the cathode side of the soil column was 4.0 initially and increased to only 6.5 after remediation for 43.6 hours, precipitate, $\text{Co}(\text{OH})_2$, was not formed in the column. The effluent rate increased with the passage of time and Co^{2+} removal in the column at the initial time were mainly controlled by ion migration. 13.1% of the total amount of Co^{2+} in the soil column was removed in 10 hours, 46.8% of the total Co^{2+} in 20.8 hours, 71.7% of the total Co^{2+} in 30.1 hours, and 94.6% of the total Co^{2+} in 43.6 hours. Meanwhile, residual concentrations in the column calculated by the developed model were similar to those by experiment.

Key Words : electrokinetic remediation, acetic acid, soil column, cobalt, precipitation

1. Introduction

South Korea has many nuclear power plants and two research reactors. The soil around the nuclear facilities could be contaminated with radionuclides during the operation and decommissioning of those facilities, especially by a nuclear accident like the one at Chernobyl in the Ukraine. Therefore, it is necessary to develop technology for remediating the soil contaminated by radionuclides such as uranium, cobalt, strontium, and cesium.

During the past decade, the need to develop

economical techniques for decontaminating a large area of contaminated soil has grown. Most existing technologies are applicable only to soils of high hydraulic conductivity. Electro-kinetics offers the possibility of transport and in-situ remediation of contaminants in cases where conventional techniques are not feasible [1, 2]. In electric field restoration, pairs of electrodes are placed in the contaminated soil and a direct current potential is applied across them. The contaminants are then transported under the action of the electric field to electrode wells from which they can be brought to the surface. Unlike soil flushing, electrorestoration

is effective in soils of low or variable permeability and does not disperse the contaminants outside the treatment zone. Meanwhile, in the case of heavy metal removal from soil by the electrokinetic method, the removal efficiency was low due to generation of precipitation in soil of high pH[3, 4]. So, a technique to restrain pH increase near the cathode of the soil column has been required to increase removal efficiency.

The objective of this study is to restrain the pH increase near the cathode of the soil column. Thus, ethanoic buffer was injected in the soil column and CH_3COOH was periodically inputted to the cathode reservoir. When the soil contaminated with Co^{2+} was decontaminated by the electrokinetic method, the effluent rate, Co^{2+} concentration, and pH were measured during the remediation period, and the removal efficiency along time was analyzed in this study. Also, a numerical model was developed to simulate residual contaminant concentrations after soil remediation and was verified by comparing the model values with experiment values.

2. Theorem and Modeling

2.1. Transport Mechanisms

The electric field drives the contaminants toward the electrodes by two mechanisms. One is electroosmosis, an electrokinetic phenomenon in which the saturating liquid and dissolved substances flow toward an electrode [5]. The electroosmotic flow rate is proportional to the product of the applied electric field strength and the ζ potential at the soil-liquid interface. The value of the ζ potential depends on the soil properties as well as the ionic strength and pH of the saturating liquid. A typical ζ potential is about -10 to -100 cmV, and in a 100V/cm electric field, water will flow toward the cathode at a velocity of around 1-10 cm/min.

The second mechanism is electromigration in which charged ions move in the electric field strength, the charge on the ion, and the mobility of the ion. Transport of charged ions by electromigration is generally more rapid than by electroosmosis. In cases where the ionic strength is high due to the presence of inorganic contaminants, the ζ potential is small and transport occurs mainly by electromigration.

The contribution of each transport to the species flux is derived from the corresponding phenomenological relationship [6] and extended to an isotropic porous medium using a vadose model. The bulk liquid velocity, u_c , in cm/min is described as the sum of the contribution due to electroosmosis, u_{eo} , in cm/min and due to any pressure gradient, u_h , in cm/min. The electroosmotic velocity is calculated from the Helmholtz-Smoluchowski relation [4]

$$u_{eo} = \frac{\epsilon \zeta}{\tau^2 \mu} \nabla \phi \equiv k_e \nabla \phi \quad (1)$$

where u_{eo} is the pore velocity due to electroosmosis in cm/min, ϵ the permittivity of the pore liquid in F/cm, ζ the zeta potential of the soil in V, τ a nondimensional tortuosity factor that accounts for capillary path and is greater than 1, μ the viscosity of the pore liquid in Pa · min, ϕ the electrostatic potential in V, and k_e in $cm^2/(V \cdot min)$ an effective electroosmotic permeability coefficient used for convenience in the numerical formulation of the model.

The pressure gradient contribution is calculated from Darcy's Law

$$u_h = -\frac{k_h}{n\mu} \nabla p \equiv k'_h \nabla p \quad (2)$$

where u_h is the pore velocity in cm/min resulting from a pressure gradient, k_h the hydraulic permeability of the medium in cm^2 , n the porosity, and p the pressure in Pa. Again, an effective

permeability coefficient k'_h in $\text{cm}^2/(\text{Pa}(\text{min}))$ is defined for convenience. The electromigration velocity, u_{ei} , in cm/min is given by [7]

$$u_{ei} = -vzF \frac{\nabla \phi}{\tau^2} \equiv k_{ei} \nabla \phi \quad (3)$$

where the migration velocity is relative to the pore liquid, v is the mobility defined as the velocity resulting from a unit force per mole, z the charge number, F Faraday's constant, and k_{ei} an effective mobility coefficient in $\text{cm}^2/(\text{V}(\text{min}))$. Finally, the contribution of diffusion to the species flux for dilute solutions are given by Fick's law.

$$j^d = -\frac{D}{\tau^2} \nabla C \quad (4)$$

where j^d is the molar flux due to diffusion in $\text{mol}/(\text{cm}^2(\text{min}))$, C in the molar concentration of species i in the pore liquid in mol/ℓ and D the diffusion coefficient in cm^2/min . Superposing the different mass-transfer mechanisms, the total flux of an individual species is given by

$$j = (u_{eo} + u_h + u_{ei})C - \frac{D}{\tau^2} \nabla C \quad (5)$$

or in terms of the gradient of pressure, electrostatic potential, and concentration by

$$j = [(k_e + k_{ei})\nabla \phi + k_h \nabla p]C - \frac{D}{\tau^2} \nabla C \quad (6)$$

where j_i is the molar flux of species i per unit pore area in $\text{mol}/(\text{cm}^2(\text{min}))$. The coefficients k_e , k_{ei} , k_h , and D/τ^2 may vary in space and time.

2.2. Equations of Change

The equation of concentration change is derived by applying conservation of mass in a control volume of porous medium which contains both the liquid and solid phases. Neglecting transport of adsorbed species, applying Gauss's divergence

theorem, and taking the limit of infinitesimal control volume leads to

$$\frac{\partial(C + C^a)}{\partial t} + \nabla \cdot j = R \quad (7)$$

C^a in mol cm^{-3} is the molar concentration in the adsorbed phase, and R is the net volumetric rates of production of chemical species due to chemical reactions.

But since the total mass of each element is conserved

$$R = 0 \quad (8)$$

Then, we may rewrite Eq.7 as follows.

$$\frac{\partial(C + C^a)}{\partial t} + \nabla \cdot ((u_{eo} + u_h + u_{ei})C - \frac{D}{\tau^2} \nabla C) = 0 \quad (9)$$

The molar concentration of species in the adsorbed phase is given by

$$C^a = \frac{\rho}{n} K_d C \quad (10)$$

where, K_d is equilibrium sorption coefficient.

Substituting the pore velocity due to electroosmosis and a pressure gradient, and electromigration velocity in Eq. 9[8] gives

$$\frac{\partial C}{\partial t} (1 + \frac{\rho}{n} K_d) = -(\frac{\epsilon \tau}{\tau^2 \mu} \nabla \phi - \frac{k_h}{n \mu} \nabla p - v z F \frac{\nabla \phi}{\tau^2}) \frac{\partial C}{\partial x} + \frac{D}{\tau^2} \frac{\partial^2 C}{\partial x^2} \quad (11)$$

Assuming that the soil is neutral prior to contact with the pore liquid, the total charge density in the system can be obtained from the concentrations of species in solution and in the solid phase. Here, since the solid phase is taken to include the thin double layer, the net charge on the soil and in the double layer must be zero. Thus, the electroneutrality condition is as follows.

$$\sum_{i=1}^N z_i c_i = 0 \quad (12)$$

2.4. Initial and Boundary Conditions

Suitable initial and boundary conditions are needed to obtain the numerical solution of Eq.14. Co^{2+} was uniformly distributed in the soil column on initial time. Since the Co^{2+} concentration of the solvent is zero and solvent constantly flows down through the bottom of the soil column, the initial and boundary conditions are as follows. Also, difference of the electric potential of both electrodes was given of 40 voltages considering the soil column length.

$$C(0, x) = C_0 \quad 0 < x < 20 \quad (\text{cm})$$

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

$$\frac{\partial C}{\partial x}(t, 20) = 0$$

$$\phi(t, 0) = 40(V)$$

2.5. Code Development

A numerical code was developed to predict the residual contaminated concentration in the soil column after soil remediation by the electrokinetic method. The code developed on the basis of the governing equation, Eq.11, 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, and a backward difference scheme for the time derivative. Also, the Thomas algorithm was used for the matrix calculation. Meanwhile, in order to avoid numerical oscillation, the space step (Δx) should be selected such that P_e (Pecret number) ≤ 2 , and the time step (Δt), such that Cu_e (Courant number) ≤ 1 .

3. Soil Remediation Experiment

The input parameters for simulation of soil

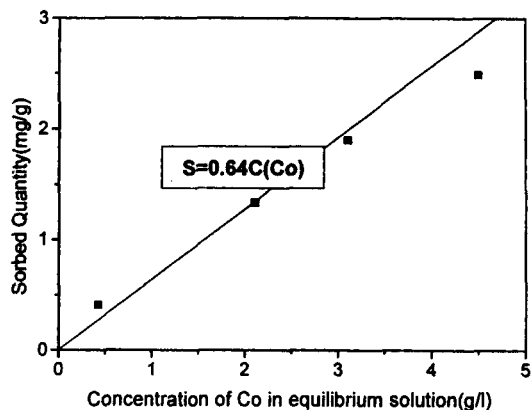


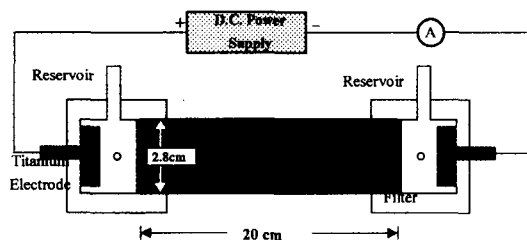
Fig.1. Equilibrium Sorption Coefficients of Co^{2+} with Kaolin Clay

remediation are listed in Table 1. The experimental method is as follows: dry bulk density (ρ_b) is the oven-dried mass of the 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 solid particles. Water content (θ) is volume of the water (V_w) divided by the total volume (V_T). And tortuosity (τ) was obtained from literatures, diffusion coefficient from comparison between experimental results and simulation results on residual concentration. In order to obtain an equilibrium sorption coefficient, 4 sets of Co^{2+} solutions of different concentrations were prepared and put into individual plastic bottles with 10g of soil. The temperature was 25°C , 100ml of Co^{2+} solution for 10g of soil was used, and the shaking time was 24 hours. Then, the Co^{2+} concentration remaining in each solution was measured by atomic absorption spectroscopy. The Co^{2+} rates sorbed in the soil were calculated. Under the above experiment conditions, the equilibrium sorption coefficient of Co^{2+} was 0.64 g/kg as shown in Fig.1.

Kaolin clay was put in a large bowl, and then 0.1 M of ethanoic buffer solution and 0.01M of CoCl_2 solution was put in it to make the saturating clay of 150cm^3 . The bowl was put in shaker and

Table 1. Parameters for Simulation

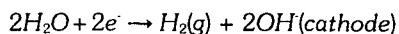
Parameter	Values
Cell dimensions, L	$\phi 2.8\text{cm} \times 20\text{ cm}$
Bulk density, ρ_b	0.77g/cm^3
Faraday's constant, F	96487 C/mol
Electroosmosis velocity,	$1.85 \times 10^{-3}\text{cm/min}$ (10.0 hours), $3.41 \times 10^{-3}\text{cm/min}$ (20.8 hours), $1.45 \times 10^{-2}\text{cm/min}$ (31.1 hours), $3.02 \times 10^{-2}\text{cm/min}$ (43.6 hours),
Potential at the anode well, ϕ_1	0.0 V
Potential at the cathode well,	40 V
Porosity, n	0.615
Tortuosity, τ	1.2
Distribution coefficient (ml/g), K_d	0.64
Diffusion coefficient(cm^2/min)	0.19

**Fig. 2. Schematic of a Cylindrical Column for Strontium Remediation**

shaken for 3 days to reach equilibrium absorption. After shaking, the saturating clay was injected into the soil column with tapping. Tapping the soil column was repeated until almost all of the air bubbles were removed. Fig. 2 shows the experimental equipment in laboratory size. The soil column is cylindrical shape with a 2.8cm diameter and a 20.0cm length. A titanium electrode, a filter, a stainless steel net, and a reservoir were established respectively at both ends of the column. The volume of the column is 123ml and the weight of kaolin clay is 94.8g. The volume of a 0.01M Co^{2+} solution injected in the column was 75.7 ml, which was calculated on the basis of the density and porosity of kaolin clay. One side of the column was connected to the anode, and the other side to the cathode. The voltage difference between both electrodes is 40 V

and an electric current is about 0.1 mA.

The pH of kaolin clay + ethanoic buffer and CoCl_2 solution in the column before the remediation experiment was 4.0. However, since the anode evolved hydrogen ions and the cathode evolved hydroxide ions directly after the experiment was run, if ethanoic buffer and acetic acid were not injected, the pH of the electrolyte in the anode reservoir would immediately change to less than 2.0 and that in the cathode reservoir to more than 12.0[9]. Then precipitate $(\text{Co}(\text{OH})_2)_2$ formed near the cathode and Co^{2+} concentration of effluent decreased. Thus the removal efficiency decreased [10].



NaOH combined little by little with 0.0056M of Co^{2+} solution in a mass cylinder which is pore solution concentration after equilibrium adsorption state between the kaolin clay and 0.01 M of Co^{2+} solution in the soil column as shown in Fig. 3. 100% of the Co^{2+} in the cylinder was precipitated at pH 12.0, 99% of Co^{2+} at pH 10.0, 65% of Co^{2+} at pH 8.0, and 0% of Co^{2+} at pH 7.3. Therefore, in order to increase the removal efficiency of Co^{2+} , a pH less than 7.0 is needed.

The option chosen for restraining the pH

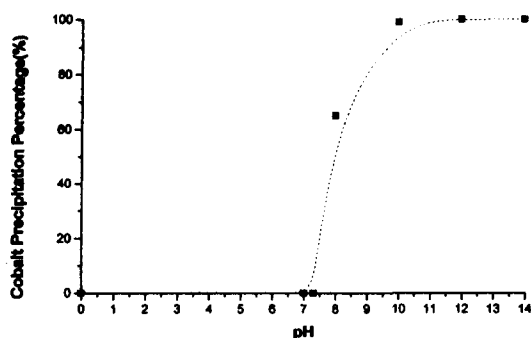


Fig.3. Cobalt Precipitation Percentage Versus pH

increase in the soil column was to supply CH_3COOK in the anode reservoir and CH_3COOH in the cathode reservoir. Also, a mixed solution of CH_3COOK and CH_3COOH was injected in the column and formed an ethanoic buffer [11]. This buffer was chosen keeping in mind the application of the process to actual in-situ situations, as it is a cheap, biodegradable and nontoxic reagent.

The initial solution with $C_{T,Ac}=0.2\text{M}$ was prepared using $C_{HAc}=C_{KAc}=0.1\text{M}$. Because $[\text{H}^+]$ and $[\text{OH}^-]$ are very small with respect to $[\text{HAc}]$ and $[\text{Ac}^-]$ in this region, the small amount of $[\text{OH}^-]$ added was assumed to react completely with $[\text{HAc}]$. Thus, $[\text{HAc}]$ decreases, and $[\text{Ac}^-]$ increases by the amount of $[\text{OH}^-]$ added per liter. The pH 12.8 equals 0.063 M of $[\text{OH}^-]$. Thus $[\text{HAc}]=0.1 - 0.063=0.027(\text{M})$ and $[\text{Ac}^-]=0.1 + 0.063=0.163(\text{M})$. Therefore, the increase of pH in the column is restrained and the pH in the column is predicted to about 5.48 in calculation as follows.

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Ac}^-]}{[\text{HAc}]} = 4.7 + 0.78 = 5.48$$

Due to this pH control, a regular electrical potential gradient is expected. The experiment process was run as follows. After the mixed kaolin clay consisted of kaolinite + ethanoic buffer solution + CoCl_2 solution have been injected into the column, the experiment was initiated under a

constant electric voltage gradient. The volumes of the anode and cathode reservoirs are 20 ml respectively. 19ml of 0.1M CH_3COOK solution was initially put in the anode reservoir, and 13ml of 0.1M CH_3COOH solution was put in the cathode reservoir. The pore solution in the column flowed toward the cathode reservoir by electroosmosis. When the cathode reservoir was filled with about 19 ml of pore solution, the experiment was suspended and then the volume of pore solution in the cathode reservoir was measured exactly. About 2ml of the pore solution was sampled and analyzed by atomic absorption spectroscopy. This process was repeated 29 times until the experiment closure. Additionally, at the end of the experiment, the kaolin clay was divided into 5 pieces. 10 ml of each piece was sampled and centrifuged for about 15 min (4000 rpm). The supernatant, i.e., the pore solution, was analyzed for Co^{2+} concentration. The experiment was conducted for only 43.6 hours due to lots of effluent rate.

4. Results and Discussion

The remediation experiment results using ethanoic buffer and CH_3COOH solution were as follows: the pH near the cathode of the column was 4.0 initially as in Fig. 4, but the pH increased to only about 6.5 after remediation for 43.6 hours and $\text{Co}(\text{OH})_2$ did not form due to the low pH. Fig. 5 shows the Co^{2+} concentration of the effluent out of the column versus the pore volume which means the total volume of pore in the soil column. The concentration of the effluent abruptly increased to 0.03M at pore volume 0.1(13 hours passage). Thus, it is predicted that plentiful Co^{2+} ions were transferred by electromigration, because this concentration is five times the Co^{2+} concentration of the pore solution, 0.0056M, at the initial time. But the Co^{2+} concentration of the

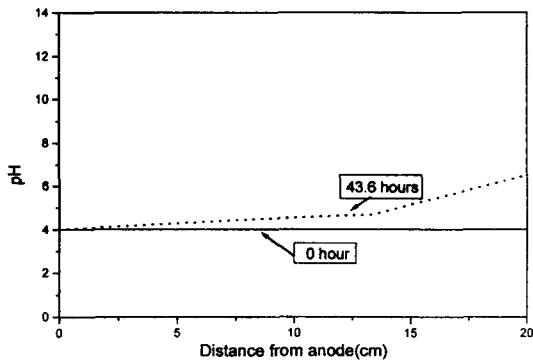


Fig.4. pH Distribution in Soil Column Measured at 0.0, and 43.6 Hours

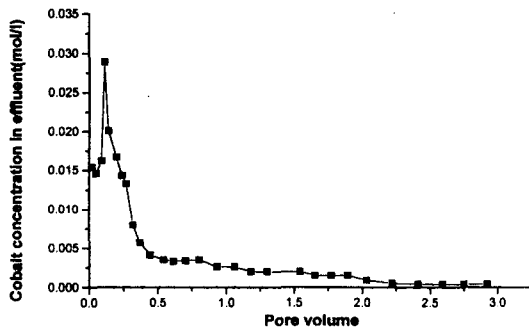


Fig.5. Cobalt Concentration in Effluent

effluent decreased to 0.004M for a pore volume of 0.1 to pore volume 0.5(28hours passage). The Co^{2+} concentration of the effluent decreased to about 0.001M for a pore volume of 0.5 to pore volume 2.0(37 hours passage). And, the Co^{2+} concentration of the effluent decreased to about 0.0004M for a pore volume of 2.0 to pore volume 2.9(44 hours passage).

Also, the flow velocities of pore solution as the experiment results were shown in Fig. 6 and Table 1. The flow velocities of pore solution increased with remediation time passage.

The total residual Co^{2+} concentration in the column versus each remediation time is shown in Fig. 7. Because no precipitate in the column formed through restraining pH increase, Fig. 7

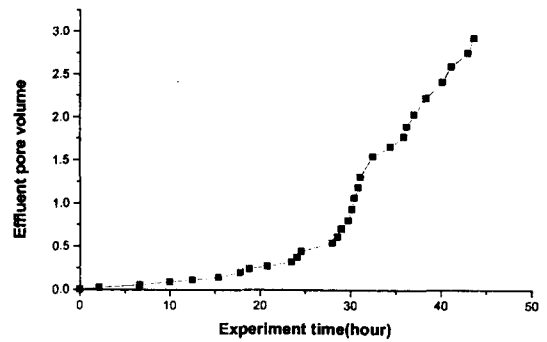


Fig.6. Effluent Pore Volume Versus Time

shows high removal efficiency. 13.1% of the total amount of Co^{2+} in the column was removed after remediation for 10.0 hours, 46.8% was removed after 20.8 hours, 71.7% was removed after 30.1 hours, and 94.6% was removed after 43.6 hours. Namely, the total amount of Co^{2+} in the column injected at the initial time was 44.6 mg. Simulation results showed that 5.8mg of Co^{2+} in the column was removed after remediation for 10.0 hours, 20.9mg of Co^{2+} was removed after 20.8 hours, 32.0mg of Co^{2+} was removed after 30.1 hours, and 42.2mg of Co^{2+} was removed after 43.6 hours. At the end of the run, the kaolin clay was drawn out and divided into 5 pieces. The concentration of the pore solution was measured by atomic absorption spectroscopy as shown in

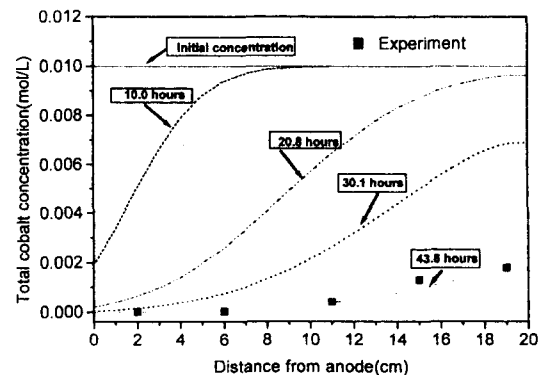


Fig.7. Distribution of Total Cobalt Concentration in Soil Column Versus Time

Fig. 7. Meanwhile, the predicted values by the developed model for calculating the residual concentration after remediation were fairly similar to the experiment values. In conclusion, 94.6% of the total amount of Co^{2+} in the column was removed through electrokinetic remediation using ethanoic buffer and acetic acid for 43.6 hours.

5. Conclusions

Ethanoic buffer was injected in the soil column and 0.1 M of CH_3COOH was continuously inputted to the cathode reservoir to restrain the pH increase. Since the pH of the cathode side of the soil column was 4.0 initially and increased to only 6.5 after remediation for 43.6 hours, precipitate, $\text{Co}(\text{OH})_2$, was not formed in the column. The effluent rate out of the soil column increased with time and Co^{2+} removal in the column at the initial time was mainly controlled by ion migration. 13.1% of the total amount of in the soil column was removed after 10.0 hours, and 46.8% of the total Co^{2+} in 20.8 hours, and 71.7% of the total in 30.1 hours, and 94.6% of the total Co^{2+} in 43.6 hours. Meanwhile, the residual concentrations in the column calculated by the developed model were similar to experimental results.

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