



Electrolyte conditioning-enhanced electrokinetic remediation of arsenic-contaminated mine tailing

Kitae Baek^{a,*}, Do-Hyung Kim^a, Sung-Woo Park^a, Byung-Gon Ryu^a,
Tserennyam Bajargal^a, Jung-Seok Yang^b

^a Department of Environmental Engineering, Kumoh National Institute of Technology, 1 Yangho-dong, Gumi, Gyeongbuk 730-701, Republic of Korea

^b Korea Institute of Science and Technology (KIST) Gangneung Institute, Gangneung, Gangwon-do 210-340, Republic of Korea

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ABSTRACT

Feasibility of electrolyte conditioning with strong acidic or alkaline solution on electrokinetic remediation of arsenic-contaminated mine tailing was investigated in the laboratory. The mine tailing contained calcium oxide of more than 50%. At alkaline condition, arsenic was precipitated with calcium, and formed calcium arsenate which is very stable solid. Catholyte conditioning with strong acidic solution and anolyte conditioning with strong alkaline solution showed similar efficiency to remove arsenic. At 4 mA cm⁻² of current density, the removal efficiency of arsenic was 62% after 28 days operation with catholyte conditioning with 0.1 M nitric acid.

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1. Introduction

Arsenic has been one of the elements of major concerns due to its highly toxicity and carcinogenicity to human beings, animals, and plants. In the world, soil and groundwater was contaminated by the anthropogenic activities including mining, smelting, agricultural use of arsenical herbicides and pesticides, disposal of chemical warfare agent, preservation of wood, industrial waste discharge and illegal dumping [1,2]. Arsenic contaminated soil has been mainly remediated by ex-situ technologies such as replacement, solidification/stabilization [3], and acid or alkaline washing [4,5]. Generally, ex-situ technology is expensive and labor consuming work. Though Korean regulation level of arsenic in soil is 6.0 mg/kg, even though two step soil washing was applied to the treatment of mine tailing, the residual concentration of arsenic after ex-situ washing was not met the regulation level [5]. As a result, in-situ technologies to remove arsenic from mine tailings are highly desired.

Electrokinetic remediation is one of in-situ remediation technologies to remove arsenic from soil and mine tailings [1,2,6,7], and electrokinetic remediation is most effective technique to be applied fine-grained contaminated soils such as clay. Electrokinetic remediation has been demonstrated to be successful and

cost-effective in removing a wide range of contaminants in many bench- and field-scale studies [8–13]. Ko et al. investigated the feasibility of BCR three-step sequential soil washing to extract As, Zn and Ni from mine tailing. Acid washing was very effective to remove As from mine tailing with >0.075 mm, while washing technique was not removed As from mine tailing with <0.075 mm [14]. As a result, electrokinetic remediation is a best available technology to remove arsenic from mine tailing containing fine-grain soil. Removal of contaminants from soil by electrokinetic remediation is accomplished by the mechanisms of electrolysis of water, electro-migration, electro-osmosis and electro-phoresis. Hydrogen ion produced by electrolysis at anode moved toward cathode, and hydroxide ion produced at cathode moved toward anode. Generally, cationic metals are desorbed due to cation exchange with hydrogen ion and moved toward cathode in electrokinetic remediation, while anionic metals are desorbed due to anionic exchange with hydroxide ion and moved toward anode. During electrokinetic remediation, pH control is very important to enhance the removal of metal from soil. pH of pore solution affects zeta potential of soil surface, desorption of metal and electro-osmotic flow rate. Conditioning of anode and/or cathode reservoirs to control pH is common choice in electrokinetic remediation [1,6,7].

In this study, the feasibility of electrolyte conditioning, that is, anolyte conditioning with strong base and catholyte conditioning with strong acid, was investigated during electrokinetic remediation of arsenic-contaminated mine tailing.

* Corresponding author. Tel.: +82 54 478 7635; fax: +82 54 478 7629.
E-mail address: kbaek@kumoh.ac.kr (K. Baek).

2. Materials and methods

2.1. Soil sample

Soil samples were collected from arsenic-contaminated areas located at the Dal-Chun abandoned mine site (Ulsan, Republic of Korea) that had been developed for iron ore [5]. Jang et al. reported that content of organic matter was 5.4%. At pH above the zero-point of charge, net change of soil surface became negative, and resulted in the repulsion of negatively charged arsenic species (2007). Soil pH is highly related to the mobility of arsenic species.

Soil sampled from this area was sieved through a 2.0 mm (no. 10) opening sieve to remove large particles and mixed to homogenize uniformly. Concentration of arsenic was analyzed by Korean standard test (KST) methods for soil adopted from the Soil Environment Preservation Act. The KST method is as follows: (1) add 50 ml of HCl (1.0 M) to each 10 g of soil sample, (2) shake the suspension at a speed of 100 rpm and 30 °C for 30 min, (3) centrifuge 10 ml of suspension at 3200 rpm for 20 min, and (4) filter the supernatant with a 0.6 μm micropore filter, dilute the filtrate if it is necessary, and acidify the filtrate with concentrated nitric acid before the arsenic analysis [5]. Arsenic concentrations of filtrates were measured using inductively coupled plasma spectrometry (ICP, Varian 730-ES, USA) at a concentration range of 0.01–10 mg L⁻¹. Initial concentration of arsenic in soil sample was 83 mg kg⁻¹.

2.2. Electrokinetic experiments

The schematic and dimension of the experimental apparatus used in this study are shown in Fig. 1. The experimental apparatus consists of four major parts: the soil cell, the electrode compartments, the electrolyte reservoir and the power supply. Ti coated with Pt was used as an anode (4 cm × 4 cm × 0.3 cm) and graphite was used as a cathode (4 cm × 4 cm × 0.8 cm). Anode was mesh type, while cathode was a plate type. Electrode compartment con-

Table 1
Experimental conditions

	Current density (mA cm ⁻²)	Anolyte	Catholyte	Duration (d)
Exp. 1	2	MgSO ₄ 0.1 M	–	28
Exp. 2	2	NaOH 0.1 M	–	28
Exp. 3	2	NaOH 0.5 M	–	28
Exp. 4	2	MgSO ₄ 0.1 M	HNO ₃ 0.1 M	28
Exp. 5	2	MgSO ₄ 0.1 M	HNO ₃ 0.5 M	28
Exp. 6	4	MgSO ₄ 0.1 M	HNO ₃ 0.1 M	28

sisted of electrode part and electrolyte part. The electrolyte part was connected to electrolyte reservoir, and the electrolyte in the reservoir was circulated with peristaltic pump to control pH of electrolyte at the flow rate of 2 ml min⁻¹. Anolyte was circulated with NaOH solution to maintain alkaline condition, while catholyte was circulated with HNO₃ solution to make acidic condition in the soil cell. Direct current power supply was used to provide electricity to the system. Overall electrokinetic experimental conditions were summarized in Table 1. Soil sample of 800 g and distilled water of 200 ml (initial water content 20 ± 0.5%) was mixed and installed in the soil cell. Experiments were carried out under the constant current condition, and voltage between anode and cathode and electro-osmotic flow were measured during experiments. After experiments, soil in the cell was sliced into 10 sections and each soil section was used to analyze water content, soil pH and arsenic concentration.

3. Results and discussions

3.1. pH distribution and voltage drop in the soil cell

Initial pH of soil was 8.47. In the conventional electrokinetic remediation (Exp. 2), pH of soil from anode was ranged from 9.8 to 10.2 except last cathode section. The pH of soil at the last cathode section was 10.94 (Fig. 2). Generally, pH of soil in electrokinetic

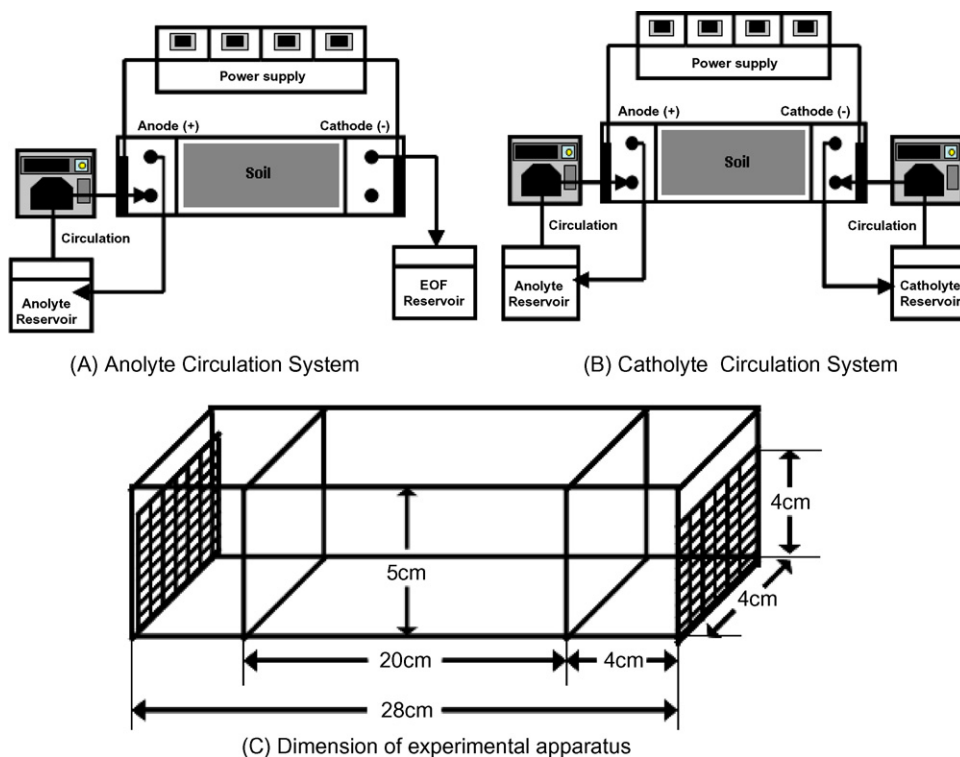


Fig. 1. Schematic and dimensions of experimental apparatus (A) anolyte circulation system, (B) catholyte circulation system, (C) dimensions of experimental apparatus.

remediation was ranged from 2 to 3 at anode section and from 10 to 12 at cathode section. However, the soil pH increased up to pH 10 compared to initial pH 8.47. In Exp. 2 and Exp. 3 in which catholyte was circulated with strong alkaline solution to maintain alkaline condition, soil pH was ranged from 10.3 to 10.6 for Exp. 2 and from 10.7 to 10.9 for Exp. 3, respectively (Fig. 2). Soil pH in Exp. 2 circulated with NaOH 0.1 M was slightly lower than the pH in Exp. 3 circulated with NaOH 0.5 M. Higher alkaline solution for the circulation of catholyte was more effective to condition soil pH.

In Exp. 4–6, strong acidic solution was circulated to maintain acidic condition for soil. Soil pH was ranged from 7.9 to 8.6 for Exp. 4, from 7.5 to 8.2 for Exp. 5 and from 7.5 to 8.3 for Exp. 6, respectively (Fig. 2). Except anode section, pH value of soil was similar to initial pH (pH 8.47). Strong acidic solution (0.5 M HNO₃) decreased more than 0.1 M HNO₃. Higher current density (4 mA cm⁻², Exp. 6) caused to decrease slightly more soil pH compared to lower current density (2 mA cm⁻², Exp. 4).

Even though circulation system was applied to control soil pH, the soil pH was not changed significantly because the contaminated soil contained high level of calcite [15]. This mineral played a role for buffering capacity. Ko et al. reported that Dal-Chun mine tailing was an alkaline soil of mean pH 7.6, and consumed 0.552 mol H⁺/kg with acid buffering due to the carbonate contents of the soil. Additionally, high concentration of calcium was detected in washing effluent in washing effluent [14].

Fig. 3 shows voltage gradient between anode and cathode. In Exp. 1, voltage gradient increased sharply up to 15 V cm⁻¹, which was a maximum value of power supply used in this study

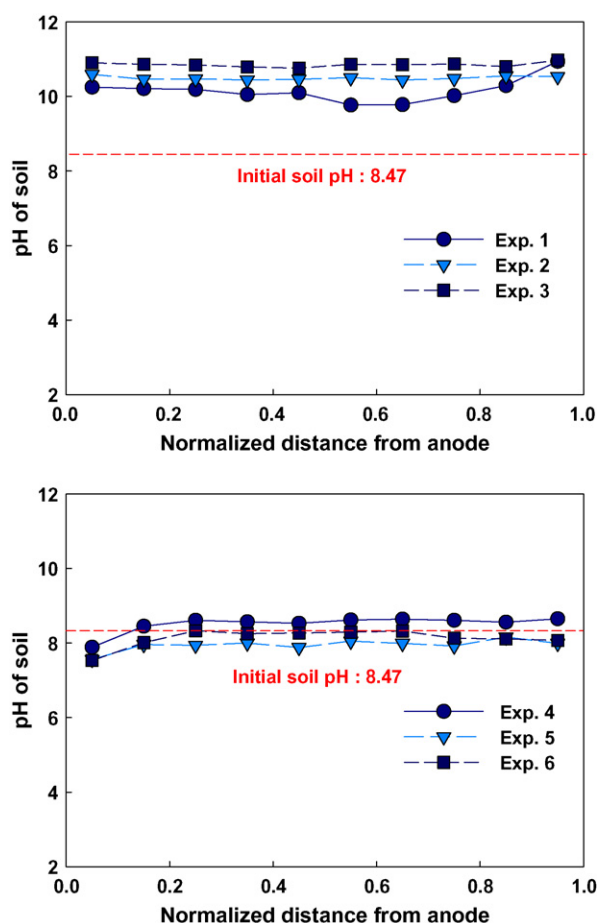


Fig. 2. pH distribution in soil cell after electrokinetic remediation.

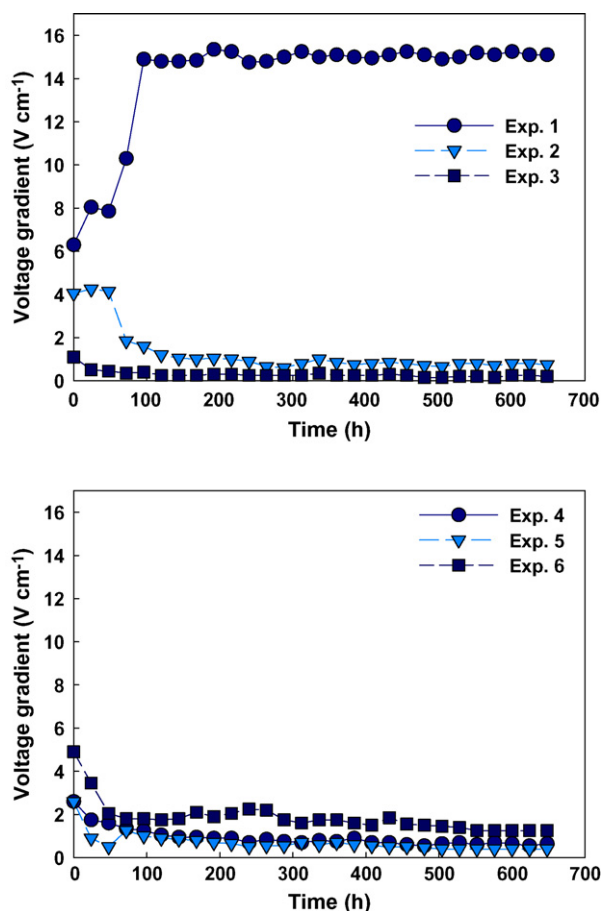


Fig. 3. Voltage gradient between anode and cathode during electrokinetic remediation.

(300V). Sharp increase in voltage gradient means sharp increase in resistance of soil. Voltage gradient increased suddenly because concentration of ion in soil pore solution decreased sharply. In Exp. 2 and Exp. 3, voltage gradient decreased gradually within 100 h, and reached constant values of 0.8 V cm⁻¹ and 0.25 V cm⁻¹ for Exp. 2 and Exp. 3, respectively. Decrease in voltage gradient comes from decrease in soil resistance because circulation of anolyte with strong alkaline solution provided sufficient cation and anion to soil pore, and alkaline condition accelerated the dissolution of soil mineral. Voltage gradient was lower at higher concentration solution of anolyte (0.5 M NaOH) than that at lower concentration solution (0.1 M NaOH).

In Exp. 4–6, voltage gradient decreased sharply and reached plateau values of 0.7 V cm⁻¹, 0.6 V cm⁻¹ and 1.6 V cm⁻¹ for Exp. 4, 5, and 6, respectively. Decrease in voltage gradient comes from providing cation and anion by circulation of catholyte and enhancing dissolution of soil mineral. Similar to anolyte circulation, voltage gradient showed less value at higher concentration for circulation solution (0.5 M HNO₃) compared to lower concentration (0.1 M HNO₃). As current density increased from 2 mA cm⁻² to 4 mA cm⁻², the voltage gradient value changed from 0.7 V cm⁻¹ to 1.6 V cm⁻¹ because voltage is proportional to current at direct current.

3.2. Electro-osmotic flow

Pore solution flows by electro-osmosis during electrokinetic process. Electro-osmosis is very important mechanisms affecting the removal of contaminants from soil with electro-migration. The Electro-osmotic flow rate is influenced by a number of factors such

as the pore water property, the zeta potential of the soil, and the electric field strength [1]. In particular, pH of pore water controls water chemistry of pore solution and zeta potential of the soil. The transported water volume by electro-osmosis was measured in cathode reservoir and anode reservoir during electrokinetic remediation (Fig. 4).

In Exp. 1–3, the direction of electro-osmotic flow was from anode to cathode. The accumulated electro-osmotic flow (EOF) was measured in cathode reservoir. EOF increased with soil pH, and EOF increased dramatically in Exp. 3 where anolyte was circulated with 0.5 M NaOH compared to Exp. 1 and 2. Generally, a zeta potential of soil surface is negative at alkaline condition, and more negative zeta potential enhanced electro-osmotic flow [1,16].

In Exp. 4, the direction of electro-osmotic flow was from anode to cathode even though strong acidic solution was circulated to control soil pH in cathode reservoir because soil pH was still slightly alkaline condition due to acid buffering capacity of soil. However, the amount of EOF was less than that of no circulation (Exp. 1). It seems that the surface charge of soil is neutral.

In Exp. 5–6, amount of EOF in cathode was negative after electrokinetic experiments, which means that the electro-osmotic flow was from cathode to anode, that is, reverse EOF. Reverse EOF occurred at positive zeta potential of soil surface. Even though soil pH was slightly basic, circulation of catholyte with strong acidic solution changed zeta potential of soil surface into positive caused from adsorption of hydrogen ion onto soil surface. In Exp. 5, the original direction of EOF was from anode to cathode up to 200 h, however, the direction changed toward anode from cathode after 200 h. The reverse EOF is due to the electro-migration of negatively charged compounds such as arsenic [13]. The amount of reverse EOF

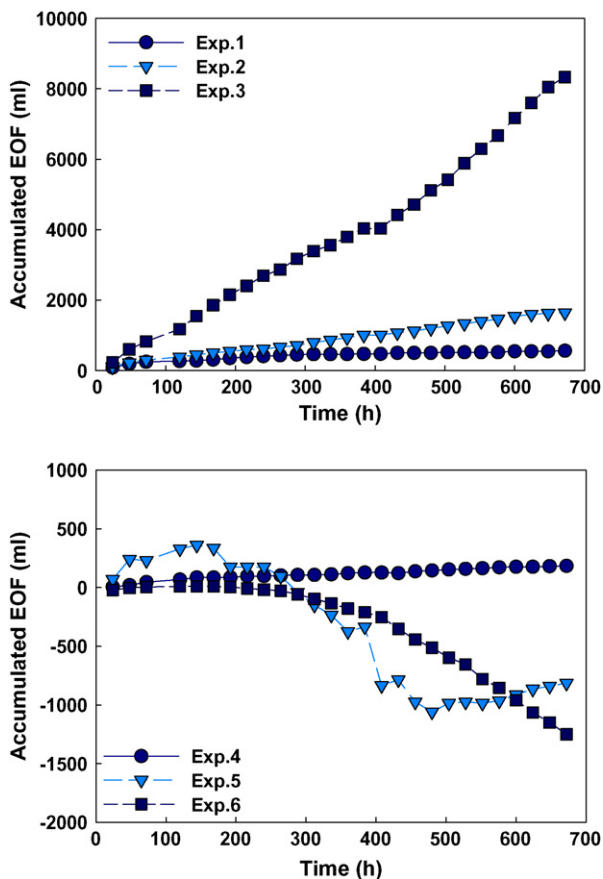


Fig. 4. Accumulated electro-osmotic flow during electrokinetic remediation.

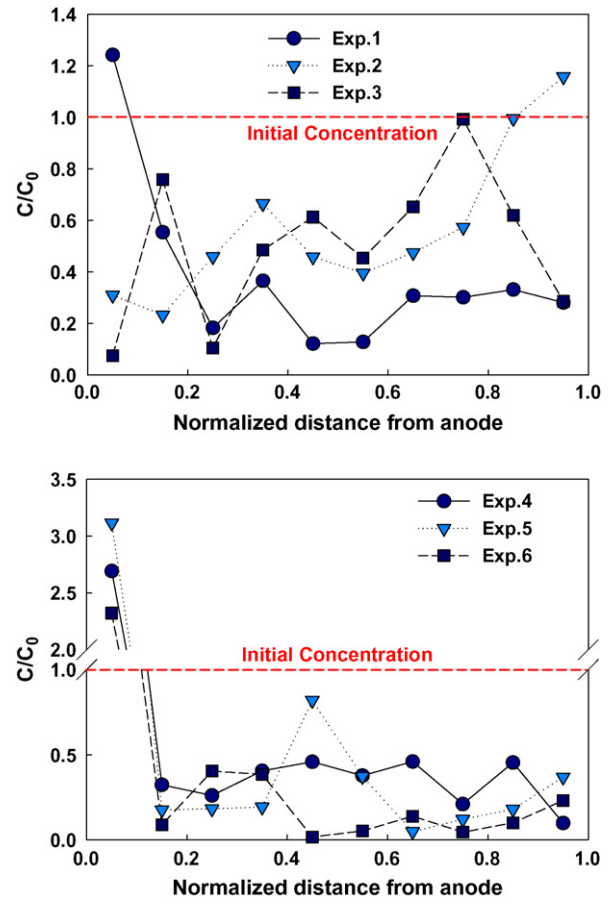


Fig. 5. Arsenic distribution after electrokinetic treatment.

increased with current density and concentration of conditioning acidic solution, but decreased with soil pH.

Acar and Alshawabkeh [8] reported that the main mechanism of electrokinetic removal of heavy metals from soils is electro-migration. However, Kim et al. reported that the electro-osmosis plays a crucial role in removing heavy metals from tailing soils during electrokinetic remediation [17]. As a result, the direction of electro-osmotic flow affects the removal of toxic metal in electrokinetic remediation.

3.3. Arsenic distribution

Fig. 5 shows arsenic distribution in soil section after electrokinetic remediation. Arsenite (As(III)) and arsenate (As(V)) are the most widespread forms in nature. As(III) may be oxidized to As(V) at oxidative condition. Under normal soil, arsenate exists as an oxyanion such as H_2AsO_4^- , HAsO_4^{2-} or AsO_4^{3-} . In electrokinetic remediation, arsenate moved from cathode to anode because it is an oxyanion. However, the direction electro-osmotic flow is from anode to cathode, that is, opposite direction of electro-migration of arsenic, at normal soil condition.

Fig. 5 shows arsenic distribution after electrokinetic experiments. In Exp. 1, arsenic moved toward anode by electro-migration, and arsenic concentration of anode region increased sharply. As shown in Fig. 3, the voltage gradient was the highest because of lack of ions in electrolyte. High voltage gradient enhanced electro-migration of arsenic from cathode to anode, and electro-osmotic flow was little. As a result, most arsenic was removed toward anode by electro-migration. In Exp. 2 and Exp. 3, arsenic was

Table 2
Summary for electrokinetic removal of arsenic

	Removal efficiency (%)	Removal amount (mg)	Energy consumption (kWh t ⁻¹)	Effective removal (mg As Wh ⁻¹)
Exp. 1	56.6	24.4	3582.7	0.009
Exp. 2	37.6	11.7	434.4	0.034
Exp. 3	44.4	16.3	91.7	0.222
Exp. 4	37.4	11.6	295.7	0.049
Exp. 5	44.3	16.2	219.84	0.092
Exp. 6	62.2	28.1	1145.28	0.031

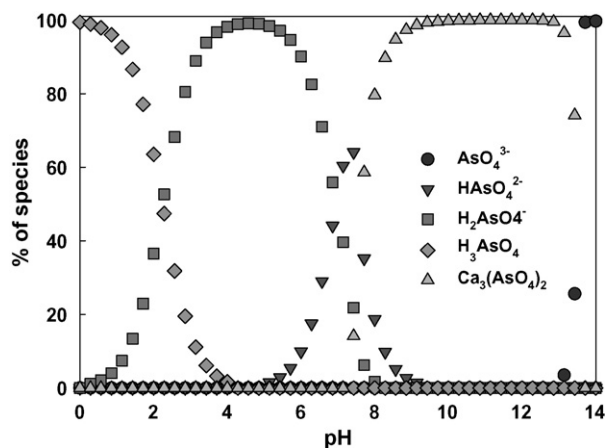


Fig. 6. Distribution of As species in presence of Ca²⁺ with MINEQL+ (version 4.5, simulated with 1000 mg/l Ca²⁺ and 100 mg/l AsO₄³⁻).

moved from anode to cathode, which means that arsenic was removed by electro-osmosis in the case of anolyte circulation with strong basic solution. As shown in Fig. 4, the electro-osmotic flow increased up to 3 times and 8 times for Exp. 2 and Exp. 3, respectively. However, the effect of enhancement in electro-osmotic flow was compensated for electro-migration because the direction of electro-osmosis was opposite to that of electro-migration. As concentration of anolyte conditioning solution increased from 0.1 M NaOH to 0.5 M NaOH, the overall removal efficiency increased from 37.6% to 44.4%, but energy consumption decreased from 434 kWh t⁻¹ to 91.7 kWh t⁻¹.

Catholyte conditioning with strong acidic solution enhanced arsenic movement toward anode, which means that the major mechanism for arsenic removal was electro-migration in Exp. 4–6. Removal of arsenic increased from 37.4% to 44.3% as concentration of catholyte conditioning solution increased from 0.1 M HNO₃ to 0.5 M HNO₃. At a concentration of 0.1 M HNO₃ for catholyte conditioning, the removal of arsenic increased from 37.4% to 62.2% with increase in current density from 2 mA cm⁻² to 4 mA cm⁻².

Generally, basic condition enhanced desorption of arsenic because hydroxide ion exchanged with arsenic in alkaline condition [1,18]. In this study, however, overall removal efficiency of anolyte conditioning was similar to that of catholyte conditioning (Table 2). Low removal of arsenic caused from (1) opposite direction of electro-migration and electro-osmosis and (2) precipitation of calcium arsenate at alkaline condition. As mentioned previously, the mine tailing used in this study contains high concentration of calcium oxide. CaO was dissolved at strong alkaline condition, and calcium ion was produced. At pH 10, arsenic was precipitated with calcium and formed very stable solid, calcium arsenate (Fig. 6). The precipitate of arsenic could not be moved by electro-migration, which decreased overall arsenic removal in electrokinetic process.

Electrolyte conditioning with strong acidic or basic solution decreased dramatically energy consumption which is a critical factor to evaluate the feasibility of electrokinetic remediation. In this

study, a new parameter, effective removal, was introduced to evaluate the feasibility (Table 2). Effective removal means amount of arsenic removed by electrokinetic remediation per unit energy consumption. Even though overall removal efficiency was the highest in Exp. 6 (highest current density), effective removal was the highest in Exp. 3 (anolyte conditioning with 0.5 M NaOH). Electrolyte conditioning enhanced overall removal efficiency of arsenic and decreased energy consumption because of enhancement in dissolution of soil mineral and supply of ions.

4. Conclusions

The feasibility of electrolyte conditioning with strong acidic or basic solution on electrokinetic remediation for arsenic contaminated-mine tailing was investigated in the laboratory scale. Anolyte conditioning with strong basic solution enhanced electro-osmosis because hydroxide ion contributed to negative zeta potential of soil surface, however catholyte conditioning with strong acidic solution increased electro-migration. Even though alkaline condition increased ion exchange between arsenic and hydroxide ion, desorbed arsenic was precipitated with calcium which was dissolved from calcite or calcium oxide at pH 10.0. Catholyte conditioning with strong acidic solution prevented increase in pH, and the arsenic has ionic form, as a result, the ionic arsenic was removed by electro-migration from cathode to anode. As a matter of fact, the remaining As in soil still over the regulated level. To meet the regulation criteria further treatment of this soil need to apply.

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