Electrokinetic remediation of cesium-contaminated soil and treatment of waste solution

*Ilgook Kim, Sung-Man Kim, June-Hyun Kim, Chan Woo Park, Hee-Man Yang and In-Ho Yoon

Decommissioning Technology Research Division, Korea Atomic Energy Research Institute, 989-111 Daedeokdaero, Yuseong-gu, Daejeon, 305-353, Korea
* *ilgook@kaeri.re.kr*

ABSTRACT

In this study, electrokinetic remediation equipment was used to remove cesium (Cs) from clay soil and waste solution was treated with sorption process. The influence of electrokinetic process on the removal of Cs was evaluated under the condition of applied electric voltage of 15.0-20.0 V. In addition to monitoring the Cs removal, electrical current and temperature of the electrolyte during experiment were investigated. The removal efficiency of Cs from soil by electrokinetic method was more than 90%. After electrokinetic remediation, Cs was selectively separated from soil waste solution using sorbents. Various adsorption agents such as potassium nickel hexacyanoferrate (KNiHCF), Prussian blue, sodium tetraphenylborate (NaTPB), and zeolite were compared and KNiHCF showed the highest Cs removal efficiency. These results demonstrated that our proposed process combined electrokinetic remediation of soil and waste solution treatment with metal ferrocyanide can be a promising technique to decontaminate Cs-polluted soil.

1. INTRODUCTION

Since the Fukushima nuclear accident, a large amount of radioactive cesium (Cs-137) has been released and consequently contaminated a widespread near area. Although a great volume of soil contaminated with Cs-137 has been generated, it was nowadays just being stored in remediation sites because of its difficulty of decontamination (Koarashi 2012, Nakao 2014). Accordingly, effective technologies for treating Cs-contaminated soil are ungently required.

Based on numerous studies of Cs retention in soil, it is well established that Cs is strongly and selectively accumulated on the phyllosilicate fraction of clay minerals, which provides a difficulty in Cs removal for remediation. With regard to the volume reduction of the contaminated soils, various techniques have been attempted for remedial treatment including physical separation, extraction, immobilization. In

particular, electrokinetic (EK) remediation is considered one of the emerging options that holds a potential for in-situ soil remediation (Virkutyte 2002, Al 2008). The EK decontamination can be used to treat soil contaminated with wide range of pollutants, such as ionorganic species and radionuclides (Reddy 2001, Yeung 2011). The main transport mechanisms of contaminants in EK technology are mainly electro-migration of the ionic species and electro-osmosis of the soil moisture. Electro-migration probably contributes significantly to the removal of contaminants, especially at high concentrations of ionic contaminants or a high hydraulic permeability of soil (Pamukcu 1992). The selected solution, also known as a purging electrolyte, should induce favorable pH conditions in the soil or interact with the incorporated heavy metals so that these heavy metals are removed from the soil (Reddy 2003). The EK remediation technique requires the presence of a pore fluid in the soil both to conduct the electrical field and to transport the species through the porous media (Acar 1995). When direct current electric field is applied to contaminated soil via electrodes, charged ions can migrate to the electrodes. The direction and quantity of contaminant movement is influenced by the contaminant concentration, soil type and structure, and the mobility of contaminant ions as well as the interfacial chemistry and the conductivity of the soil pore water.

Previous studies have shown that EK technique is effective for remediation of Cs in low-permeability soil such as clay (Kim 2003, Al-Shahrani 2005, Jung 2015). In this study, therefore, we explored the applicability of the EK technique for clay soil contaminated by Cs. The EK equipment was manufactured to remove Cs from the contaminated fine soil. The electric current, the temperature of the electrolyte, and the Cs removal efficiency according to the lapsed time were evaluated through several experiments. In addition, soil waste solution generated from EK process was treated with various sorbents.

2. Materials and methods

2.1 Preparation of Cs-contaminated soil

The soil was sampled near a site of the Kori nuclear power plant, Korea. The collected soil was preliminarily sieved to remove gravel, plant roots and impurities. The fine soil particle fraction (< 0.075 mm) was selected for the Cs removal experiments. The fine soil was mixed in an aqueous 3 mM CsCl solution for 7 days to be fully saturated. The Cs-sorbed soil was collected by centrifugation and washed three times with deionized water, followed by drying at 60°C.

2.2 EK remediation experiment

EK remediation equipment was manufactured for the experiments. A schematic diagram of the EK equipment is shown in Fig. 1. The EK equipment consists of a horizontal soil cell, two electrode chambers (anode/cathode rooms), an electrolyte reservoir, an electrolyte effluent reservoir, and a power supply, and a soil chamber was placed into a horizontal soil cell of 4.0×8.0×6.0 cm for the experiment. A filter sack made of polypropylene was inserted in the soil chamber to prevent an outflow of soil and was filled up with 100 g of fine soil contaminated with Cs. The electrolyte in

reservoir was supplied to the anode room at 0.5-1 mL/min. The impellor was installed in the middle of the horizontal soil cell. Meanwhile, an anion exchange membrane was inserted between the anode room and the contaminated soil to prevent an influx of Cs ions.
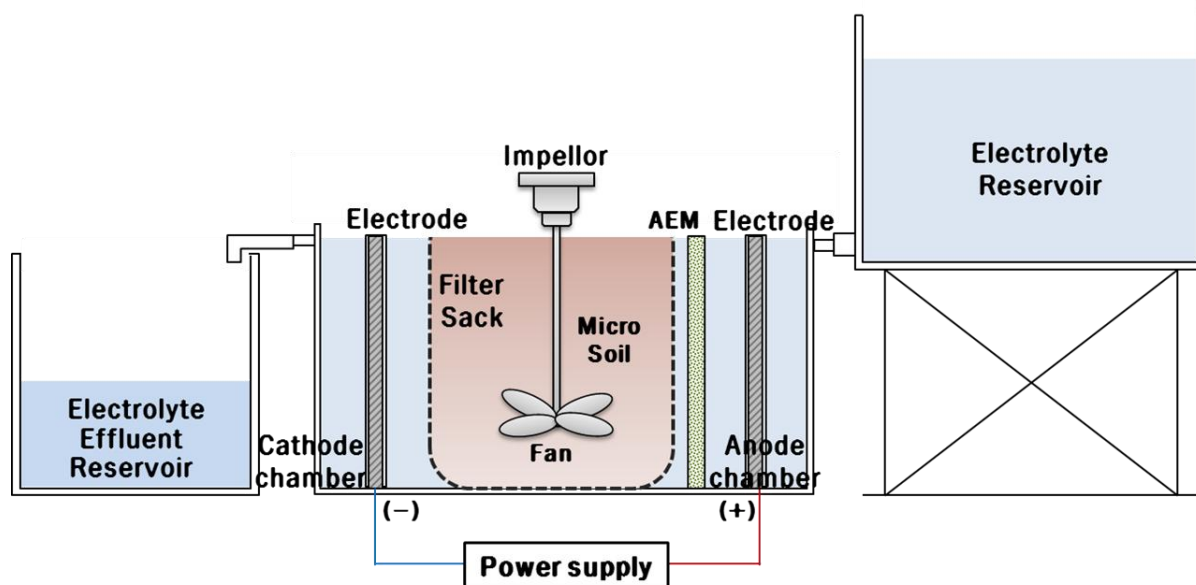

Fig. 1 Schematic diagram of EK remediation equipment

The experiment to remove Cs from fine soil was carried out using EK equipment. The electric voltage between electrodes is 10.0-20.0 V. The temperature in the soil chamber was 45-75°C. In addition, the initial Cs concentration of fine soil was 3.84 mg Cs/g soil and the rpm of the impellor in soil chamber was 150-200/min. 0.1 M HNO_3 was used as electrolyte to accelerate the Cs desorption from soil upon stirring. The period of EK decontamination operation was 24 h. The rate and concentration of electrolyte effluent from the cathode chamber were occasionally measured during the decontamination period. After the decontamination experiment had completed, the concentration of residual Cs of the decontaminated fine soil was also measured.

2.3 Adsorption experiment for treatment of soil waste solution
An adsorption experiment to remove Cs from soil waste solution was carried out using several adsorbents. Potassium nickel hexacyanoferrate (KNiHCF) was synthesized according to a previously reported procedure (Qing 2015). Prussian blue, sodium tetraphenylborate (NaTPB), and zeolite (IONSIV R9160-G) were also compared to adsorb Cs from waste solution. For adsorption reaction, the waste solutions mixed with the adsorbents were stirred for 3 h. After the desired contact time, the supernatants were measured for the determination of the final Cs concentration. The Cs concentration in the supernatant was determined using Atomic absorption spectrometry (AAS, Analytik Jena, Germany).

3. Results and discussion

3.1 EK decontamination for Cs removal

Cs in the contaminated fine soil during the EK process was removed by electro-osmosis, electro-migration, and a hydraulic pressure flow, as in the following Eq. (1):

$$j = [(k_o + k_m)R\nabla I + k_h \nabla p]C - \frac{D}{\tau^2}\nabla C \tag{1}$$

where j is the molar flux of the species per unit pore area, K_o is the electro-osmotic permeability, K_m is the electro-migration coefficient, R is the electric resistance, I is the electric current, K_h is the hydraulic permeability, P is the pressure, C is the molar concentration, D is the diffusion coefficient, and τ is a non-dimensional tortuosity. The pH achieved in the soil cell upon using 0.1 M of HNO_3 as an electrolyte was below 0.5, which accelerated the desorption of Cs ions by ion-exchange and prevented the formation of metal hydroxides on the cathode. Therefore, Cs in the fine soil can be removed during the EK decontamination process with acid electrolyte by electro-osmosis, electro-migration, and acid dissolution.

As shown in Fig. 2(a), it can be observed that with the increase of the applied voltage, the current also increased. The higher the current is, the stronger the effect of electro-migration is, which improves the Cs extraction. It has been generally known that the amount of mobile ions in the soil solution have effect on the electric current. At the voltage of 20 V, therefore, the current increased at the beginning of EK operation due to the increase in ions from soil in the electric field, and then decreased because of the reduced ions. Fig. 2(b) shows the changes in the temperature of the soil cell with elapsed time. At 10 V and 15 V, the temperature rapidly increased within 4 h, and then gradually increased. While at 20 V, the temperature reached a peak at 8 h and then gradually decreased. This change in the temperature of the soil is primarily dependent on the electric current and resistance of the soil, which is a function of the moisture and salt concentration (Fu 2017).
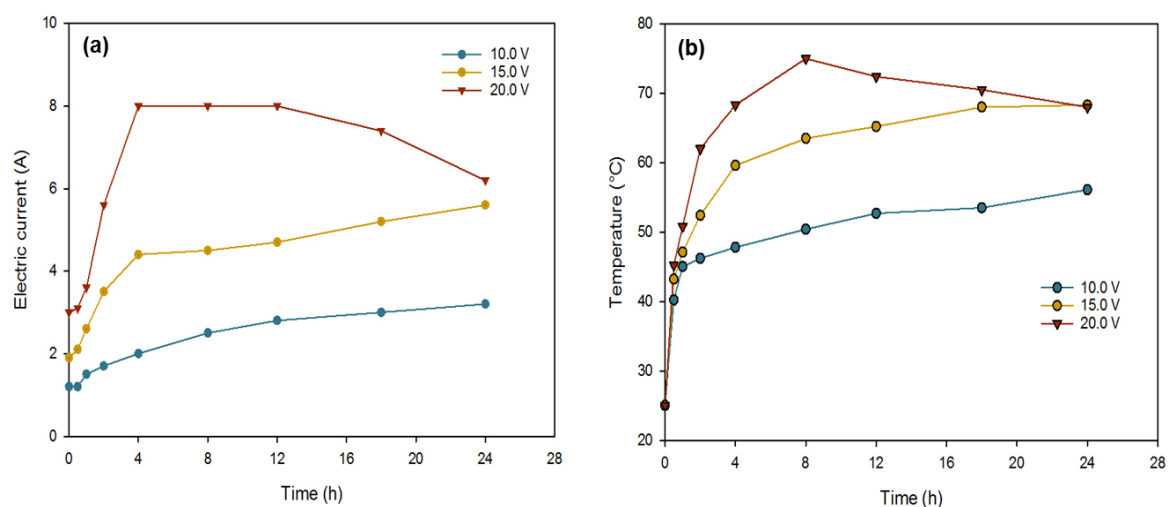

Fig. 2 Variations of (a) electric current and (b) temperature with time during EK remediation

. The removal efficiencies of Cs from soil in the EK experiment with different electric voltages are compared in Fig. 3. In EK operation, cations including Cs can be migrated toward cathode chamber and finally collected to the electrolyte effluent reservoir. The higher the voltage applied, the more significant the migration is. When the different gradient voltages applied, the Cs removal efficiency increased with time and 20 V showed the highest Cs removal of 92.8%. At the higher electric voltage, the free ionic pollutants which can migrate in the electric field easily were transformed from soil-bound state by protons and consequently readily desorbed from the soil.
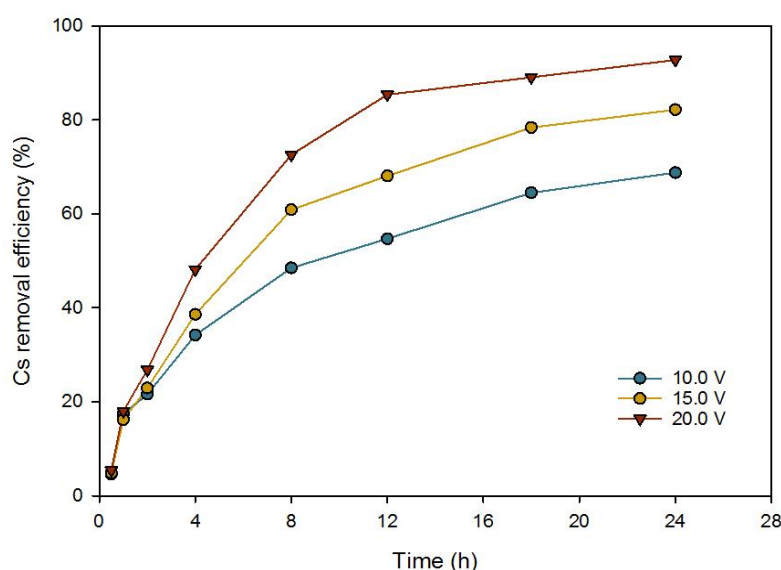

Fig. 3 Variations of Cs removal efficiency with time during EK remediation

3.2 Treatment of soil waste solution

After EK operation, the liquid fraction collected in electrolyte effluent reservoir was separated for waste solution treatment experiments. The concentrations of major metals in soil waste solution are shown in Table 1. The principal metals extracted from soil in electrolyte are Al, K, Ca, Mg, Fe, Si and Cs.

Table 1 Concentration of principal metals in soil waste solution

Metals	Concentration (mg/L)
Al	846.1
K	475.7
Ca	456.4
Mg	352.0
Fe	204.6
Si	124.2
Cs	20.9

For Cs adsorption experiments, KNiHCF, NaTPB, Prussian blue, zeolite were used to adsorb Cs in waste solution at a constant adsorbent dosage of 1 g/L, 25°C for 180 min by varying solution pH. Fig. 4 shows Cs removal efficiency from soil waste solution with various adsorbents at pH 0.9 (original) and pH 7.0 (adjusted). As the results of adsorption test, KNiHCF was determined as the optimum adsorbent indicating the highest Cs removal with coexisting cations under both acid and neutral pH conditions. In general, transition metal hexacyanoferrates exhibit an open zeolite-type structure consisting of a cubic network of iron centers bound by bridging cyanide ligand, which facilitates the interaction of alkali metal ions into the cubic structure required for maintaining its charge neutrality in solution (Keggin 1936). Thus, due to the specific structure characteristics of transition metal hexacyanoferrates, the high selectivity of Cs adsorption can be achieved (Jin 2003). With KNiHCF, Cs^+ is exchanged by K^+ in the sorption process and has the trend of moving toward face-centered clearance of KNiHCF, indicating high sorption capacity and selectivity. The results are also in good agreement with work done by Kim (2017) who compared adsorption agents for removing Cs-137 from ash and soil waste solutions.
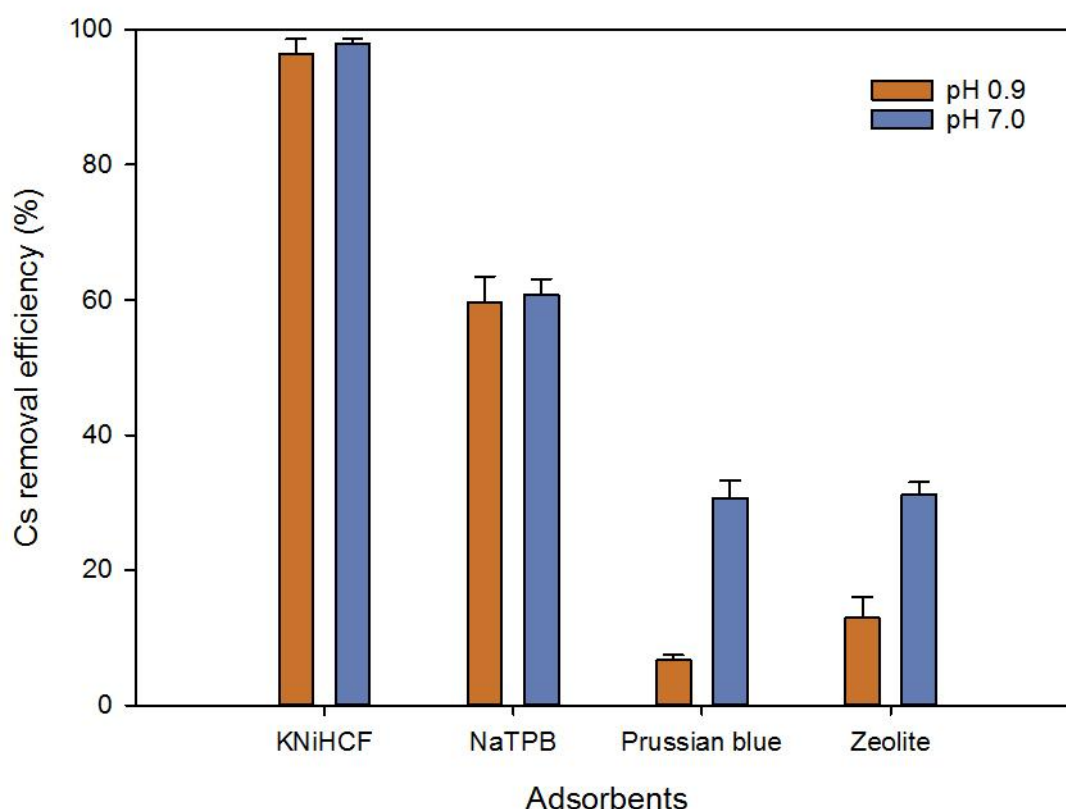

Fig. 4 Comparison of Cs removal efficiency from soil waste solution using different adsorbents

4. CONCLUSIONS

In this study, the EK remediation equipment was manufactured to treat fine soil contaminated with Cs and then KNiHCF was used to remove Cs from soil waste solution. The variations of electric current, temperature and Cs removal efficiency according to the lapsed time by EK process were investigated with varying the voltage. At 20 V of the EK process, the removal efficiency of Cs from the fine soil was 92.8%. In addition, KNiHCF showed the high Cs sorption capacity and selectivity in soil waste solution among various adsorbents. This overall process, therefore, appears to have high potential to be remediation option for the treatment of Cs-polluted soil.

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