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ORIGINAL PAPER

Electrokinetic removal of chloride and sodium from tidelands

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Abstract A laboratory-scale investigation was carried out to study the characteristics of electrokinetic (EK) movement for separation of salts from tideland. The salinity of tideland material, including the sodium and chloride contents, was investigated as a function of operation time under a constant voltage gradient of 1 V/cm. As the operation period increased, the salinity of tideland material decreased gradually. However, the rate of decrease gradually diminished with an increase in the operation period. The electrical current increased gradually with the operation time. Ten days of electrokinetic operation decreased the electrical conductivity of the tideland material to 65.5% of the initial value. Sodium was removed completely, but the removal efficiency of chloride was 58.5% after 10 days. The lower removal of chloride was due to the formation of complexes with magnesium and calcium. High concentrations of chloride formed chlorine gas in the anolyte, and aqueous chlorine oxidized the circulation tube. The pH distribution after electrokinetic treatment showed a typical shape, and the change in water content was negligible. The results demonstrate that the electrokinetic process is a suitable means to remove salinity from tidelands.

Keywords Tidelands · Electrokinetic remediation · Salinity · Electromigration · Ionic mobility · Solubility

1 Introduction

Korea is surrounded by sea on three sides. The West Sea and the South Sea are shallow with numerous islands, while the East Sea is characterized by deep water and its proximity to the ocean. Because of their Rias physiography caused by sedimentation, the West and South Seas have complex coastlines [1]. The tidelands are wide and the tidal difference is very large. Because of these regional characteristics, in the western and southern parts of Korea, many tidelands have been changed into agricultural land, and on others, there have been land reclamation projects for creating agricultural land and buffer zones for urbanization. In the 50 years preceding 2001, a total of 40,189 ha of tideland were reclaimed under a series of reclamation programs. Initially, the major objective of tideland reclamation was the creation of agricultural land for self sufficiency in food production. Specially, Korean law states that agricultural land should be at least 30% of the reclaimed land. Na^+ and Cl^- are major problematic ions for agricultural lands. However, because of rapid urbanization and industrialization in Korea, a very large number of construction sites were required. Consequently, the major reason for tideland reclamation became the establishment of sites for new cities or for residential, industrial, and/or commercial use.

The reclaimed tidelands contained high concentrations of salts, mainly sodium chloride, which caused numerous

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problems for their use. The salts inhibited the growth of plants because of reverse osmotic pressure. When concrete buildings or structures were built in the tideland, the chloride diffused into the concrete and the reinforced rebar was corroded by the chloride ions [1]. As a result, the high concentration of salts caused problems regarding stability and durability for concrete structures built on the tideland.

The tidelands mainly consist of clay minerals. Transport or movement of heavy metals, salts, nutrients and oxidants through clay pores is very difficult [2–5]. Electrokinetic technology (EK) is a technique that employs low direct current to facilitate the transport or movement of ionic material through porous media [6]. Electrokinetic technology has been applied to control or remediate various inorganic and organic pollutants in soils and sediments [6–14]. Cho et al. [2] reported that salts such as nitrate, chloride, potassium and sodium were removed effectively by EK from saline greenhouse soil. Jia et al. [9] reported that nitrate was transported through the soil by an electrokinetics process against the hydraulic gradient. The results of these studies show that chlorides and nitrates were significantly removed by this technology, but sulfate removal was less effective.

The mobility of ions is a key parameter in determining the performance of the EK process, because electromigration is a major removal mechanism for ions. The effective mobility of ions was calculated by the following equation [2, 7]:

$$u_j = \frac{D_j z_j F}{RT}$$

$$u_j^* = u_j \tau n$$

where, D_j is the diffusion coefficient, u_j is the theoretical ionic mobility, u_j* is effective ionic mobility, z_j is the valence, F is Faraday's constant (96,847 C/mol), R is the universal gas constant (8.3144 J/kmol), T means the absolute temperature, τ is the tortuosity factor (0.2–0.5), and n is the porosity (0.1–0.7).

The effective ionic mobility of chloride (166.3×10^6 cm^2/Vs) is 1.5 times higher than that of sodium (108.9×10^6 cm^2/Vs), which means that the removal of chloride is faster than of sodium. Therefore, EK is accepted as the most suitable technology for separating salts such as chloride and sodium from tideland because the major part of the salts is ionic in form in tidelands, and the soil texture of tidelands are silty clay and more homogeneous than other soils.

In this study, the feasibility of the EK process for the removal of salts from tidelands was investigated in terms of operation time. We analyzed the electrical conductivity (EC) of tidelands and the removal characteristics of ions such as chloride and sodium.

2 Materials and methods

2.1 Characteristics of tidelands

The tideland samples used in this experiment were obtained from the Songdo area in the western part of Korea. They were used without any pretreatment. The target elements were chloride and sodium ions. The initial concentrations of chloride ions, sodium ions and EC were 3551.7, 3922.5 mg/kg, and 20.74 dS/m, respectively. But the soluble calcium was not detected in the initial soil. The EC and concentration of NaCl were higher than Korean southern coast tideland even though it was different by seasonal wind or crossed by period by a large mountain chain [1]. The tideland sample consisted of 48.8% of silt and 51.2% of clay. Table 1 shows the physico-chemical properties and initial condition of the tideland sample used in this experiment.

2.2 EK cell

The diagram of the anolyte circulation system used in this experiment is shown in Fig. 1. The EK cell consists of electrodes, a soil compartment, electrolyte chambers and an electrolyte reservoir. The dimensions of the soil compartment were 4 cm × 4 cm × 20 cm. The electrolyte chambers were located at both sides of the soil compartment (4 cm × 4 cm × 4 cm) and electrodes were installed at the ends of the electrolyte chambers. Both the anode and the cathode consisted of graphite electrodes. Filter paper was placed between the soil compartment and the electrolyte chambers to prevent the loss of soil into the chambers. The anolyte solution was circulated into the anolyte reservoir by a peristaltic pump at a flow rate of 2.4 mL/min to reduce the hyperaccumulation of chloride and chlorine gas in anolyte

Table 1 Physico-chemical properties and initial condition of soil

Characteristic	Value
pH	6.43
EC (dS/m)	20.7
Organic content (wt%)	3.45
CEC (meq/100 g)	10.53
Water content (wt%)	31.9
Particle size distribution (wt%)	
Sand	0
Silt	48.8
Clay	51.2
Initial soluble concentration (mg/kg)	
Cl^-	3551.7
Na^+	3922.5
Ca^{2+}	N.D.
Mg^{2+}	243.75

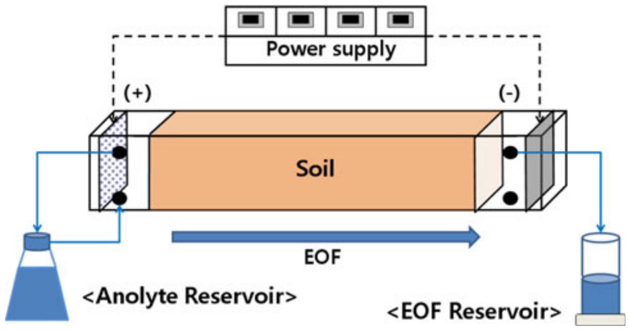

Fig. 1 The schematic of electrokinetic experimental system

and a bottle was connected to the cathode chamber to collect the electroosmosis flow (EOF).

2.3 EK experiments

All experiments were executed under a constant voltage gradient of 1 V/cm, tap water was used as the anolyte, and the duration of the experiments was 5, 8, 10, and 15 days. The experiments focused on the effect of operation time. First, the tideland sample was placed in the soil compartment. The cathode and anode chambers were then filled with tap water to just below the overflow level and the anolyte was circulated in the anode reservoir by a peristaltic pump. The EOF that overflowed the cathode chamber was collected and measured every day.

Under a constant voltage gradient, the current was measured at desired time intervals. At the end of the tests, the soil compartment was divided into ten equal sections (each 2 cm in length), and each section was analyzed.

2.4 Analysis

Soil samples were dried at 105 °C for 5 h and pulverized. A mass of 10 g of dried soil was mixed with 50 mL of distilled water for 1 h and then filtered out. The filtrate was used to analyze EC, pH, salinity, and ion concentrations such as Cl^-, Ca^{2+}, and Na^+. The pH and EC were determined by a pH/ISE meter (Istek 735P, Korea) and a conductivity meter (Istek 455C, Korea). ICP-MASS (Agilent, USA) equipment and ion chromatography (Futecs, Korea) were used for the analysis of cations and anions.

3 Results and discussion

3.1 Variation with time of soil pH and current density

The variations in pH for the soil section after the completion of the EK experiments are presented in Fig. 2. The electrolysis reaction at the electrodes produced hydrogen and hydroxide ions at the anode and the cathode, respectively [2, 3, 11–14]. The hydrogen ions produced at the anode were transported towards the cathode by electro-migration and electro-osmotic flow. Also, the hydroxide ions generated at the cathode moved towards the anode. However, since the velocity of hydrogen ions is 1.8 times higher than that of hydroxide ions, the pH decreased around the anode, but increased near the cathode. With time, the acid and base fronts moved gradually towards the cathode and the anode, and consequently, there was a general pH distribution in the EK treatment of tideland material.

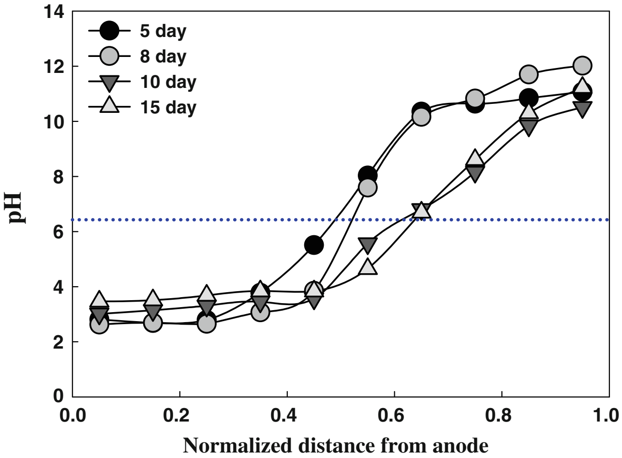

Fig. 2 The variation of pH in soil section after EK treatment

Figure 3 shows the variations with time of electrical current density for each experiment. The desorption of ions from the soil surface increased as the electric current flowed through the soil compartment. The increase in the number of desorbed ions decreased the electrical resistance of the soil. So the current density increased gradually until 100 h. After that, the ion removal increased because of electromigration or electro-osmotic flow, and the total number of ions balanced out in the soil compartments. After that, the change in current density was negligible. Cho et al. [2] reported similar trend of current density in the electrokinetic restoration of saline soil. Each experiment showed slightly different trends because of heterogeneity not only in the tideland materials but also in the exchangeable ions even though the tideland mixed well before experiment. The linear increase in the current density implies that the expenditure of electrical energy increases in proportion to the square of the operation time. The gradual increase in current density makes the EK process for removing salts from tideland very expensive.

3.2 Electrical conductivity change in the soil section after EK experiments

Generally, EC of tidelands is very high due to an abundance of soluble anions and substitutable cations, and the major

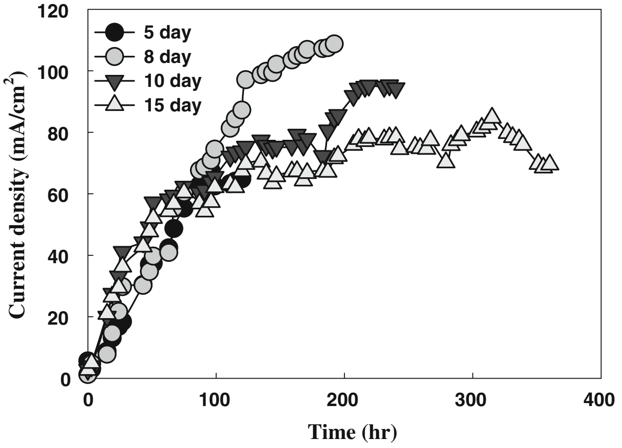

Fig. 3 The variation of electrical current density during experiment

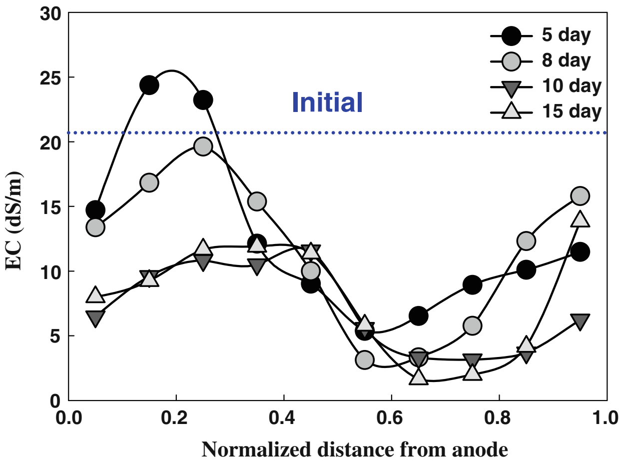

Fig. 4 The variation of electrical conductivity (EC) in soil section after EK treatment

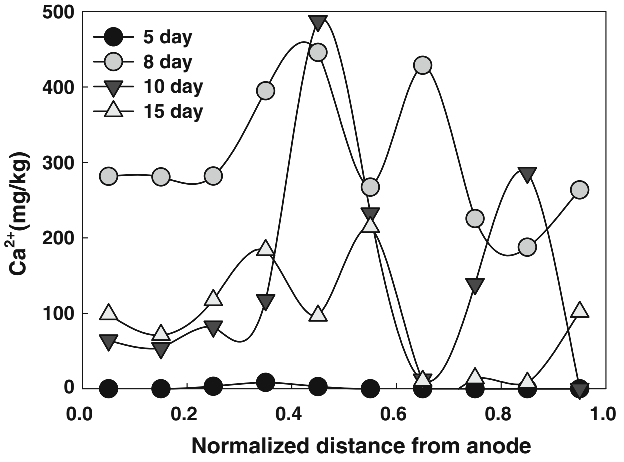

Fig. 5 The calcium concentration in soil section after EK treatment

Table 2 Summary of electrokinetic treatment

	Duration (days)			
	5	8	10	15
Residual EC (dS/m)	12.6	11.6	7.2	8.1
Removal efficiency (%)	39.2	44.3	65.5	61.2
Energy consumption (kWh/m^3)	96.3	266.1	316.9	463.5
Effective removal ((dS/m)/(kWh/m^3))	0.084	0.034	0.043	0.027

constituents of EC are chlorides and sodium. The variations in the EC in the soil section after the EK treatments are presented in Fig. 4. When a constant voltage was applied to the soil compartment, the positively charged sodium ions and the negatively charged chloride ions accumulated at each electrode chamber and electrode section. As shown in Fig. 4, after 5 days, the EC of the anode region increased slightly while that of the cathode region decreased. As the operation time increased, the EC in the anode and cathode regions gradually decreased. The cause of the initial increase of the EC in the anode region was that the mobility of chloride ions was 1.5 times higher than that of sodium ions. Soluble calcium ions were not detected in the original tideland sample. The variation of calcium in the soil section after EK treatment is presented in Fig. 5. The detection of calcium after the EK treatment was due to the pH change in the tideland material. The acidic or basic conditions enhanced the desorption of calcium. The average calcium concentration increased for 8 days, after which it decreased. The highest concentration of calcium was observed in the middle section (0.4–0.7 of normalized distance). The leached calcium ion by acid front was moved toward cathode by electro-migration and EOF. At the middle section, the soil pH was changed from acidic condition to alkaline condition, which caused to precipitate calcium as a calcium hydroxide. Soil in the middle section was relatively harder than in the other sections after EK treatment. Table 2 shows the reduction in EC of soil after EK treatment. EC decreased gradually for up to 10 days, and then increased slightly. The increase in EC was related to the increase in soluble cations, especially calcium.

3.3 Distribution of chloride and sodium

Figure 6 shows the variation of salt concentration in the soil section after the EK treatment. Under the electric field, the chloride moved towards the anode. Some chloride could have been converted into chlorine gas during the electrolysis of water at the anode as follows:

$$2Cl^- \rightarrow Cl_2(g) + 2e^-.$$

A green color was observed in the anolyte and the circulation tube which changed into white because of the oxidation reaction by chlorine gas. High concentration of chloride in the anolyte solution may inhibit the removal of

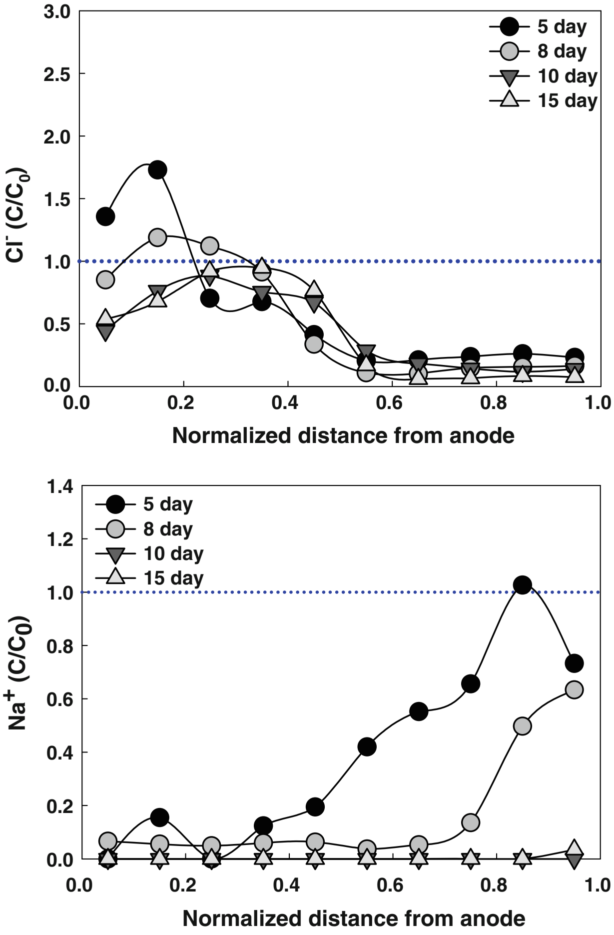

Fig. 6 The distribution of chloride and sodium after EK treatment

chloride from the tideland material because of back diffusion into the soil section from the anolyte solution. In the case of sodium, it was desorbed from the soil surface by the ion exchange reaction between the sodium adsorbed onto the soil surface and hydrogen ions transported by electromigration. The desorbed sodium was transported towards the cathode. Sodium accumulated at the cathode region, but it was removed rapidly from the soil section to the catholyte chamber. It can be expected that the removal efficiency of chloride be higher than that of sodium due to its higher ionic mobility, however, the actual removal efficiency of sodium was higher than that of chloride ions. The sodium ion is inert and more than 97% of sodium exists as the ionic form of Na^+. The ionic sodium was removed by electromigration and electro-osmotic flow. However, the chloride formed complexes with magnesium and calcium such as $[MgCl]^+$ or $[CaCl]^+$. The complexes having positive charges, moved towards the cathode, that is, in the direction opposite to that of chloride migration. Also, some chlorides form a complex with sodium as dissolved [NaCl]. Based on the simulation using MINTEQ, some chlorides form a complex with sodium as dissolved [NaCl]. The complex is a non-charge species, and it cannot be migrated by an electric field, which is one explanation for the lower removal of chloride compared to sodium. Another reason is related to the removal mechanism and the direction of the mechanism. As is well known, sodium was removed by electromigration and electro-osmosis and the direction of both mechanisms is exactly the same and does not precipitate with hydroxide ion [2]. In the case of chloride, however, the direction of electromigration is towards the anode, but the direction of electro-osmotic flow is towards the cathode. Even though the major removal mechanism of chloride is electromigration, the transport of chloride is inhibited by the electro-osmotic flow.

3.4 Energy consumption during EK experiments

The cumulative energy consumption is shown in Fig. 7. With increasing operation time, the cumulative energy consumption was proportional to the square of the operation time. Under a constant voltage gradient, the current in the soil compartment plays a role in determining total energy consumption. The current density linearly increased with the operation time, and thus the energy expenditure during the desired time interval also increased with the operation time. As a result, the total energy consumption increased dramatically with the operation time. Especially, the energy consumption increased significantly in the initial stage of the experiment because of the rapid increase in current density. Effective removal efficiency was calculated by dividing reduction of EC into energy consumption. The effective removal efficiency dramatically decreased in the 5- to 8-day period, and then increased slightly at 10 days, however, the value at 15 days decreased to one-third of the value for 5 days. The effective removal efficiency implies that a 10 day-period is more energy-effective than a 15-day period. As the results of effective

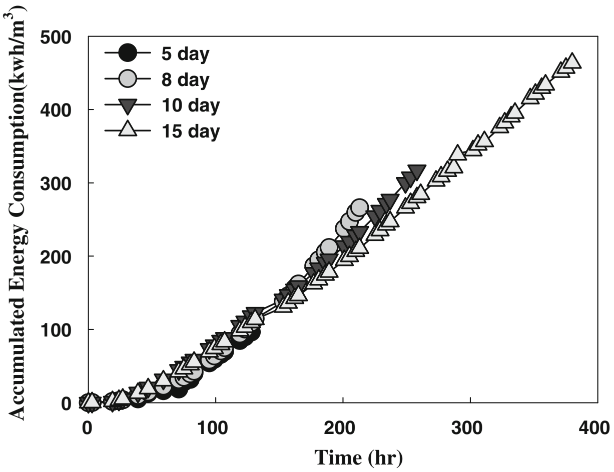

Fig. 7 Accumulated energy consumption during EK treatment

removal efficiency with Na^+ and Cl^- considering energy expenditure, the 10-day operation was more effective in removing chloride and sodium from tideland material than the 15-day operation because there was no significant difference of removal efficiency between the 10 and 15 days shown in Fig. 6.

4 Conclusions

Electrokinetic experiments to remove chloride and sodium from tideland material were carried out in the laboratory. Under a 1 V/cm constant voltage gradient, the removal efficiencies of sodium and chloride after 10 days were 100 and 58.5%, respectively, after which they decreased slightly because of the increased desorption of exchangeable cations. Sodium was removed by electromigration and electro-osmotic flow towards the cathode, but chloride transport due to electromigration and electroosmosis took place in the opposite direction. After EK treatment, soluble calcium was observed in the soil section because the desorption of calcium was significantly influenced by the soil pH. Soil EC was lowered to 65.5% of the initial value after 10 days, and then increased slightly. After 10 days, the removal efficiency slightly decreased and energy consumption increased. Consequently, an optimum time exists for the removal of chloride and sodium by electrokinetic treatment of tideland material.

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