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중금속으로 오염된 점성토의 동전기영동에 의한 침강 거동에 관한 연구

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Electrophoretic Particle Movement in Suspension Considering the Gravitational Settling and Sedimentation of Clayey Soil

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ABSTRACT

Contaminated sediments more than 30 million/m^3 is generated from dredging work for harbours and coastal maintenance in Korea. Approximately 300 million/m^3 of sediments is dredged to deepen harbours and shipping lanes in US and of which 3~12 million/m^3 is highly contaminated. Although much is known about technologies for the remediation of heavy metal contaminated soil, much less is known about the treatment of contaminated sediment. In general, negatively charged fine particles will migrate towards positively charged system of electrodes under the influence of electrophoresis. However, the electrically induced migration of colloidal particles contaminated with heavy metals may be hindered by the positively charged heavy metal contaminants adsorbed onto the soil surfaces depending on the contamination level. This paper demonstrates settling behaviour of clayey soil by comparison with electrophoretic particle movement under the effects of heavy metal contamination, applied electric field strength, and its polarity changed by the electrode configuration.

Key words : clayey soil, electrophoresis, heavy metal, precipitation, sedimentation

요 약 문

다공질매체를 통한 미세 입자의 이동은 고함수비 오염준설토의 탈수 및 오염물질의 제거와 같은 지반의 안정화 처리 및 토양의 정화에 있어서 중요한 메커니즘이 되고 있다. 일반적으로 음전하를 갖는 미세 입자들은 동전기영동의 영향으로 양극(+)방향으로 이동하게 된다. 그러나 중금속과 같은 양전하를 띤 오염물질로 흡착된 미세 입자의 경우 중금속의 종류 및 오염도에 따라 동전기영동에 의한 움직임은 제약을 받을 수 있다. 본 연구에서는 자연상태의 미세 토립자의 침강거동 및 직류전류의 영향 하에서 발생되는 동전기영동에 의한 침강 거동에 대하여 조사하였다.

주제어 : 점성토, 동전기영동, 침강, 중금속, 침전

1. Introduction

Cadmium, copper, lead, mercury, nickel and zinc are considered as the most hazardous heavy metals, and the decontamination of sediments has recently received the highest priority in US (Mulligan et al., 2001a).

Approximately 300 million/m^3 of sediments is dredged to deepen harbours and shipping lanes in US and of which 3~12 million/m^3 is highly contaminated (US EPA, 1999). Approximately 10% of the sediments in underlying waters in US are contaminated, which will require removal or remediation of sediments that are contaminated within 10

years.

Contaminants tend to adsorb the smaller particle sizes due to higher surface area to volume ratios and higher organic matter contents, and metals also have been shown to associate with sulfides (Zagula and Beltinger, 1993). The properties of sediments can differ significantly from soils, and therefore, technologies that work for soils may not be as efficient for sediments (Mulligan et al., 2001b).

The fundamental electrokinetic (EK) processes are transport of ionic species and water through porous media based on the phenomena known as electromigration (EM), electrophoresis (EP), and electroosmosis (EO) along with other related effects including dissolution/precipitation, electrolysis, and the resultant acid/base fronts (Acar and Alshawabkeh, 1993; Mitchell, 1993; Yeung, 1994; Rødsand et al., 1995). A number of field-scale and laboratory-scale studies for the EK remediation to date have reported encouraging results of removal efficiencies for metals and soluble organic pollutants on clayey soils; the EK processes removed greater than 80% of heavy metals and organic contaminants (Lageman, 1993; Probstein, 1994; Acar et al., 1995).
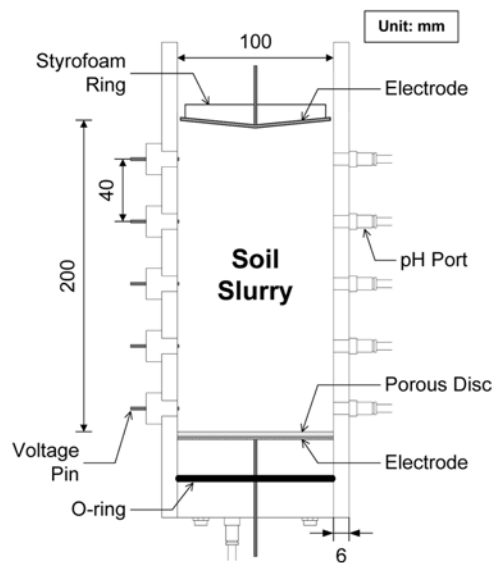
The purpose of this paper is to investigate several variables affecting the fundamental sedimentation processes, such as the effects of intensity of the applied electric field,

electrode configuration, and heavy metal contamination level on the settling behaviour of contaminated dredged soft materials under the influence of EK processes. The characteristic features of surface settling rate, heavy metal removal, correlations of electric current, slurry pH, and voltage gradient in the presence of a DC electric field are examined and evaluated.
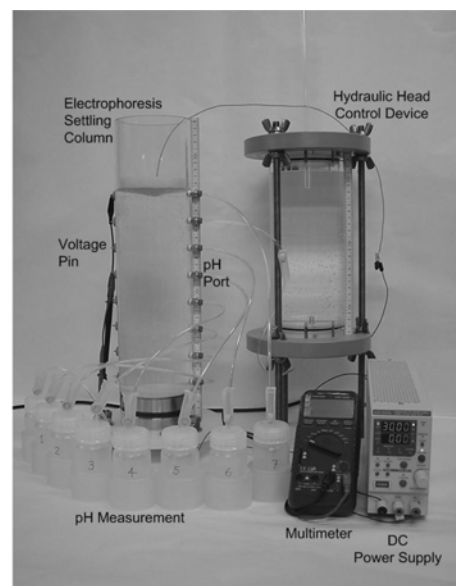
2. Apparatus and Procedure

2.1. Apparatus

A schematic diagram of electrophoresis settling column (ESC) used in this experimental programme is presented in Fig. 1. The column of 100 mm diameter and 300mm long was constructed from a clear acrylic tube, equipped with each of 5 voltage pins and pH ports along the side of the wall. The voltage pins and pH ports were embedded in contact with the slurry sample at regular intervals in order to measure local voltage and pH gradient within the specimen. An end cap was inserted into the column with an 'O'-ring sealant installed between the column and the end cap in order to prevent any leakage of fluid during tests. A disc shape stainless steel electrode was located at the bottom with a cone shape floating electrode on the slurry surface. Thus, the gases generated at the electrode

Fig. 1. The electrokinetic apparatus.

floating on the surface move along the surface gradient of 3.5 degrees and escape into the atmosphere.

2.2. Materials

A number of bench-scale laboratory tests were carried out using kaolin clay in order to investigate the effects of electrophoresis on the settling behaviour of charged clay particles in suspension. Kaolinite is relatively inert compared to the other active clay minerals, and the electrochemical and mechanical properties are well known. The chemical content and typical properties are presented in Table 1, and the experimental details are summarised in Table 2.

2.3. Procedure

Initial slurry densities were prepared by mixing the required mass of soil with de-aired water in an electrically operated mixer and measured using a densimeter (PAAR DMA35) accurate to ± 0.001 g/cc. For the metal contaminated slurry, zinc nitrate (i.e. $Zn(NO_3)_2 \cdot 6H_2O$) powder was added to the tap water for making 700 mg/L zinc solution, which was then mixed with kaolin clay. The mixing period was approximately 2 hours before the start of each test to promote a uniform mixture. The slurry was then introduced into the testing cell and the monitoring begun. A constant electric field, rather than a constant electric current, was applied to the soil specimen. The

constant field better simulates the field condition and also significant power loss may occur due to the increase of soil resistance by the depletion of ions resulting in the premature termination of experiment (Yeung et al., 1997). New electrodes and tubing were used for each test to avoid any cross-contamination between the tests. The ESC and valves were soaked in a dilute acid solution for 24 hours, and thereafter rinsed with de-ionised tap water. The key measurements were surface settlement, electric current, local voltage gradient, pH, and zinc concentration.

2.4. Chemical analysis

The overlying water was collected in regular interval during each experiment, and the sedimented soil specimen was sectioned into five after the completion of each test for the chemical analyses. The different soil sections were acid digested to collect the pore fluid for the determination of total zinc concentration and the removal rates of contaminants from the soil specimen. The zinc concentration was measured using inductively coupled plasma (ICPS-8000 Shimazu).

3. Results and Discussion

3.1. Settling behaviour of clayey particles in suspension

Fig. 2(a) shows surface settlement versus time results for case1 and case4. As seen, the amount of settlement under gravity for about 10 hours was 57% (110 mm), and the settling rate of zinc contaminated slurry was much faster than that of case1 (i.e. the sample height becoming approximately half after 1 hour of gravitational settling) and the amount of sedimentation became 70% after about 10 hours of gravitational sedimentation. A typical example of gravitational settling behaviour can be seen from the

Table 1. Summary of kaolin properties

Chemical Properties	Content (%)	Typical Properties	Value
SiO_2	45.4	Average Particle Size	0.4 μm
Al_2O_3	38.5	325 Mesh Residue	0.01%
K_2O	0.1	pH	6.0~8.0
Fe_2O_3	0.5	Specific Gravity	2.58
MgO	0.02	Moisture Content	1.0 % max.
Na_2O	0.2	Oil Absorption	40~45 g/100 g

Table 2. Experimental conditions

Test Series	Electrode Configuration	Electrolyte Solution	Voltage Gradient	Slurry pH	Processing Time
Case1	–	Tap	–	6.7	12 hr
Case2	Cathode Top	Tap	200 V/m	6.7	12 hr
Case3	Anode Top	Tap	200 V/m	6.7	30 hr
Case4	–	700 mg/L Zn	–	5.2	11 hr
Case5	Anode Top	700 mg/L Zn	200 V/m	5.2	8 hr
Case6	Anode Top	700 mg/L Zn	100 V/m	5.2	9 hr

surface settling curve indicated by case1 (Kynch, 1952; McRoberts and Nixon, 1976; Bowden, 1988; Lee, 2000; Shang, 2001), which includes an initial stage of stability followed by a period of relatively rapid settling, and finally a long period of slow settling at a decreasing rate (see Fig. 3). Different electrolyte solution may have induced faster settling processes due to the contract of diffuse double layer as indicated by case4.

Fig. 2(b) shows EP settling behaviour under different polarities by comparison with gravitational sedimentation: the anode at the bottom and the cathode at the slurry top (i.e. cathode top condition) for case2 and the cathode at the

bottom and the anode at the slurry top (i.e. anode top condition) for case3. Note that the electric field was applied to each of the sample for EK sedimentation after the completion of initial period of stability when the slurry height became approximately 185 mm. As shown by case2 and case3, the electrically induced surface settlements for the first 1 hour are almost identical to the gravitational settling processes and thereafter the EP settling rate became relatively faster during the hindered settling stage compared to the gravitational one. For about 4 hours of the EK sedimentation, the slurry height became approximately 40mm and no more surface settlement was observed. As
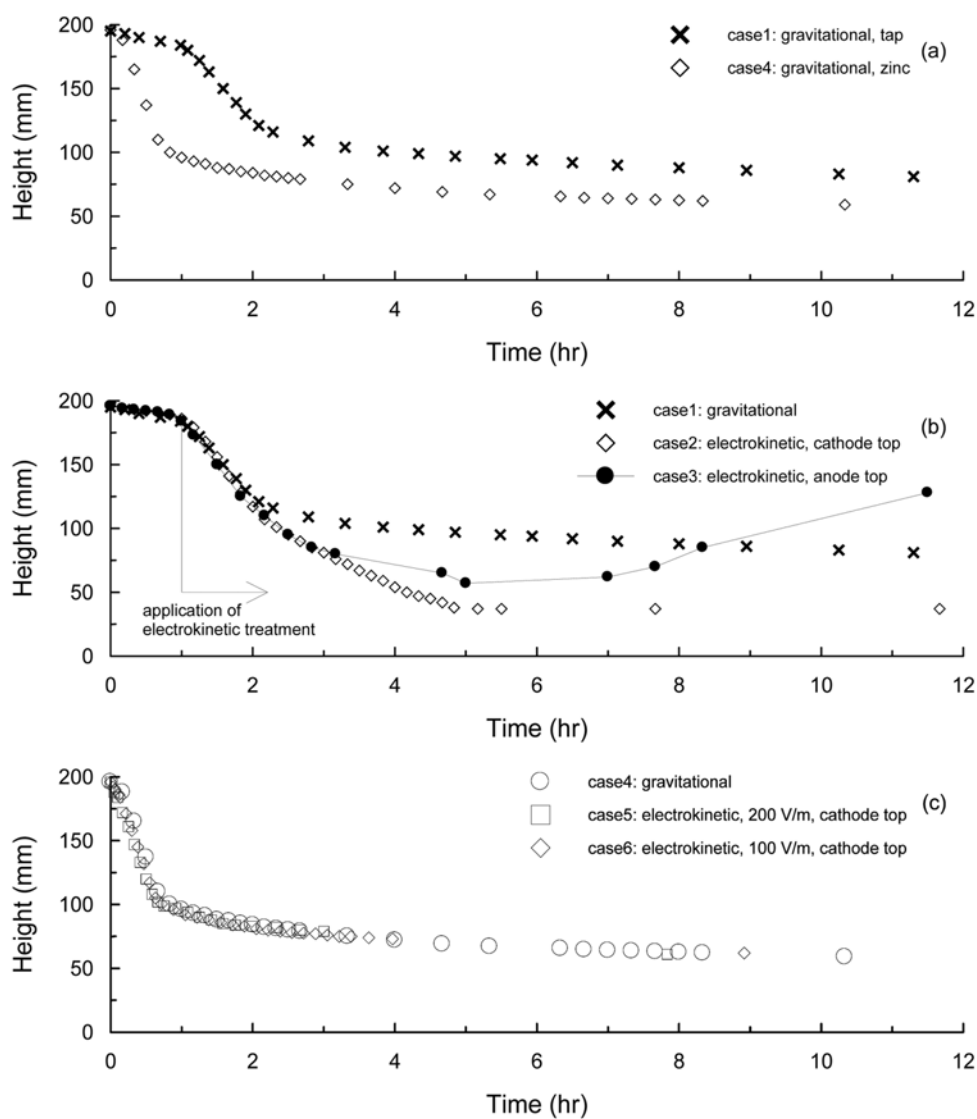

Fig. 2. Surface settlement vs. time, case1 to case6: (a) effects of electrolyte solution; (b) effects of electrode configuration; (c) effects of applied electrical intensity.

shown by case2 and case3, the electrically induced surface settlements for the first 1 hour are almost identical to the gravitational settling processes: no remarkable effect of electrophoresis during the free settling stage. It is interesting to note that the EP settling rate became relatively faster during the hindered settling stage compared to the gravitational one. It seems that the EP particle movement starts during the hindered settling stage.

It was expected from case3 that the EP settling rate under the anode top condition would be significantly reduced by the upwards particle movement due to the effects of electrophoresis. However, the EP settling rate was almost identical to that under the cathode top condition for the first 2 hours, and thereafter the electrophoretic settling rate became relatively slower, followed by the surprising upwards movement of slurry surface during the hindered settling and consolidation stage. It appears that the EP effects start to occur in the hindered settling stage when the negatively charged colloidal particles have complicate electrochemical interactions.

Unlike case1, case2 and case3, the slurry samples used for case4, case5 and case6 were contaminated with zinc as shown in Fig. 2(c). The gravitational settling curve obtained from test case4 shows that the settling rate is relatively faster in the initial and free settling stages by comparison with the settling curve observed from case1 as

already noted in Fig. 2(a). As seen from case4, case5 and case6, the effects of electrophoresis were not observed with the slurry sample contaminated with zinc. The addition of zinc might have changed the surface charge of soil particles (e.g. loosing their negative charges), so that the EP particle movements appear to be hindered during the whole processes.

3.2. Variation of pH and heavy metal removal

The final pH profiles after the completion of settling processes are shown in Fig. 4. The initial pH of tap water was about 7.5, and the pH value for the kaolin slurry became approximately 6.7 after mixing process. In the case of zinc contaminated kaolin slurry, the pH value became lower to about 5.2: the initial total zinc concentration of kaolin slurry being approximately 700 mg/L.

The variations of pH during and after EK soil processing are dependent on the electrode configuration as shown in Fig. 4(a). As seen from case2 conducted under the cathode top condition, the pH in the upper part (i.e. overlying water) increased up to approximately 11 and that in the lower part (i.e. sediment bed) decreased to less than 5 after EK treatment. However, the pH profile of slurry sample conducted under the anode top condition (see case3) represents the opposite pH distribution compared to that observed from case2 (see Fig. 4(a)). A similar pattern of decreasing pH near the anode and the increasing pH near the cathode can also be seen from the pH profiles of zinc contaminated slurry samples as shown in Fig. 4(b).

The pH decreased throughout most of the soil sediment, ranging between 2 and 4, and the pH near the anode became less than 2.5 after the EK process. It appears that the H^+ ions produced in the base chamber entered into the sample and advanced half way up the soil, producing an acid front, and base front created by OH^- ions produced at the cathode remained in the cathode region during the EK process, resulting in soil acidification occurring in the majority of the soil specimen.

The pH changes begin to occur from the region close to the electrodes as a result of electrolytic reactions at the surface of electrodes: the acidity from the anode and the alkalinity from the cathode. Thus, the resultant ion migrations (i.e. acid/base fronts) develop a region of high
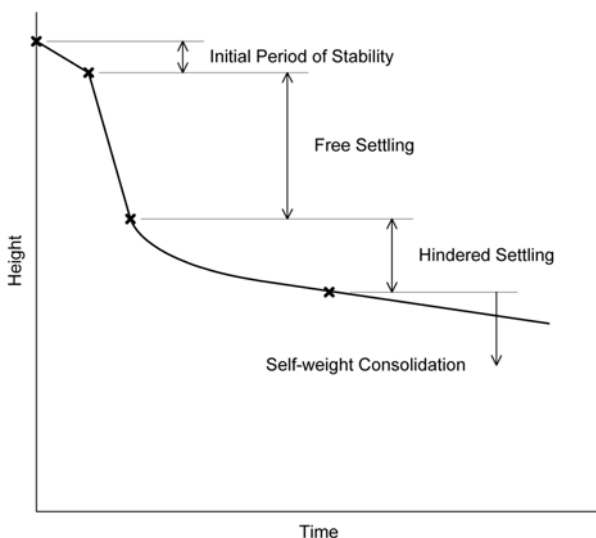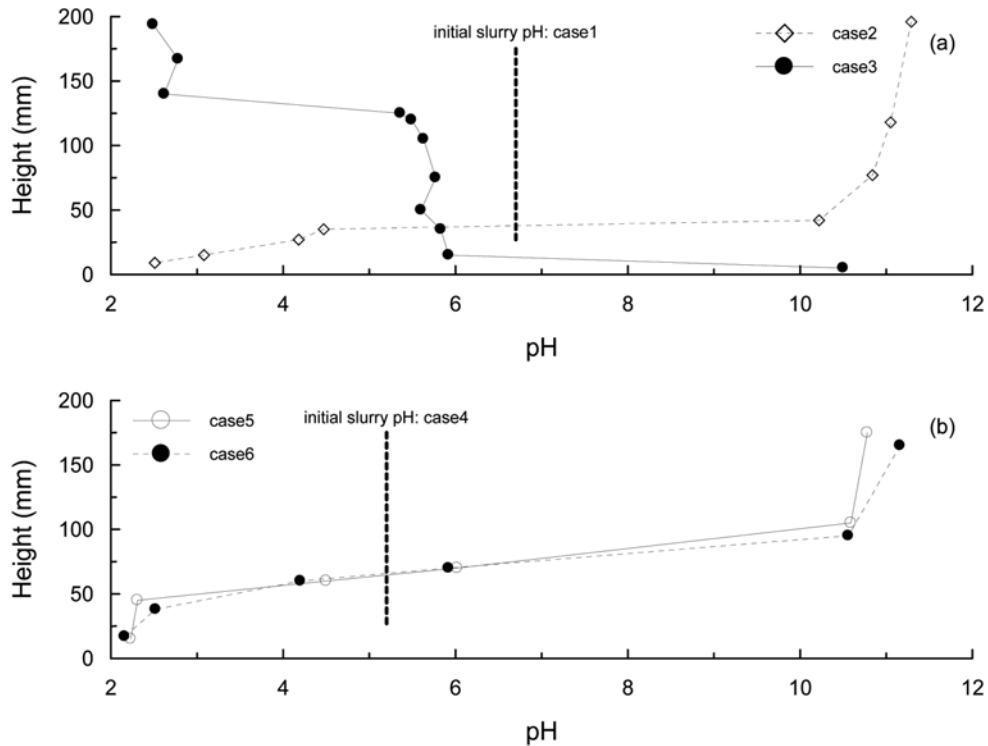

Fig. 3. Schematic of settling stage.

Fig. 4. pH vs. height, case1 to case6: (a) case2 – cathode top, case3 – anode top; (b) case5 – 200 V/m, case6 – 100 V/m.

resistance due to the neutralisation, resulting in the variation of electric current and local voltage gradient. It appears that the relatively higher mobility of the acid front may be due to the EO water flow from the anode towards the cathode reinforcing the migration of the H^+ ions but retarding OH^- ions.

3.3. Electric current and voltage gradient

Fig. 5 shows electric current versus time results for case2, case3, case5 and case6. The initial value of electric current under the fixed voltage condition was approximately 13 mA under the applied voltage gradient of 200 V/m as seen from case2, which gradually increased for about 4 hours due to electrolytic reactions. By that time, the advancing acid front from the anode may have reached to the surface of slurry sample, and met the base front from the cathode. Thus, the electric current started to decrease after about 4 hours due to the neutralisation at the slurry surface. On the other hand, the electric current continuously decreased under the anode top condition (see case3) during EK treatment. As case3 was conducted under the anode top condition, the immediate formation of

neutralisation can be expected from the beginning of test due to the high pH environment, resulting in the reduction of electric current on the EK treatment as shown in Fig. 5(a).

Fig. 5(b) shows a general pattern of decreasing electric current passing through the slurry sample as a function of time. The decreasing rate of electric current appears to be related to the initial slurry pH and the applied electric field strength. For example, the electric current of zinc contaminated slurry sample quickly increased up to 260 mA under the applied voltage gradient of 200 V/m, and thereafter sharply decreased to 80 mA within 3 hours of the EK treatment. On the other hand, the initial electric current under the applied voltage gradient of 100 V/m was about half of that under the voltage gradient of 200 V/m. The reduction of electric current under a constant (i.e. fixed) applied electric field implies the increase in resistance due to the neutralisation in the system as already noted in the pH profiles. The pH of zinc contaminated slurries for case5 and case6 was low (i.e. acidic), so that the hydroxyl ions generated by electrolysis at the cathode could have immediate reactions with the existing positive
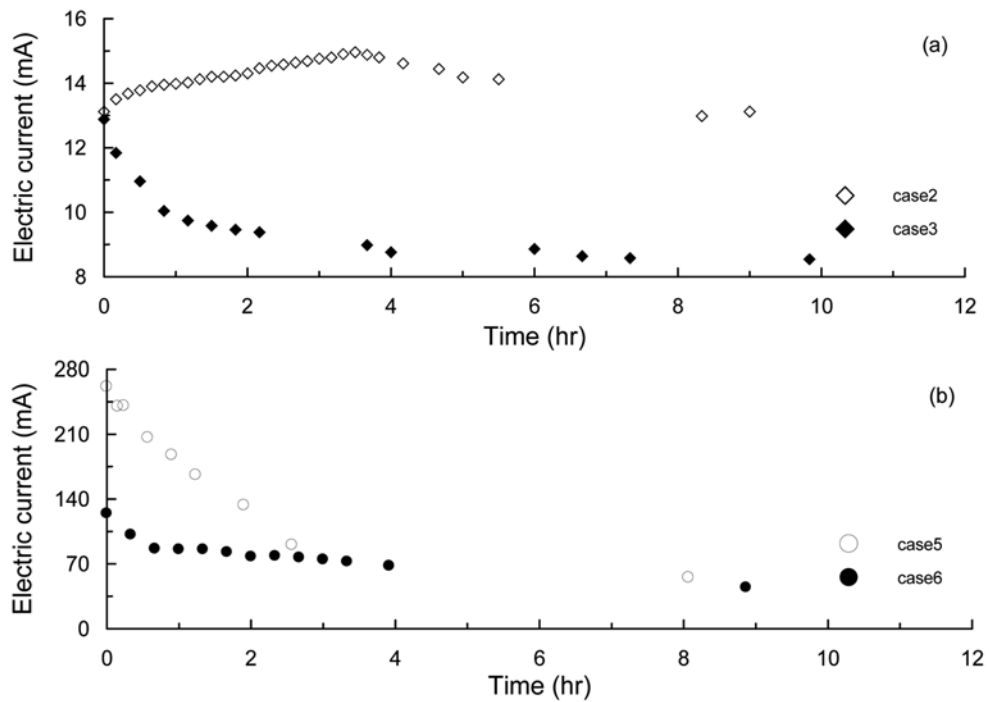
Fig. 5. Electric current vs. time: (a) case2 – cathode top, tap, case3 – anode top, tap; (b) case5 – 200 V/m, zinc, case6 – 100 V/m, zinc.
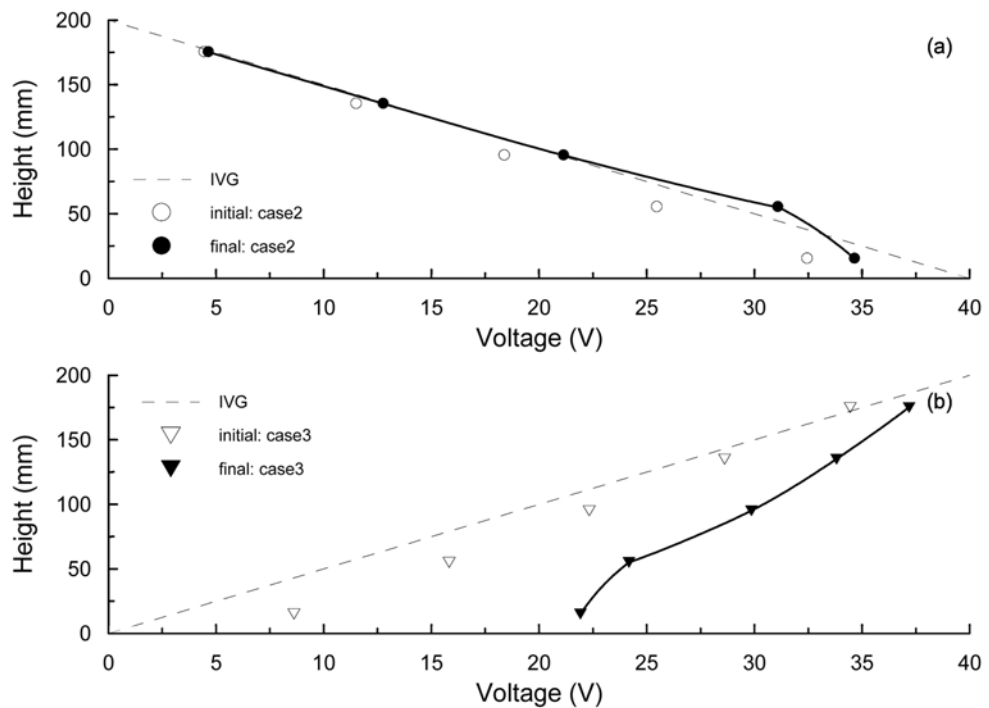

Fig. 6. Voltage gradient profiles: (a) case2 – cathode top, 200 V/m, tap; (b) case3 – anode top, 200 V/m, tap.

ions (e.g. Zn^{2+}) in the acidic overlying solution, resulting in the formation of neutralisation zone and zinc precipitation in the region close to the cathode.

The variation of local voltage gradients throughout the slurry sample are shown in Figs. 6 and 7 as a function of time and distance. The initial voltage gradients for all tests
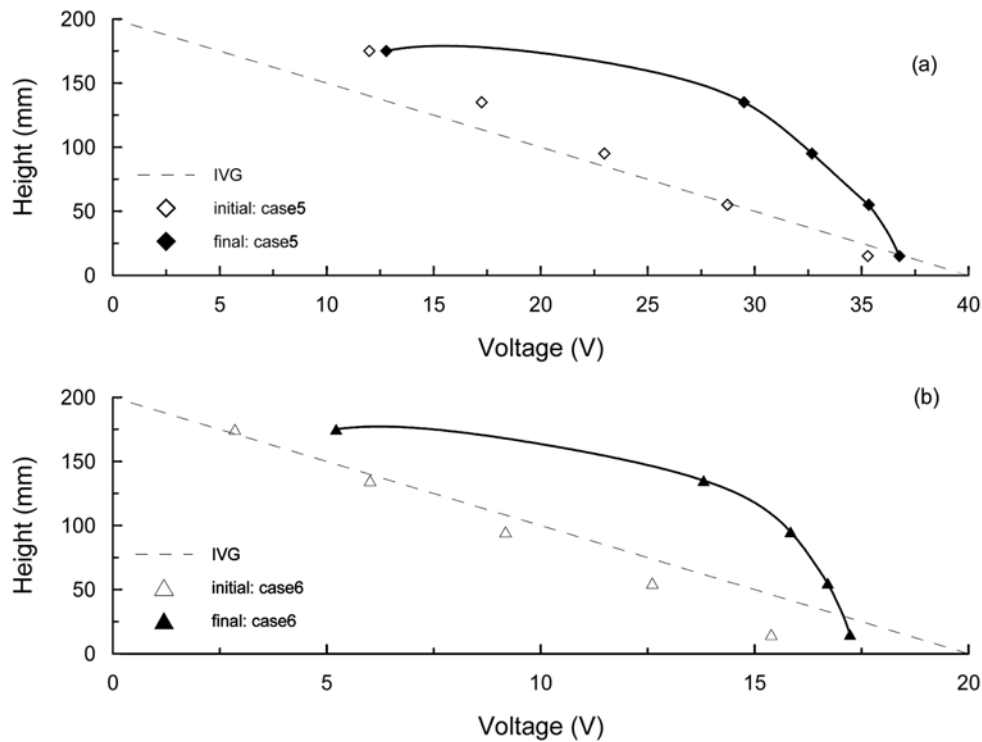
Fig. 7. Voltage gradient profiles: (a) case5 – cathode top, 200 V/m, zinc; (b) case6 – cathode top, 100 V/m, zinc.
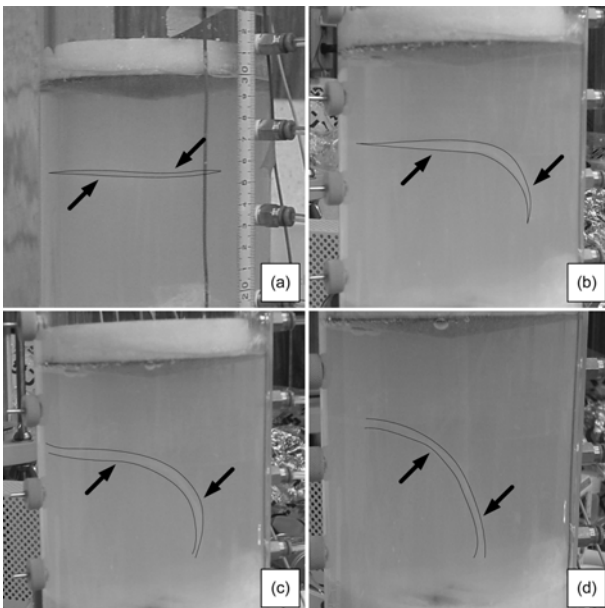

Fig. 8. Zinc precipitation during EK treatment: (a) t = t₁; (b) t = t₂; (c) t = t₃; (d) t = t₄.

immediately after the application of electric field are approximately linear, by comparison with the idealised voltage gradients (IVG), indicating the ionic distribution of the slurry is fairly uniform throughout the specimen. The electrical potential difference rose in the cathode region due to the reactions of acid/base fronts within the first few hours, which remained rather constant throughout the rest of the test depending on the variation of pH.

3.4. Heavy metal removal

It was found from ICP analysis that metal contaminants in a dilute suspension can be removed by EK soil processing; zinc removal efficiency was up to 80%. However, most of the migrating metal contaminants appear to precipitate in the overlying solution due to the neutralisation occurring in the high pH environment, and settle down on the surface of slurry sample as shown in Fig. 8.

4. Summary and Conclusions

The effects of electrophoresis during EK treatment in a dilute suspension have been demonstrated by the laboratory column tests under different electric field strength and polarity. From the experimental investigations, the followidsandng conclusions were achieved:

(1). The effect of electrophoresis was significant during the hindered settling stage after the free settling due to the influence of electrochemical interactions between the charged clay particles.

(2). The electrophoretic particle movement could be controlled by changing the slurry density and pH, depending on the soil properties.

(3). The electrically induced sedimentation was greater in magnitude and faster in rate than that under the gravitational sedimentation.

(4). The formation of acid/base fronts due to electrolytic reactions under the influence of electrokinetics has been demonstrated experimentally and identified by the measurement of pH during and after EK treatment.

(5). It was found from ICP analysis that metal contaminants in a dilute suspension can be removed by EK soil processing: the removal efficiency of zinc up to 80 %. However, most of the migrating metal contaminants appear to precipitate in the overlying solution due to the neutralisation occurring during EK processing.

Acknowledgements

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