



Impact of carbonate on the efficiency of heavy metal removal from kaolinite soil by the electrokinetic soil remediation method

V.R. Ouhadi^{a,*}, R.N. Yong^b, N. Shariatmadari^c, S. Saeidijam^a, A.R. Goodarzi^a, M. Safari-Zanjani^a

^a Faculty of Engineering, Bu-Ali Sina University, Hamedan, Iran

^b RNY Geoenvironmental Research, North Saanich, Canada

^c Iran University of Science and Technology, Tehran, Iran

ARTICLE INFO

Article history:

Received 4 December 2008

Received in revised form 11 August 2009

Accepted 12 August 2009

Available online 20 August 2009

Keywords:

Electrokinetic
Electro-osmosis
Soil remediation
Carbonate
Kaolinite

ABSTRACT

While the feasibility of using electrokinetics to decontaminate soils has been studied by several authors, the effects of soil composition on the efficiency of this method of decontamination has yet to be fully studied. This study focuses its attention on the effect of “calcite or carbonate” (CaCO_3) on removal efficiency in electrokinetic soil remediation. Bench scale experiments were conducted on two soils: kaolinite and natural-soil of a landfill in Hamedan, Iran. Prescribed quantities of carbonates were mixed with these soils which were subsequently contaminated with zinc nitrate. After that, electrokinetic experiments were conducted to determine the efficiency of electrokinetic remediation. The results showed that an increase in the quantity of carbonate caused a noticeable increase on the contaminant retention of soil and on the resistance of soil to the contaminant removal by electrokinetic method. Because the presence of carbonates in the soil increases its buffering capacity, acidification is reduced, resulting in a decrease in the rate of heavy metal removed from the contaminant soil. This conclusion was validated by the evaluation of efficiency of electrokinetic method on a soil sample from the liner of a waste disposal site, with 28% carbonates.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

In geo-environmental engineering projects the application of electrokinetics for contaminant removal in soils involves the application of direct electrical current (DC) with low potential and intensity on two electrodes in a contaminated soil. When electrical potential is applied across a wet soil mass, cations are attracted to the cathode and anions to the anode. In order to be mobile in the electric field, heavy metals must be present in the dissolved phase of the soil. The desorption and mobilization of most heavy metals during the remediation process is catalyzed by an acidic front that develops from the anode end of the soil. When the acidic front reaches all through the soil, the remediation action is complete [1]. Recently, electrokinetics has been employed successfully for the removal of different types of heavy metals, including lead [2], caesium [3], copper [4,5] and cadmium [6,7] from contaminated soil. Generally, electrokinetic remediation can be used to treat soils contaminated with inorganic species [8–10], organic compounds [11–13], and radionuclides [14,15].

Electro-osmosis, which is the movement of water relative to the soil under the influence of an imposed electric field [15], is the

principal process used for electrokinetic remediation. In this process the ions carry water as they migrate, exerting a pull on the water around them. Since there are more cations than anions in soil containing negatively charged clay particles, there is a net water flow towards the cathode. This flow is termed electro-osmosis [16]. Electro-migration, which applies to the movement of ions due to the application of an electrical current, is another process of contaminant removal with electrokinetic remediation. Electro-migration does not depend on the pore size; it is equally applicable to coarse and fine-grained soils [17,18]. Electrokinetics and specifically electro-osmosis are commonly used in various geotechnical and geo-environmental engineering projects. These methods have been used to speed up the consolidation of soft clay [16,19–21], to increase the stability of slopes [22–24], to increase the flow rate of reservoir fluids during petroleum recovery [25], and for drainage and sedimentation of clay suspensions [26]. Recently, Voinitchi et al. [27] have shown how the use of an electrokinetic technique can have an impact on chloride transport through cement based-materials. In a recent report, the latest developments in electrokinetics were reviewed [28].

Of late, several experimental research projects have been undertaken to investigate contaminant removal from kaolinite soil [7,29–31]. Prior research showed that the most influential factor on the success of contaminant removal is the pH of the soil, which must be low in order to mobilize heavy metal ions [10,31].

* Corresponding author. Tel.: +98 918 812 4592; fax: +98 811 8221316.

E-mail address: vahidouhadi@yahoo.ca (V.R. Ouhadi).

Carbonates are one of the major fractions of soils in semi-arid and arid areas of the world. Heavy metals are retained in clay soils by several soil phases or mechanisms, such as exchangeable, carbonate, hydroxide, and organic. Nevertheless, of all of these mechanisms contributing to contaminant attenuation, carbonates play the most essential role [32,33]. In this regard, usually at a pH of more than five, the carbonate phase contributes to the contaminant retention process. It has been shown [34] that buffering capacities of soils are strongly influenced by the carbonate content and CEC (cation exchange capacity) value. Calcite mineral functions well as a buffer for pH changes in the soil-water. This mineral is believed to be effective at absorbing heavy metals and phosphates [35,36]. Investigation of the distribution of heavy metals in stream sediments showed that Cu and Zn were found mainly in carbonate phases [37].

When it comes to clay minerals, kaolinite has a very low cation exchange capacity (CEC), and thus shows a much lower buffering capacity than that of other clay minerals, such as illite and montmorillonite [35]. As a result, it is an appropriate soil sample for an investigation of the impact of the buffering capacity of carbonate on the efficiency of electrokinetic remediation of soils.

Previous studies have taken into account the impact of current voltage, different clay minerals, the contaminant types and pH on the efficiency of the electrokinetic method [31,38–40]. However, little attention is generally paid to the influence of carbonate on the efficiency of the electrokinetic method. The primary purpose of this study was to investigate the impact of carbonates on the efficiency of the electrokinetic method for contaminant removal from kaolinite soils rich in carbonate.

2. Materials and methods

2.1. Geo-environmental engineering characterization of soil samples

Two types of soil samples were used in this study. The first is a kaolinite soil identified as “super zenous kaolinite” (kaolinite-z) from northwest Iran. In this research a series of samples were prepared which included the kaolinite-z samples at different percentages of calcite (laboratory added calcite). The variations of added calcite was 6%, 11%, 16%, 21% and 26%, respectively. Since the kaolinite-z sample has an initial 4% concentration of calcite, the total quantity of calcite present in the sample was 4% (for kaolinite-z soil in the “as is” condition), 10%, 15%, 20%, 25% and 30%, respectively. The second soil sample used in the study, for the purposes of comparison, was representative of the soil used in the clay liner at a waste disposal site in Hamedan, a city located in the west part of Iran. This sample was identified as a “representative soil sample” from the region. The geo-environmental engineering properties of kaolinite-z and the Hamedan sample are presented

in Table 1. In this Table, the geo-environmental engineering properties of kaolinite-z sample are compared to the characteristics of Georgia kaolinite-PX. Several investigators have used Georgia kaolinite as a soil sample in their research [41–43]. Physical properties, including specific gravity, particle size distribution, Atterberg limits, organic content and moisture content were determined according to ASTM methods [44]. According to the results in Table 1, the Hamedan soil sample has a carbonate concentration of 28%, which means it is a suitable sample for investigation of the impact of carbonate on the electrokinetic soil remediation process. Kaolinite, illite, quartz and feldspars were also found in this natural-soil sample.

For the geo-environmental engineering analyses, the kaolinite soil was air-dried and sieved through a #200 mesh. Then, geo-environmental engineering tests were performed according to test procedures as detailed in the laboratory manual of the Geotechnical Research Centre of McGill University. The cation exchange capacity (CEC) was determined using the BaCl₂ replacement method [45]. XRD analysis was performed using the method suggested in studies by Moore and Reynolds [46], and Ouhadi and Yong [47]. The XRD spectra were obtained by scanning in the 2θ range of 10–60°. A Bruker (Siemens) D8 Advance apparatus with Cu Kα radiation was used to obtain the X-ray diffraction patterns of the soil samples. Specific surface area (SSA) was determined using the ethylene glycol–monoethyl ether (EGME) method, according to the procedure described by Elthantaway and Arnold [48]. The carbonate content of the soil was determined with titration [49]. Soil pH was measured in a 1:10 soil-solution.

2.2. Sample preparation and experimental methods

To investigate heavy metal (HM) interaction with kaolinite from the point of view of geo-environmental engineering, soil samples were prepared by adding solutions of zinc nitrate (Zn(NO₃)₂·6H₂O) to the kaolinite sample. The suspensions of soil-electrolyte were prepared at a 1:10 soil-solution ratio. A series of batch equilibrium tests were performed according to EPA [50]. The soil suspension samples (prepared by the aforementioned method) were equilibrated (shaken for 24 h) after the solution was applied to the soil. Then, samples were centrifuged at 3000 rpm for about 10–15 min. The amounts of HM remaining in the supernatant were analyzed using an atomic absorption spectro-photometer (GBC 932 AB Plus). A titration experiment is usually used to obtain the buffering capacity of soils. The buffering capacity of soil is a function of the mineral type, specific surface area and the CEC of minerals, along with the quantity of calcite in the soil [34]. A series of titration experiments was performed to investigate the influence of laboratory added carbonate on the buffering capacity of kaolinite. For this purpose, several mixtures of kaolinite at different percentages of carbonate were prepared. Various concentrations of nitric acid were added

Table 1
Physico-chemical properties of soil samples.

Physico-chemical characteristics	Kaolinite-z	Georgia kaolinite	Soil sample of liner of waste disposal site
Soil Classification	CL (lean clay)	CH (fat clay)	CL-ML (silty clay)
Analysis XRD	Kaolinite, Quartz, Calcite	Kaolinite	Illite, Calcite, Quartz, Feldspars
CEC (meq/100g)	13.6	4.2–8	12.5
SSA (m ² /g)	61	12	118
LL (%)	24.1	64	22.1
PI (%)	11.2	30	6.2
Sulphate Content (%)	0	0	0
Organic Content (%)	0	0	0
Carbonate Content (%)	4	0	28
W _{opt} (%)	17.5	31	12.8
γ _{dmax} (g/cm ³)	1.96	1.37	1.9
Initial pH	9.05	4.7–5	8.6
G _s	2.75	2.65	2.7

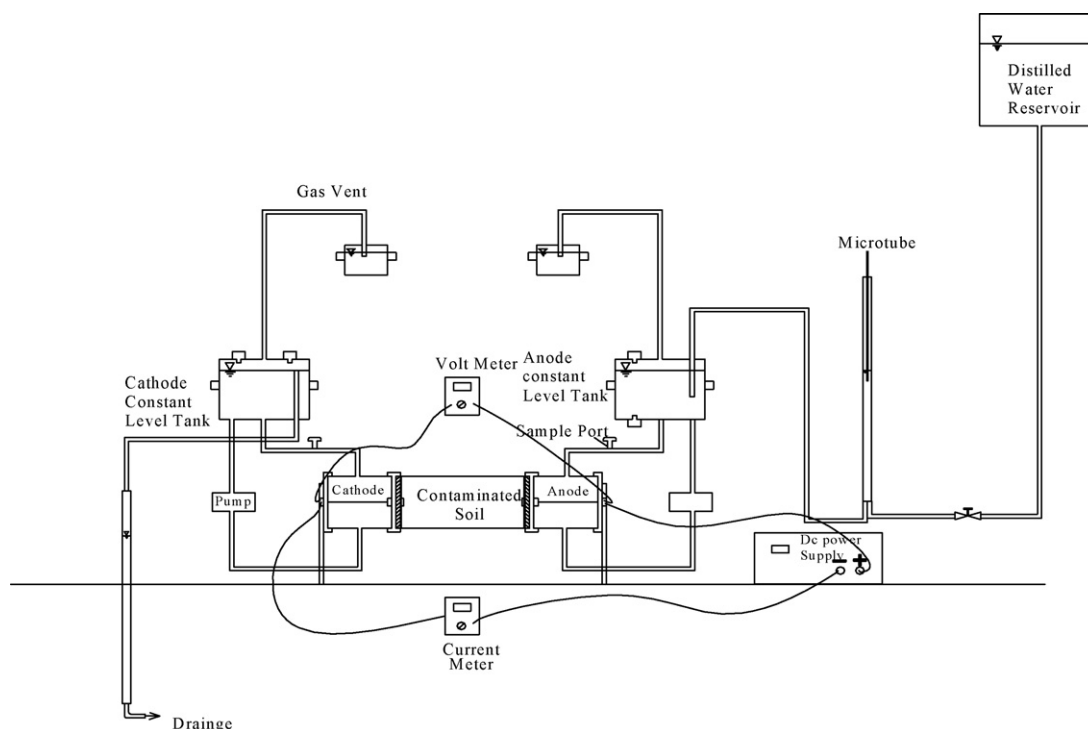


Fig. 1. Schematic diagram of electrokinetic test set-up.

to these samples. After equilibrium, the pH of the mixtures was measured in 1–10 soil:electrolyte solution ratios. To investigate the effect of carbonate on the soil–contaminant interaction, artificial calcite was added to the kaolinite soil sample in different percentages as stated previously. Triplicate samples were prepared for each test to verify the reproducibility of results. For electrokinetic experiments, the initial densities, void ratios, and water content of all the samples were initially maintained at the same level to prevent differing tortuosity and transport hindrance in samples.

2.3. Experimental procedure

Fig. 1 shows the schematic diagram of the electrokinetic experiment. In Fig. 2 the details of an electrokinetic cell are presented. The main cell is constructed of Plexiglas, with an internal diameter of 72 mm and a length of 145 mm. At one end of this cell is an anode and at the other a cathode, which are connected to the

anode and cathode reservoirs, respectively. Reservoirs serve as an electrolyte source for electrolysis. The electrolyte solutions were re-circulated by a pump from the electrodes compartment to the reservoirs. At the beginning of the test de-ionised water was used in the anode and cathode compartments. Two graphite electrodes, each of which has a filter paper on the contact line with the soil, are located at the end of the cells. The two ends of the cell are connected to the power supply. The power supply provides a direct current (DC) with a maximum 10 A and 240 V current. A voltage of 30 V was used in this research. By applying this voltage to the two ends of the cell, the quantity of electric current in the soil sample of the cell could be measured. Laboratory contaminated soil samples were placed in the cell and electrical current was applied to the two ends of the cells, and consequently to the soil samples of the cells. For soil sample preparation, the dry soil was sieved through a #10 mesh and mixed with 30% laboratory contaminated distilled water (Hamedan soil with 24%). The initial concentration of zinc

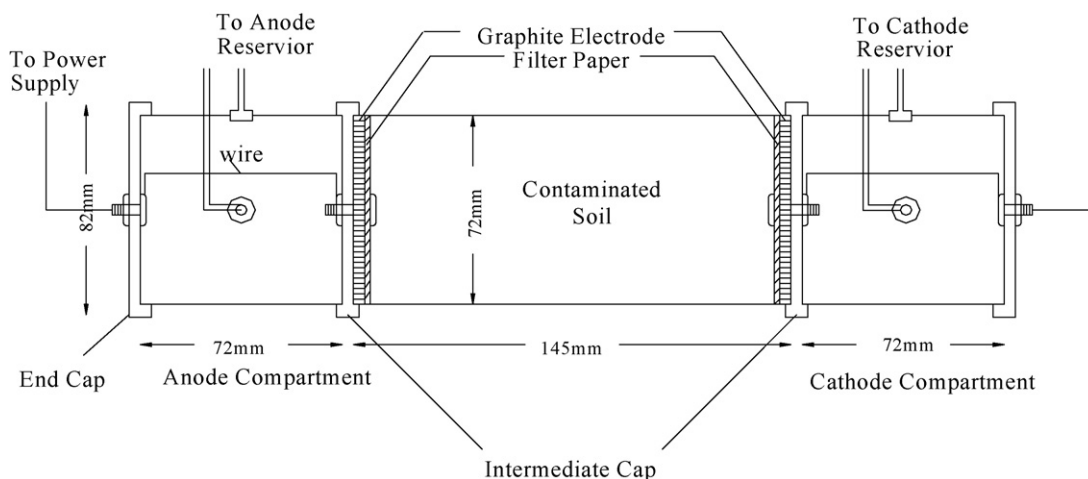


Fig. 2. Details of the electrokinetic test cell.

Table 2
Characteristics of electrokinetics experiments.

Experiment number	Test 1 (kaolin+4% carbonate)	Test 2 (kaolin+10% carbonate)	Test 3 (kaolin+15% carbonate)	Test 4 (kaolin+20% carbonate)	Test 5 (kaolin+25% carbonate)	Test 6 (kaolin+30% carbonate)	Test 7 (natural-soil sample)
Max. dry density (g/cm ³)	1.33	1.37	1.39	1.28	1.30	1.35	1.32
Water content%	30.3	30.0	29.0	31.6	31.1	30.3	24.2
Void ratio (e)	1.03	0.97	0.94	1.1	1.07	1.00	1.00
Saturation ratio (S _r)	80.9	85	84.8	79	79.9	83.3	65.3
Porosity (n)	0.51	0.49	0.48	0.52	0.52	0.5	0.5
Volume of Voids (cm ³)	234.6	225.4	220.8	239.2	239.2	230	230
Voltage (V)	30	30	30	30	30	30	30
Time (h)	100	100	100	100	100	100	100
Initial contaminant concentration (ppm)	1973	2054	2133	1982	2444	2288	2078

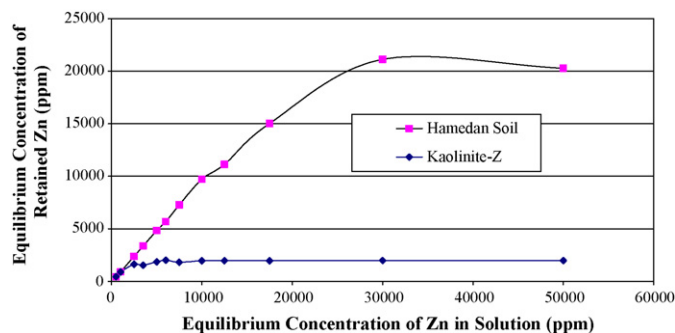


Fig. 3. Adsorption isotherm for kaolinite-z and the natural-soil from batch equilibrium test.

nitrate used to artificially contaminate the soil sample was chosen according to the results of other studies on industrial waste disposal sites [39,41]. The suggested concentration for Zn ions is 101–27,800 ppm with a mean value of 2790 ppm [51]. A zinc concentration of 2500 ppm was used in this research. Soil–contaminant mixtures were shaken for a period of 10 min in a mechanical mixer. Samples were kept in a plastic bag for 24 h to reach an equilibrium condition in terms of soil–contaminant interaction. This laboratory contaminated sample was then placed into the electrokinetic cell in 10 layers, with each layer compacted 25 tamps using a 0.5 kg tamper. From the soil sample of each cell a sample was taken for water content, pH, and heavy metal (HM) concentration measurements. After each electrokinetic experiment, the soil sample was extracted from the cell and was separated into five slices. Each sample was oven dried and mixed carefully. Then, a part of this sample was used to measure the quantity of soluble and retained HM according to the EPA method [50]. Each electrokinetic experiment was run for 100 h according to the recommendation of prior researchers [39]. To investigate the impact of carbonate on the efficiency of contaminant removal from the kaolinite sample in electrokinetic procedure, a series of seven experiments were performed. The details of these experiments are presented in Table 2. In this Table, the percent of carbonate is reported according to the dry weight of the soil.

3. Results and discussion

Fig. 3 compares the adsorption of zinc ions to the kaolinite-z sample and to the soil sample of waste disposal liner for Hamedan. Both samples follow the Langmir adsorption model [52]. The results in Fig. 3 for the kaolinite-z sample show that the maximum adsorption of Zn ions to the kaolinite sample is 1700 ppm. Therefore, the concentration of 2500 ppm which was used in the electrokinetic experiment is more than the maximum quantity of HMs which can be retained by kaolinite sample. On the other hand, the Hamedan soil is able to retain 21,000 ppm of zinc ions, which disparity can be attributed to the larger quantity of carbonate in Hamedan soil compared to that of the kaolinite sample. The major difference between the retention capacity of Hamedan soil and kaolinite-z can be attributed to both SSA and carbonate contribution for heavy metal retention. As the results of Table 1 show, the specific surface area of Hamedan soil is almost twice that of kaolinite-z. In addition, according to the results of Table 1, the Hamedan soil contains 28% carbonate, while the kaolinite-z sample has only 4% carbonate. Both factors contribute to higher heavy metal retention of natural-soil in comparison with that for the kaolinite-z sample.

The impact of pH variations on the retention of Zn ions by kaolinite samples is presented in Fig. 4. Different concentrations of nitric acid (HNO₃) and sodium hydroxide (NaOH) were used to adjust the pH of soil–electrolyte through a range of pH values. As the results in Fig. 4 show, with an increase in the pH of soil–electrolyte, HM

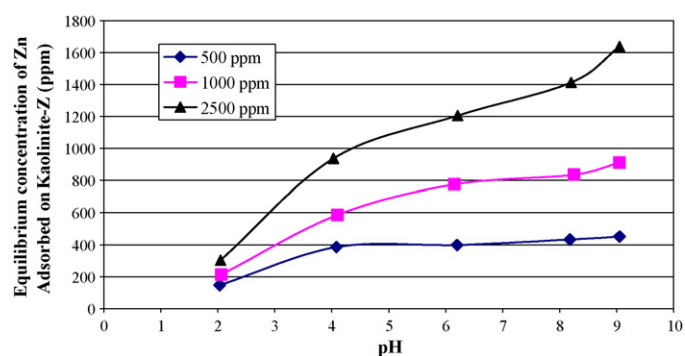


Fig. 4. Influence of pH variations on the retention of Zn by kaolinite sample.

retention of soil increases. This can be attributed primarily to the precipitation of zinc hydroxide ($Zn(OH)_2$) [41]. In addition, since kaolinite has a pH dependent charge, at high pH levels it has a greater tendency to adsorb heavy metals, due to its higher negative charge in this range of pH.

To further investigate the influence of pH variations on the retention properties of kaolinite, titration experiments were performed on the Hamedan soil and several samples of kaolinite with different percentages of laboratory added carbonate. As the results in Fig. 5 show, the presence of carbonate in the kaolinite sample caused a noticeable change on the extent and trend of pH variation in the presence of different concentrations of acid. According to the results in Fig. 5, the addition of carbonate to the kaolinite sample decreases the slope of the pH-acid added curve, which means it increases the buffering capacity of kaolinite. This shows that the addition of carbonate decreases the sensitivity of soil to the pH variation of pore fluid. It is interesting to note that the pattern of the curve for the Hamedan soil sample and mixtures of kaolinite (20–30%) carbonate is relatively similar. This may be due to the fact that all these samples have relatively high carbonate fractions. In other words, since these samples have a relatively similar CEC and they are composed of non-active clay minerals, the presence of carbonate controls the extent of their contaminant retention.

Prior research has shown that samples with a large cation exchange capacity (CEC) and a large specific surface area (SSA) demonstrate a greater buffering capacity. Since kaolinite has a low SSA and CEC, one may conclude that the different results obtained in the buffering capacity experiments for different mixtures of kaolinite-carbonate are not due to the difference between the SSA and/or CEC of these samples. In fact, the difference in results seen in Fig. 5 (i.e. two mixtures of kaolinite with 4% and 10% carbonate) is mainly due to the carbonate content of these samples. In addition,

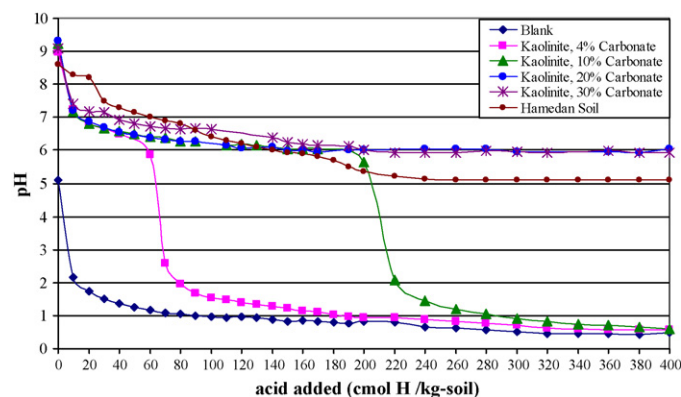


Fig. 5. Impact of carbonate on the buffering capacity variations of kaolinite-z sample in comparison with the natural sample.

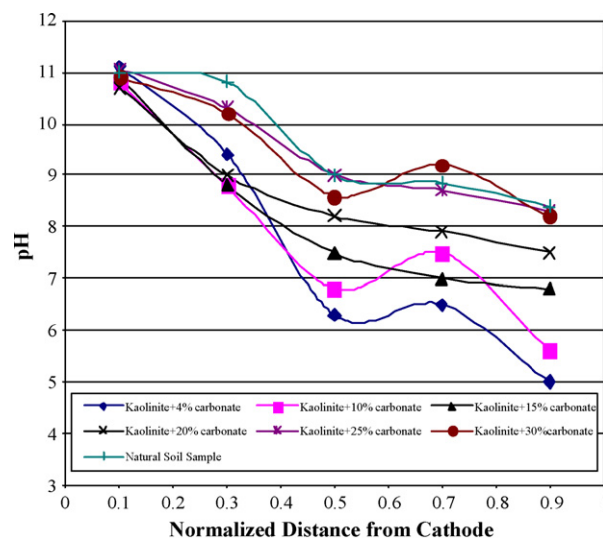
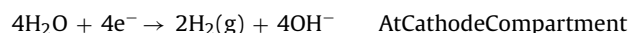
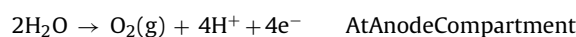


Fig. 6. pH variations of the soil sample of electrokinetic cell at the end of the experiment, sample length 145 mm, applied voltage 30 V.

tion, the more the concentration of carbonate increases, the less the buffering capacity experiment is able to differentiate between the behaviour of mixtures of kaolinite and different concentrations of carbonate. Furthermore, due to the low CEC of the samples studied and their high retention properties, the cation exchange phenomenon has little impact on the contaminant retention of soil. In this case, as the quantity of carbonate increases in soil samples, retention also increases because of the retention of heavy metals in $HM-CO_3$ forms. Finally, the buffering capacity patterns of Hamedan soil and kaolinite+30% carbonate are close to each other, which might be due to the relatively similar concentration of carbonate in these two samples.

3.1. Results of electrokinetic experiments

In electrokinetic experiments the electrolysis of water produces H^+ ions at the anode and OH^- ions at the cathode according to the following equations:



These interactions cause the formation of acidic conditions at the anode side and alkaline conditions at the cathode side. For this reason, a few hours after applying the electrical current around the anode, the pH drops as low as 3.5. On the other hand, the pH around the cathode rises as high as 11. The hydrogen ions (H^+) produced on the anode side move towards the cathode while the hydroxyl ions (OH^-) which are produced tend to transfer to the anode [2].

Fig. 6 shows the pH variation along the soil samples in electrokinetic cells at the end of experiments for seven different samples (test numbers 1–7, the details of which are presented in Table 2). The results in this Figure help to understand the impact of carbonate on the acid front phenomena in the electrokinetic experiment. In fact, desorption of cationic species from clay surfaces is essential in contaminant removal from fine-grained deposits. Electrolytic generation of H^+ at the anode and its transport into the soil mass by migration (secondarily by electroosmotic advection and diffusion) enhances desorption of the retained species. The pH of pore fluid also significantly controls this mechanism. An increase in H^+ concentration results in desorption of cations in an amount controlled by the soil type [2]. As can be seen in Fig. 6, test number 1 has the lowest quantity of carbonate, and the pH varies from 11 at the

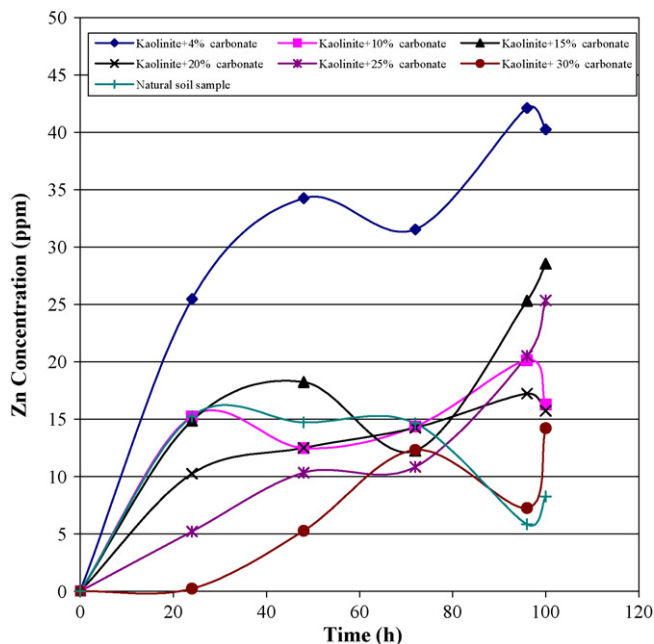


Fig. 7. Variations of Zn concentrations on the cathode compartment of electrokinetic cell.

cathode side to five at the anode side. It should be noted that with a high pH, most of the zinc is retained in the hydroxide and carbonate phases [15]. However, as the quantity of carbonate increases in soil samples, the range of pH variations along the electrokinetic cell decreases. For instance, in test number 6, which is a mixture of kaolinite and 30% carbonate, the pH varies from 11 to 9 from the cathode side to the anode side. In the electrokinetic experiment of the Hamedan soil, (test number 7) a pattern similar to that of test number 6 is observed. Therefore, one may conclude that the relatively identical concentration of calcite in these two samples is the reason for similar pH variation patterns in electrokinetic cells. In other words, due to the presence of such a high quantity of carbonate, the soil sample buffers against the reduction of pH. Therefore, the H⁺ ions transformation from anode towards cathode will not be able to significantly reduce the soil pH in cell.

To investigate contaminant transport in the electrokinetic process, the concentrations of Zn ions in the cathode compartment are measured and reported. Fig. 7 shows the variations of Zn ions for seven different samples at the cathode compartment during the electrokinetic experiments (time zero to 100 h). As can be seen, in all seven experiments there is a very limited quantity of zinc ions released at cathode compartment. In other words, at the end of the electrokinetic experiment only one percent of the HMs had been removed from the contaminated soil. Still, one could argue that this negligible amount of contaminant removed in the cathode compartment is due to the diffusion of heavy metal from the soil sample to the cathode compartment and not due to electrokinetic phenomena. To investigate further the impact of carbonate on the efficiency of electrokinetic remediation, the final concentrations of Zn ions for all seven samples along the soil in the electrokinetic cell were measured. Fig. 8 shows the results of these measurements. As can be seen in this Figure, in test number one, which is the kaolinite-z sample, the HMs moved from the anode side towards the cathode side. However, this movement stops around 5 cm before the cathode electrode. A similar pattern can be observed for experiment numbers 3 and 4. However, in experiment numbers 5, 6 and 7, this variation in HM concentration along the electrokinetic cell is quite minimal. For instance, in experiment number 6, the Zn concentration at the end of the experiment is almost uniform along

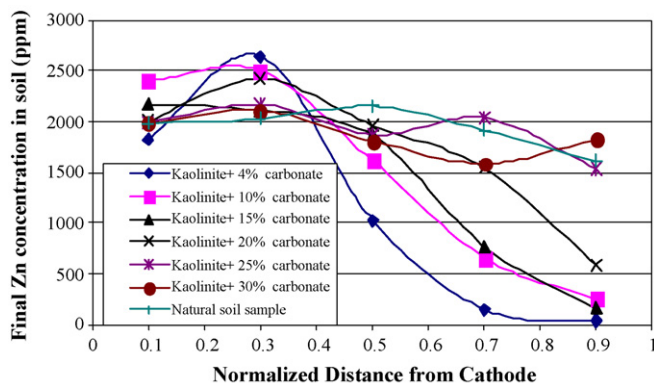


Fig. 8. Variations of Zn concentrations in the electrokinetic cell at the end of experiment, sample length 145 mm, applied voltage 30 V.

the electrokinetic cell. According to the results in Fig. 8, similar behaviour is observed for the soil sample of liner from the waste disposal site at Hamedan. In addition, for all curves in Fig. 8, the maximum concentration is observed at 5 cm from the cathode.

Fig. 9 shows the final variations of moisture content along the soil samples in different electrokinetic experiments. As can be seen in this Figure, due to the electrokinetic phenomena, water moves from the anode side to the cathode side. This causes an increase in the moisture content at the cathode side in comparison to that of the anode side. In addition, in all cases the final moisture content at the cathode side is much higher than that of its initial water content in the cells. This could be attributed to electro-osmosis and its consolidation effect. In fact, in spite of electro-migration, which caused the movement of HMs from the anode side to the cathode side, the transportation of pore fluid from the anode side to the cathode side causes an increase in effective stress at the anode side, which in turn leads to an increase in soil density (consolidation). This movement of water contributes to the transportation of HMs by advection from the anode side to the cathode side.

Another point which can be observed in these experiments is the variation of current density in samples during the performance of the experiment. Due to the applied 30 V differential voltage, an electrical flow of 60 A passed through the samples. This electrical flow is equal to a flow density of 1.47 mA/cm². 40 h from the beginning of the test, this flow rate diminished greatly and decreased to 5–6 mA by the end of the test, which is equal to a current density

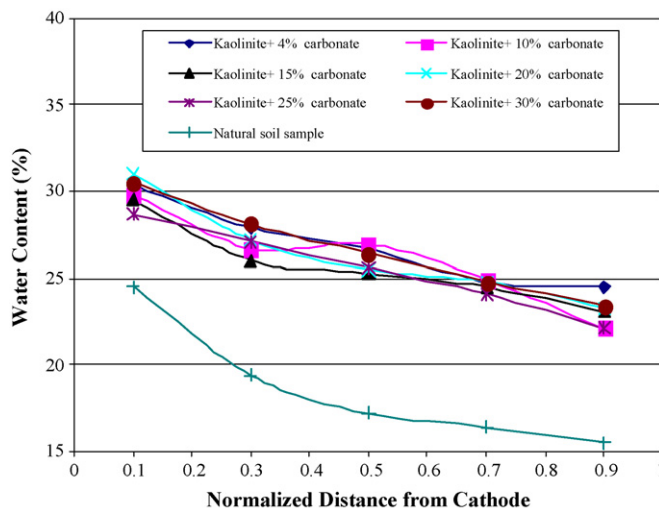


Fig. 9. Moisture content variations in the electrokinetic cell at the end of experiment, sample length 145 mm, applied voltage 30 V.

of 0.12–0.15 mA/cm². This reduction in flow rate can be attributed to an increase in resistance of the sample which will be explained further in this paper.

3.2. General discussion

In electrokinetic contaminant remediation, it is important to pay particular attention to the impact of the soil type and contaminant type on the applicability and efficiency of this method. Kaolinite, due to its low CEC and low activity coefficient, is the soil most suitable for electrokinetic remediation. However, the presence of carbonate in kaolinite, as previously addressed, causes a noticeable increase in the buffering capacity of soil. This increase in buffering capacity is the basis for a delay in the formation and development of acid front phenomena (Fig. 6). Therefore, as the results in Fig. 6 show, with an increase in carbonate concentration during electrokinetic remediation, soil tends to maintain its alkaline condition. This alkaline property is an appropriate condition for the precipitation of Zn in the form of Zn(OH)₂. Furthermore, the lack of acid front formation in Hamedan soil, which is due to its high concentration of carbonate (28% carbonate), prevents the solubility and release of zinc ions from soil during electrokinetic remediation (Fig. 8, test 7). For this reason a relatively low removal of contaminant in this sample occurred. In addition, as the results in Fig. 8 show, in test numbers 1–4 the contaminant moved from the anode side to the cathode side, but stopped around 5 cm before cathode itself. However, when the quantity of calcite exceeds 20%, a very small difference between the variations of contaminant along different parts of sample in the electrokinetic cell is found. In other words, the extent of contaminant removal from anode side towards the cathode side is negligible. The increase in buffering capacity produces a resistance against acid front in electrokinetic remediation. Therefore, we were faced with a very low contaminant removal from anode side towards the cathode side in test numbers 5–7, which caused an unacceptable time requirement for remediation. The impact of carbonate on the efficiency of heavy metal removal from kaolinite soil by electrokinetic soil remediation can be summarized as follows: (1) Delay in development of acid front; (2) increase in buffering capacity; (3) soil maintains its alkaline condition; (4) precipitation of Zn(OH)₂. All of these factors cause a low removal of contaminant transport in electrokinetics application.

4. Conclusions

- 1- Since the presence of carbonate in soils causes an increase in buffering capacity, the alkaline pH of soil rich in carbonate does not significantly vary in electrokinetic contaminant remediation. Consequently, heavy metal contamination is retained in precipitated hydroxide/carbonate forms. As a result, the efficiency of electrokinetic remediation decreases.
- 2- The lack of formation of acid front in carbonate rich kaolinite causes a resistance in pH variation during electrokinetic soil remediation. Therefore, the soil washing with the produced H⁺ ions will not form. The 95% efficiency of contaminant removal in the kaolinite sample around the anode electrode and a noticeable reduction in this efficiency to 5% in the sample of kaolinite with 30% carbonate shows the impact of carbonate on the efficiency of heavy metal removal by electrokinetic method. The low efficiency of this method of soil remediation on the laboratory contaminated soil sample of liner from the waste disposal site at Hamedan, which has 28% carbonate, supports the above conclusion.
- 3- The noticeable water content variation along the soil sample after the electrokinetic procedure proves that the presence of

carbonate does not prevent the electro-osmosis phenomena. For this reason, the low contaminant removal in electrokinetic remediation of carbonate rich soils is attributed to electro-osmosis. Due to the electrolysis of water around the cathode electrode, the movement of hydroxyl ions (OH)⁻ contributes to the reduction of the electrokinetic phenomena. This movement of hydroxyl ions is virtually independent of the concentration of carbonate in soil. Furthermore, the calcium precipitation close to the cathode clogged the soil pores; restraining further transport of heavy metal ions for removal.

Acknowledgements

This paper was a part of a joint research project involving Bu-Ali Sina University and the Iran University of Science and Industry. The authors would like to acknowledge the financial support for the experimental material and equipment which was obtained from the Office of the Vice-President of Research of Bu-Ali Sina University and Iran University of Science and Industry.

References

- [1] L.M. Ottosen, H.K. Hansen, A.B. Ribeiro, A. Villumsen, Removal of Cu, Pb and Zn in an applied electric field in calcareous and non-calcareous soils, *J. Hazard. Mater.* B85 (2001) 291–299.
- [2] Y.B. Acar, A.N. Alshawabkeh, Principles of electrokinetic remediation, *Environ. Sci. Technol.* 27 (13) (1993) 2638–2647.
- [3] S.S. Al-Shahrani, E.P.L. Roberts, Electrokinetic removal of caesium from kaolin, *J. Hazard. Mater.* B122 (2005) 91–101.
- [4] G. Maini, A.K. Sharman, G. Sunderland, C.J. Knowles, S.A. Jackman, An integrated method incorporating sulfur-oxidizing bacteria and electrokinetics to enhance of copper from contaminated soil, *Environ. Sci. Technol.* 34 (2000) 1081–1087.
- [5] D.M. Zhou, L. Cang, A.N. Alshawabkeh, Y.J. Wang, X.Z. Hao, Pilot-Scale electrokinetic treatment of a Cu contaminated red soil, *Chemosphere* 63 (2006) 964–971.
- [6] D.B. Gent, R.M. Bricka, A.N. Alshawabkeh, L.L. Larson, G. Fabian, S. Granade, Bench- and field-scale evaluation of chromium and cadmium extraction by electrokinetics, *J. Hazard. Mater.* 110 (2004) 53–62.
- [7] M. Mascia, S. Palmas, A.M. Polcaro, A. Vacca, A. Muntonia, Experimental study and mathematical model on remediation of Cd spiked kaolinite by electrokinetics, *Electrochim. Acta* 52 (10) (2007) 3360–3365.
- [8] K. Reddy, C.Y. Xu, S. Chinthamreddy, Assessment of electrokinetic removal of heavy metals from soils by sequential extraction analysis, *J. Hazard. Mater.* B84 (2001) 279–296.
- [9] R.F. Probst, R.E. Hicks, Removal of contaminants from soils by electric fields, *Science* 260 (1993) 498–503.
- [10] A. Giannis, E. Gidarakos, Washing enhanced electrokinetic remediation for removal cadmium from real contaminated soil, *J. Hazard. Mater.* B123 (2005) 165–175.
- [11] K.R. Reddy, R.E. Saichek, Enhanced electrokinetic removal of phenanthrene from clay soil by periodic electric potential application, *J. Environ. Sci. A39* (5) (2004) 1189–1212.
- [12] J. Kim, K. Lee, Effects of electric field directions on surfactant enhanced electrokinetic remediation of diesel-contaminated sand column, *J. Environ. Sci. Health A* 34 (4) (1999) 863–877.
- [13] A. Karagunduz, A. Gezer, G. Karasuloglu, Surfactant enhanced electrokinetic remediation of DDT from soils, *Sci. Total Environ.* 385 (1–3) (2007) 1–11.
- [14] Y.B. Acar, R.J. Gale, A.N. Alshawabkeh, R.E. Marks, S. Puppala, M. Bricka, R. Parker, Electrokinetic remediation: basics and technology status, *J. Hazard. Mater.* 40 (1995) 117–137.
- [15] J. Virkutyte, M. Sillanpaa, P. Latostenmaa, Electrokinetic soil remediation-critical overview, *Sci. Total Environ.* 289 (2002) 97–121.
- [16] J.K. Mitchell, T.C. Wan, Electro-osmotic consolidation: its effects on soft soils, *Proceeding of IX ICSMFE, Tokyo, Japan, 1, 1977*, pp. 219–224.
- [17] L. van Cauwenbergh, Electrokinetics: technology overview report, *Groundwater Remediation Technologies Analysis Centre* (1997) 1–17.
- [18] R.J. Lynch, A. Muntoni, R. Ruggeri, K.C. Winfield, Preliminary tests of an electrokinetic barrier to prevent heavy metal pollution of soils, *Electrochim. Acta* 52 (10) (2007) 3432–3440.
- [19] L. Casagrande, Electro-osmosis, *Proceedings of Second International Conference on Soil Mechanics and Foundation*, 1, 1948, pp. 65–78.
- [20] L. Bjerrum, J. Mowm, O. Eide, Application of electro-osmosis to a foundation problem in a norwegian quick clay, *Geotech., Lond.* 17 (1967) 214–235.
- [21] D.G. Buckland, K.Y. Lo, Electrokinetic enhanced sedimentation of contaminated welland river sediment, M.Sc. Thesis, Department of Civil and Environmental Engineering, The University of Western Ontario, Canada, 2000.
- [22] L. Casagrande, Electro-osmosis in soils, *Geotechnique* 3 (1) (1949) 159–177.
- [23] B.A. Chappell, P.L. Burton, Electro-osmosis applied to unstable embankment, *J. Geotech. Eng. Div., ASCE* 101 (8) (1975) 733–740.

- [24] L. Casagrande, Stabilization of soils by means of electro-osmosis: state of the art, *J. Boston Soc. Civil Eng., ASCE* 69 (2) (1983) 255–302.
- [25] S.A. Amba, G.V. Chilingirian, C.M. Beeson, Use of direct electrical current for increasing the flow rate of reservoir fluids during petroleum recovery, *J. Can. Petroleum Tech.* 3 (1) (1964) 8–14.
- [26] J.Q. Shang, Electrokinetic in geotechnical and environmental engineering applications, in: *Proceedings of 53rd Annual Conference of the Canadian Geotechnical Society*, Montreal, 2000, pp. 5–23.
- [27] D. Voinitchi, S. Julien, S. Lorente, The relation between electrokinetics and chloride transport through cement-based materials, *Cement Concrete Composites* 30 (3) (2008) 157–166.
- [28] A.V. Delgado, F. Gonzalez-Caballero, R.J. Hunter, L.K. Koopal, J. Lyklema, *J. Colloid interface Sci.* 309 (2) (2007) 194–224.
- [29] Y.B. Acar, A.N. Alshawabkeh, Electrokinetic remediation. I: pilot-scale tests with lead-spiked kaolinite, *J. Geotech. Eng.* 122 (3) (1996) 173–185.
- [30] J.Y. Wang, X.J. Huang, J.C.M. Kao, O. Stabnikova, Removal of heavy metals from kaolin using an upward electrokinetic soil remedial (UESR) technology, *J. Hazard. Mater.* B136 (2006) 532–541.
- [31] L.M. Ottosen, K. Lepkova, M. Kubal, Comparison of electro-dialytic removal of Cu from spiked kaolinite, spiked soil and industrially polluted soil, *J. Hazard. Mater.* B137 (2006) 113–120.
- [32] R.A. Griffin, N.F. Shimp, J.D. Steele, R.R. Ruch, W.A. White, G.M. Hughes, Attenuation of pollutants in municipal leachate by passage through clay, *Environ. Sci. Technol.* 10 (1976) 1262–1268.
- [33] F. Plassard, T. Winiarski, M. Petit-Ramel, Retention and distribution of three heavy metals in a carbonated soil: comparison between batch and unsaturated column studies, *J. Contam. Hydrol.* 42 (2000) 99–111.
- [34] R.N. Yong, B.P. Warkentin, Y. Phadangchewit, R. Galvez, Buffer capacity and lead retention in some clay minerals, *Water, Air, Soil, Pollut. J.* 53 (1990) 53–67.
- [35] R.N. Yong, *Geoenvironmental engineering, contaminated soils, pollutant fate and mitigation*, CRC Press, Boca Raton, 2001.
- [36] P. Sipos, T. Németh, I. Mohai, I. Dódon, Effect of soil composition on adsorption of lead as reflected by a study on a natural forest soil profile, *Geoderma* 124 (3–4) (2005) 363–374.
- [37] R. Segura, V. Arancibia, M.C. Zúñiga, P. Pastén, Distribution of copper, zinc, lead and cadmium concentrations in stream sediments from the Mapocho River in Santiago, Chile *J. Geochem. Explor.* 91 (1–3) (2005) 71–80.
- [38] K.R. Reddy, U.S. Parupudi, S.N. Devulapalli, C.Y. Xu, Effects of soil composition on the removal of chromium by electrokinetic, *J. Hazard. Mater.* 55 (1997) 135–158.
- [39] J. Hamed, A. Bhadra, Influence of current density and pH on electrokinetic, *J. Hazard. Mater.* 55 (1997) 279–294.
- [40] Y.B. Acar, J.T. Hamed, A.N. Alshawabkeh, R.J. Gale, Cd(II) removal from saturated kaolinite by application of electrical current, *Geotechnique, Geotech., Lond.* 44 (3) (1994) 239–254.
- [41] R.N. Yong, A.M.O. Mohamed, B.P. Warkentin, *Principles of Contaminant Transport in Soils*, Elsevier, Holland, 1992.
- [42] R.N. Yong, Y. Phadangchewit, pH influence on selectivity and retention of heavy metals in some clay soils, *Can. Geotech. J.* 30 (1993) 821–833.
- [43] A.K. Darban, A. Foriero, R.N. Yong, Concentration effects of EDTA and chloride on the retention of trace metals in clays, *Eng. Geol.* 57 (2000) 81–94.
- [44] ASTM, *Annual book of ASTM standards*, Philadelphia, American Society for Testing and Materials, 4(8) (1992).
- [45] W.H. Hendershot, M. Duquette, A simple barium chloride method for determining cation exchange capacity and exchangeable cations, *Soil Sci. Am. J.* 50 (1986) 605–608.
- [46] D.M. Moore, R.C. Reynolds, *X-Ray diffraction and identification and analysis of clay minerals*, Oxford University Press, New York, 1989.
- [47] V.R. Ouhadi, R.N. Yong, Impact of clay microstructure and mass absorption coefficient on the quantitative mineral evaluation by XRD analysis, *Appl. Clay Sci.* J. 23 (1–4) (2003) 141–148.
- [48] I.N. Elthantany, P.W. Arnold, Reappraisal of ethylene glycol mono-ethyl ether, (EGME) method for surface area estimation of clays, *Soil Sci.* 24 (1973) 232–238.
- [49] P.R. Hesse, *A Textbook of Soil Chemical Analysis*, William Clowes & Sons, 1971.
- [50] EPA, *Process design manual: land application of municipal sludge*, Municipal Environ. (1983) Res. Lab. EPA-625/1-83-016.
- [51] V.R. Ouhadi, R.N. Yong, M. Sedighi, Influence of heavy metal contaminants at variable pH regimes on rheological behaviour of bentonite, *Appl. Clay Sci. J.* 32 (3–4) (2006) 217–231.
- [52] A.T. Yeung, C. Hsu, R.M. Menon, EDTA-enhanced electrokinetic extraction of lead, *J. Geotech. Eng., ASCE* 122 (8) (1996) 666–673.