Electrokinetic removal of caesium from kaolin

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Abstract

Soil, in the form of kaolin and a sample of natural soil from an industrial site, was artificially contaminated with caesium and subjected to electrokinetic treatment. The effect of catholyte pH control on the process was investigated using different acids to control the catholyte pH. During treatment the in situ pH distribution, the current flow, and the potential distribution were monitored. At the end of the treatment the pore fluid conductivity and the caesium concentration distribution was measured. The results of these experiments showed that for caesium contamination, catholyte pH control is essential in order to create a suitable environment throughout the soil to enable contaminant removal. It was found that the type of acid used to control the catholyte pH affected the rate of caesium removal (nitric, sulphuric, acetic and citric acids were tested). All of the acids tested were effective, but the highest caesium extraction was achieved when nitric acid was used to control the catholyte pH. The relatively high adsorption capacity of the soil for caesium was found to significantly reduce the rate of removal. After 240 h of treatment at $1\,V\,cm^{-1}$ (using sulphuric acid to control the catholyte pH), less than 80% of the caesium was removed from a 30 cm long sample of kaolin. Electrokinetic treatment of the industrial soil sample was slower than for the kaolin, but a significant extraction rate for caesium was achieved.
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1. Introduction

Electrokinetic treatment is a promising technology for in situ soil decontamination. Electrokinetic remediation can be performed by applying a low direct current across electrodes placed in the ground to remove inorganic and organic contamination from the soil [1–4]. When an electric field is applied to saturated soil electrolysis reactions are induced at the electrodes and electrokinetic transport phenomena (electroosmosis, electromigration, and electrophoresis) occur in the porous medium. In general, the electrode reactions can be considered to produce O_2 gas and H^+ ions in solution at the anode and H_2 gas and OH^- ions in solution at the cathode [1,5].

A major factor which influences the mobility of contaminants in soil is the soil pH. Applying a dc current to the soil results in the generation of acid at the anode and alkali at the cathode [1,6]. This leads to an acid front at the anode and a basic front at the cathode. In the presence of the electric field, the acid front tends to migrate towards the cathode and the basic front advances towards the anode by electromigration.

A common problem with electrokinetic removal of heavy metals is precipitation of the metal ions which has been found to occur close to the cathode, hindering the extraction process [7–10]. The generation of alkali conditions at the cathode tends to immobilise heavy metal contaminants by hydroxide precipitation. A low pH environment can promote the removal of metallic contaminant from fine grain soils as a low pH promotes desorption (by ion exchange) of most heavy metals and cations from the soil surface.

In some studies, the area around the cathode was treated to adjust the pH in order to prevent precipitation of metals in the soil, for example for the removal of zinc, nickel and cadmium [2,11]. On the other hand, chromium and uranium contaminated soils have been treated to give high pH conditions so that mobile anionic complexes were formed [9].

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Radioactive isotopes of caesium are common contaminants which can result from activities such as dumping of nuclear waste, nuclear plant accidents, and the use of nuclear weapons [12,13]. Only a few studies have been reported on the electrokinetic removal of caesium from soil [14,15] and further research on the use of electrokinetic treatment for this contaminant is desirable. The objective of this paper is to evaluate the application of the electrokinetic technique for the removal of radioactive caesium pollution from kaolin, by investigating the treatment of kaolinite spiked with a non-radioactive caesium nitrate. The chemical and electrokinetic behaviour of the radioactive and non-radioactive isotopes of caesium are expected to be identical, so that simple, safe experiments can be carried out.

2. Experimental

2.1. Set-up

A multi-compartment cell was used to investigate the electrokinetic remediation process of soil contaminated with caesium. The cell was constructed from Perspex, to enable direct observation of the effect of the electrokinetic process on the specimen. The cell, which is shown schematically in Fig. 1, consisted of a sample vessel and two electrode compartments. The cylindrical shaped sample vessel had an inside diameter of 50 mm, and a length of up to 30 cm. The sample vessel was divided into compartments, each 3 cm in length and vinyl gaskets were used to prevent leakage between the compartments. Each compartment had a hole sealed with a rubber bung, which could be removed during experiments in order to measure the local pH and electrical potential.

The electrode compartments had the same inside diameter as the specimen vessel and were 50 mm in length. The top of each electrode compartment was open to allow insertion of the electrodes, enable the release of any gases generated at the electrodes and for measurement of the catholyte and anolyte pH. Two tubes were fitted to the top and the bottom of the catholyte compartment to enable continuous circulation and pH control of the catholyte. The cathode was a 50 mm diameter disc of stainless steel mesh, which provided a large surface area. The anode was a titanium mesh coated with iridium mixed-metal oxide and was also 50 mm in diameter. The soil specimen was separated from the electrode compartment using two circular micro-porous flat sheet membranes consisting of ultrahigh molecular weight polyethylene and amorphous silica (Daramic®) with an average pore size of 0.1 μm. This membrane was chosen due to its low cost, high conductivity and stability under acidic condition. The contaminants could pass through the pores of the membrane during the extraction process, but the kaolin or soil particles were separated from the electrolytes.

The electrode compartments were initially filled with deionised water. The cathode compartment fluid was recycled using a peristaltic pump through a reservoir which was maintained at pH = 3.0. The pH of the reservoir solution was controlled using a pH controller and a make up solution of acid at pH = 1.5. The electrodes were connected to a dc power supply. The current flow through the specimen was measured using an ammeter.

2.2. Soil characteristics

2.2.1. Kaolin

The electrokinetic remediation process was studied using kaolin contaminated with caesium nitrate. One of the advantages of electrokinetic treatment (compared to alternative techniques) is that it is effective for low porosity, clayey soils. Kaolin, a hydrated aluminium silicate material, has been widely used for the study of electrokinetic treatment of soil [4,5,9,11,16,17], as it provides a model, reproducible, low-buffering clayey soil. For this study Kaolin was purchased from Sigma Aldrich Co. Ltd., in the form of a fine white powder with a particle size distribution (when dry) of between 0.1 and 4 μm. This kaolin was found to be naturally acidic; when
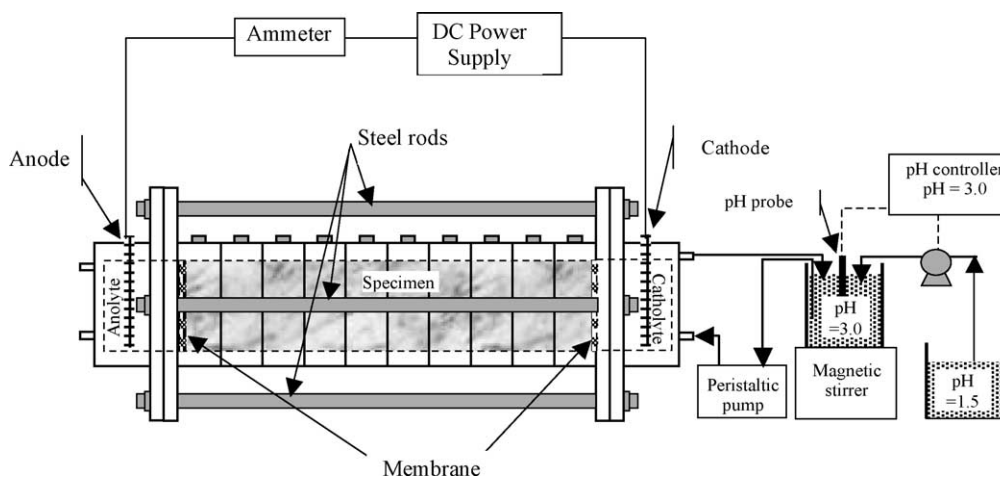

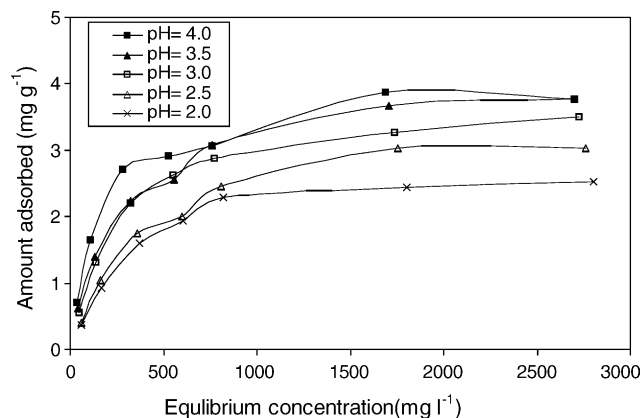Fig. 1. Schematic diagram of the experimental set-up.

Fig. 2. The effect of pH on the adsorption isotherm for caesium on kaolin. Operating conditions: mixing time = 48 h, shaker speed = 250 rpm, temperature = 22 °C.

mixed with deionised water (using a water/kaolin mass ratio of 1.8) the supernatant pH was 3.78.

Measurements of the bulk density and the particle density (measured using a helium pycnometer) were used to estimate the porosity of the kaolin sludge (see Section 2.3), giving a value of $\varepsilon = 0.81$. The tortuosity of the kaolin sludge was found to be 0.545 from measurements of the conductivity of the sludge and pore fluid.

Clay minerals are known to exhibit strong Cs adsorption characteristics [18]. Although Cs adsorption on clays and soils has been widely studied [e.g. 18–22] only a few of these studies have addressed acidic (pH < 4) environments [19,21]. The mechanism of caesium adsorption on clay minerals is complex, with sorption occurring at both edge and interlayer sites [20]. Experiments were carried out to determine the adsorption behaviour of caesium on kaolin as a function of pH under acidic conditions. Kaolin (2 g) was mixed with deionised water (25 ml) at a range of caesium concentrations (100–3000 mg l^{-1}) and the mixtures were shaken to ensure complete interaction between contaminants and kaolin. The kaolin mixtures were mixed for 48 h at room temperature using a horizontal shaker at 250 rpm, which was found to be sufficient mixing time to achieve equilibrium. The pH was monitored every few hours and adjusted to the desired value by adding 1 M HNO$_3$ or 1 M NaOH. The samples were then centrifuged for 15 min at 4000 rpm and the caesium concentrations of the supernatant was measured by atomic absorption spectroscopy.

The effect of pH on the adsorption isotherm for caesium on kaolin is shown in Fig. 2. It is clear from Fig. 2 that the kaolin has a relatively high adsorption capacity for caesium (2–4 mg g^{-1}). The distribution coefficient observed at low concentrations varies from 6.1 ml g^{-1} at pH 2.0 to 20.9 ml g^{-1} at pH 4.0, consistent with the data reported by Shahwan and Erten [22] under neutral conditions. As expected [21,23,24], increasing the solution pH increases the adsorption capacity. On the other hand, a low pH en-

vironment promotes desorption of caesium into the pore fluid [8–10], probably by an ion exchange mechanism [22]. In all cases the adsorption capacity of the kaolin was approached for equilibrium caesium concentrations in excess of 1000 mg l^{-1}.

The results confirm that a low pH environment is desirable to give higher concentrations of caesium in the pore fluid and thus to enhance the electrokinetic treatment process. Allowing acid through the soil during electrokinetic remediation will promote ion exchange and desorb metals from the clay surface. It is expected that in most cases a significant proportion of the caesium contaminant will be adsorbed on the kaolin, unless the total caesium concentration is around 3000 ppm or higher.

2.2.2. Soil sample

The soil sample, which was supplied by BNFL, was not suitable to use directly in the experiments as it contained an unknown amount of ground water and large stones were present in the soil. Therefore, a drying, sieving and crushing process was carried out before the soil was used in the experiments, in order to provide a reproducible soil sample. Unfortunately, due to the limited amount of soil material supplied, it was not possible to carry out caesium adsorption tests on the soil. However, the cation exchange capacity of the soil was measured and found to be high at 20.6 meq per 100 g, compared to 5.2 meq per 100 g for kaolin. This indicates that the soil had a high buffering capacity, which may slow the advance of the acid front from the anode.

2.3. Sludge preparation

The kaolin or the soil sample used in the experimental work was spiked with caesium nitrate [CsNO$_3$] solution. The sludge was prepared by mixing dry kaolin or soil with the prepared solution in a mass ratio (liquid to solid) of 1.8 or 0.5 (for kaolin and soil respectively) in order to achieve a desired caesium concentration in mg Cs kg^{-1} dry kaolin/soil. The initial water content in the sludge was thus 64% for kaolin and 33% for the soil, these values having been chosen to obtain a saturated sludge. The prepared kaolin sludge behaved like a viscous fluid which settled under gravity, facilitating the filling of the sample vessel.

The sludge was mixed vigorously to ensure homogeneity and to equilibrate the Cs between the pore fluid and the solid phase. A stirrer fitted with six impellers was used to mix the sludge for 5 h. Samples from different parts of the sludge were analysed by atomic absorption spectrophotometer (AAS) to verify its homogeneity.

The resulting sludge was left for a further 48 h to equilibrate the contaminant between the pore fluid and the solid phase. When the sludge was left for 8 days after mixing, no significant change in the pore fluid concentration was obtained, indicating that 48 h was sufficient time to achieve equilibrium.

2.4. Procedures

In order to aid loading of the sample vessel, it was assembled vertically. One of the electrolyte compartments, a membrane and the first few compartments (along with the necessary gaskets) were assembled and the compartments filled with sludge, taking care to avoid air pockets. Further compartments were added and filled with sludge, and finally the second membrane and electrode compartment were fitted. Bolts were fitted to the steel rods and tightened to seal the assembled cell. The cell was then rotated into its normal horizontal orientation. The electrode compartments were filled with deionised water prior to each experiment. During the experiment the anolyte level was topped up with deionised water as necessary.

In all cases a potential corresponding to $1 \, V \, cm^{-1}$ of sample was applied across the cell (i.e. 30 V for the 30 cm sample vessel). This is a typical voltage gradient used for electrokinetic treatment which can be safely used in the field [1–3]. The current was measured during the experiments using a digital ammeter and the in situ pH distribution was measured by inserting a pH electrode through the holes on the top of each compartment. It was found that the sludge was sufficiently soft to allow insertion of the pH probe to a depth of 25 mm, and sufficient moisture was present to give a reproducible measurement of pH. For drier clays this approach may not be suitable. The power supply was disconnected when measuring in situ pH to eliminate any interference.

The electrical potential at different locations in the specimen was measured using two 2 mm diameter stainless steel probes inserted to a depth of 25 mm in the sample and connected to a voltmeter. The electrical potential in each compartment was measured relative to the compartment adjacent to the anode (1.5 cm from the anode compartment) using a digital voltmeter. Differences in the interface potential at the stainless steel due to variations in local conditions will lead to errors in these measurements. However, these errors were found to be of order 10 mV, small compared to the potential difference measurements of order 1 V.

At the end of the experiment, the steel rods which clamped the compartments together were loosened and a thin sheet of rigid plastic was inserted between each compartment. This enabled separation of the kaolin/soil in each compartment for subsequent analysis. The pore fluid conductivity and the caesium concentration were determined for the kaolin/soil from each compartment. Nitric acid (HNO_3), which is known to be effective for the extraction of heavy metals from soil [5,23], was used to "digest" the caesium in the sample. Dilute nitric acid at pH $\approx$ 0.3 (20 ml) was added to 4 g of the sample, and the mixture was shaken at room temperature for 24 h. The pore fluid was then separated from the specimen by centrifugation at 4000 rpm for 10 min. The caesium concentration in the specimen was determined by measuring the metal concentration in the supernatant liquid using AAS. The developed method was significantly simpler than the standard methods for analysis of heavy metal contaminants in soil. For

the system under study, the method gave reproducible results and achieved >95% extraction of caesium.

In order to express the caesium concentration in the soil as $mg \, Cs \, kg^{-1}$ dry soil, the water content of the soil from each compartment was also determined by drying (at 120 °C for 24 h) and weighing a known mass of the soil sludge. In order to determine the conductivity of the pore fluid, a known mass of the specimen was centrifuged at 4000 rpm for 15 min. The conductivity of the supernatant pore fluid was then measured using a conductivity meter.

3. Results and discussion

3.1. Catholyte pH control

The adsorption results confirm that pH control is required in order to increase the rate of caesium removal from kaolin. In this section, the effect of the catholyte pH control on the electrokinetic treatment of kaolin contaminated with caesium nitrate is discussed. Two experiments were conducted on kaolin contaminated with caesium to investigate the effect of pH control on caesium removal. In the first experiment, the catholyte pH was not controlled while in the second experiment the catholyte pH was controlled at a value of 3.0 using sulphuric acid. When the catholyte pH was not controlled, a filter paper (Whatman No. 5) was used to separate the kaolin from the catholyte, as the polyethylene membrane was unstable under the alkaline conditions generated. The experiments were conducted for 120 h with kaolin that had been contaminated with caesium nitrate to give an initial caesium concentration of $450 \, mg \, Cs \, kg^{-1}$ of dry kaolin. The in situ pH was measured during the experiments while total caesium concentration was measured at the end of each experiment.

Fig. 3 shows the caesium distribution in the cell after 120 h of treatment. When the catholyte pH was not controlled, the caesium concentration was significantly reduced in most of the cell. However, significant accumulation of caesium was
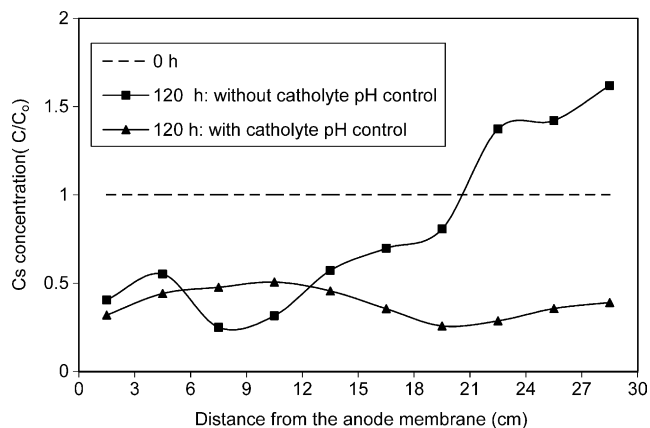
Fig. 3. Distribution of final caesium concentration across the soil specimen with and without catholyte pH control. Operating conditions: treatment time = 120 h, $C_0 = 450 \, mg \, Cs \, kg^{-1}$ dry kaolin, $E = 1 \, V \, cm^{-1}$.

Table 1
Material balance of caesium removal experiments

Process	Cs collected in the anolyte (mg)	Cs remaining in the cell (mg)	Cs collected in the catholyte (mg)	Total Cs (mg)	Initial Cs present (mg)	Cs extracted (%)	Discrepancy in material balance (%)
pH controlled	<0.1	47	74	121	124	60	2.5
pH not controlled	<0.1	106	22	128	132	17	3

Operating conditions: time = 120 h, C_0 = 450 mg Cs kg^{-1} dry kaolin, E = 1 V cm^{-1}.

observed in the area close to the cathode. The accumulation of caesium close to the cathode was probably associated with a high pH environment, where migration of OH$^-$ from the catholyte into the kaolin precipitated caesium as CsOH. When the catholyte pH was controlled, a decrease in caesium concentration was observed throughout the cell. In total, only 17% of the caesium initially present was removed without pH control, compared to 60% removal when the catholyte pH was controlled, as shown in Table 1. These percentages are based on the amount of caesium collected in the catholyte, rather than the caesium concentrations measured in the kaolin at the end of the experiment. A material balance (Table 1) indicates that the experimental methodology is sound, with a maximum discrepancy of 3.0%.

The in situ pH distribution in the electrokinetic cell measured during these experiments is shown in Fig. 4. When the catholyte pH was not controlled, the anolyte pH decreased with time to a value of 2.0 and the catholyte pH increased to a value of 11.3. After 120 h of treatment, the in situ pH increased monotonically with distance from the anode. The kaolin pH in the area close to the anode decreased to a value less than its initial value as a result of migration of H$^+$ ions from the anolyte into the kaolin. The kaolin pH increased throughout most of the cell due to the migration of OH$^-$ ions from the catholyte. The high pH area close to the cathode probably caused the precipitation of CsOH, which blocked the pore fluid and hindered the caesium removal.

When the catholyte pH was controlled, a low pH environment was maintained throughout the cell. The low pH

improved the caesium removal by improving desorption of caesium into the pore fluid, enabling caesium transport by electromigration.

The effective resistivity of the kaolin soil in the area close to the anode ($r_{1,2}$) and that close to the cathode ($r_{9,10}$) was calculated from the potential measurements as follows:

$$r_{ij} = \frac{\Phi_{ij} A}{Il} \tag{1}$$

where Φ_{ij} is the measured potential difference between compartments i and j, I the current passing through the cell A is the cross-sectional area of the sample vessel and l the distance between the measuring points. The results shown in Table 2 indicate that at the start of each experiment the effective resistivity was fairly uniform, and was similar in both experiments. After 120 h of treatment, the effective resistivity decreased in the area close to the anode in both experiments, probably due to an increase in the concentration of H$^+$ ions. On the other hand, the effective resistivity increased in the area close to the cathode. This increase in the effective resistivity near the cathode may be due to the increased pH, reduced cross sectional area (due to consolidation of the kaolin), precipitation blocking the soil pores, or depletion (by electromigration) of ions present in the original kaolin. It is likely that the increase in the effective resistivity observed in the region close to the cathode when catholyte pH control was applied was largely due to the latter of these effects. The other effects were more significant in the absence of catholyte pH control, and in particular severe consolidation was observed in the region of the cell close to the cathode. Fig. 5 shows photographs of the cell prior to treatment and after 120 h of electrokinetic treatment both with and without catholyte pH control. Although some consolidation was observed when catholyte pH was controlled, the effect was much more severe in the absence of pH control. The consolidation would normally be expected to occur in the direction of the electric gradient, and the observed vertical consolidation in Fig. 5(b) and
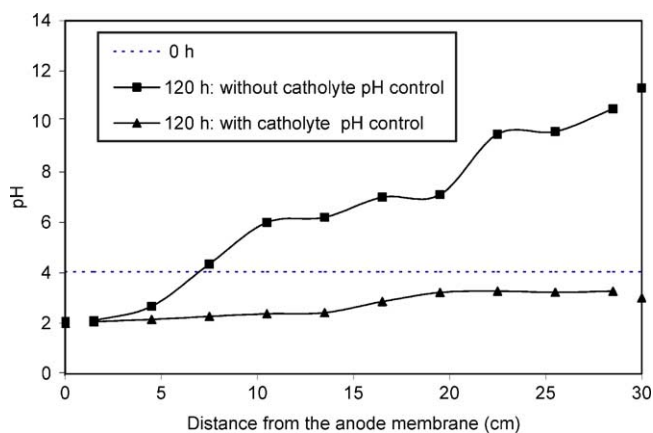

Fig. 4. In situ pH profiles as a function of distance from the anode membrane when sulphuric acid was used to control catholyte pH. Operating conditions: time = 120 h, C_0 = 450 mg Cs kg^{-1} dry kaolin, E = 1 V cm^{-1}. The data points at 0 and 30 cm indicate the electrolyte pH.

Table 2
Resistance calculated using potential difference in the area close to the anode and that close to the cathode

Process	Time (h)	$r_{1,2}$ (Ω m)	$r_{9,10}$ (Ω m)
pH controlled	0	58	55
	120	3.1	70
pH not controlled	0	52	53
	120	11	93

Operating conditions: time = 120 h, C_0 = 450 mg Cs kg^{-1} dry kaolin, E = 1 V cm^{-1}.

(a) Before the experiment

(b) After treatment, with catholyte pH control

(c) After treatment, without catholyte pH control
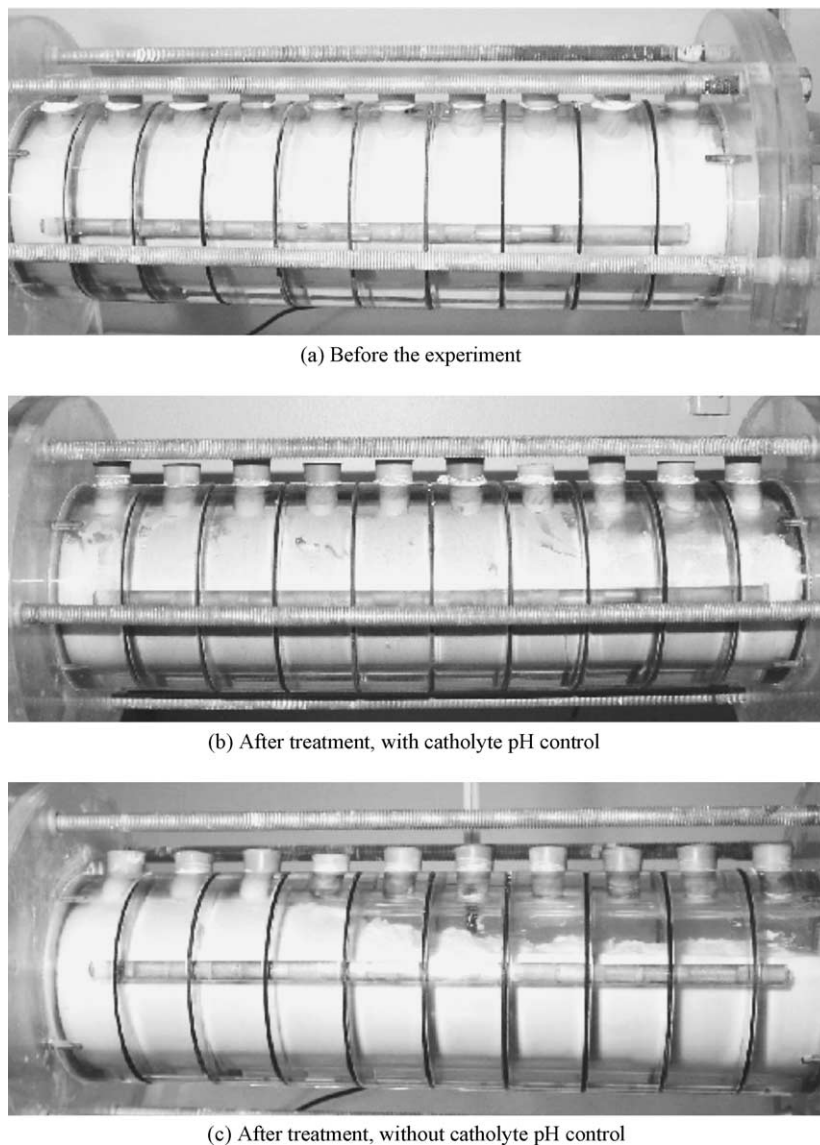
Fig. 5. Effect of catholyte pH control on the kaolin consolidation. Operating conditions: time = 120 h, C_0 = 450 mg Cs g^{-1} dry kaolin, E = 1 V cm^{-1}. (a) Before the experiment; (b) experiment with catholyte pH control; (c) experiment without catholyte pH control.

(c) was probably due to gravity settling of the consolidated sludge.

3.2. Choice of acid

Experiments were carried out using a range of different acids to control the catholyte pH. It was found that the choice of acid could significantly affect the performance of the electrokinetic treatment. In addition, consideration should also be given to the potential for contamination of the soil by the anion associated with the acid used. Electrokinetic extraction of caesium from kaolin was carried out for 48 h using sulphuric acid, nitric acid, acetic acid and citric acid for catholyte pH control. It was found that nitric and sulphuric acids gave higher removal rates that the weaker citric and acetic acids. The caesium concentration distribution obtained after 48 h of

electrokinetic treatment are shown in Fig. 6. The material balance results for these experiments, shown in Table 3, indicate that the use of nitric and sulphuric acids resulted in a slightly higher removal of caesium than citric or acetic acids, with acetic acid giving the worst performance. A maximum extraction percentage of 38% was obtained when nitric acid was used to control the catholyte pH. When citric, nitric or sulphuric acid was used to control the catholyte pH, the caesium concentration profile (Fig. 6) was relatively uniform across the cell. Slightly higher concentrations of caesium were observed in the compartments close to the cathode when acetic acid was used to control the catholyte pH.

These findings are supported by the measurements of the pH distribution. Fig. 7 shows the in situ pH distribution in the cell. When nitric acid was used to control the catholyte pH, a uniform low pH (<3.0) was observed. When sulphuric acid

Table 3
Material balance of caesium removal experiments using different acids to control the catholyte pH

Acid	Cs collected in the anolyte (mg)	Cs remaining in the cell (mg)	Cs collected in the catholyte (mg)	Total Cs (mg)	Initial Cs present (mg)	% Cs extracted (%)	Discrepancy in material balance (%)
Nitric acid	<0.1	69	46	115	121	38	5
Sulphuric acid	<0.1	75	44	119	123	36	3
Citric acid	<0.1	85	31	116	123	26	6
Acetic acid	<0.1	89	28	117	124	23	6

Operating conditions: treatment time = 48 h, $C_0 = 450$ mg Cs kg^{-1} dry kaolin, catholyte pH = 3.0, $E = 1$ V cm^{-1}.
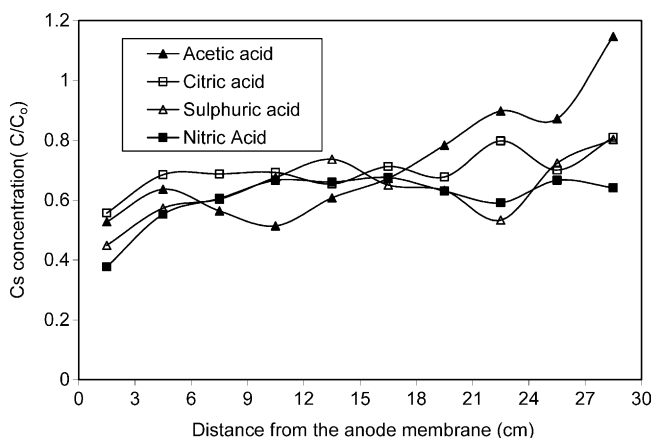
Fig. 6. Distribution of final caesium concentration across the soil specimen using a range of acids for catholyte pH control. Operating conditions: treatment time = 48 h, $C_0 = 450$ mg Cs kg^{-1} dry kaolin, catholyte pH = 3.0, $E = 1$ V cm^{-1}.

was used to control the catholyte pH, a slightly higher pH (compared to the use of nitric acid) was obtained throughout the cell. However, the pH was below 3.0 throughout most of the cell after 48 h of operation. In general, the pH distribution in the cell was more uniform when nitric and sulphuric acids were used to control the catholyte pH compared to acetic and citric acids. The pH distributions observed are consistent with the caesium removal results, with a lower in situ
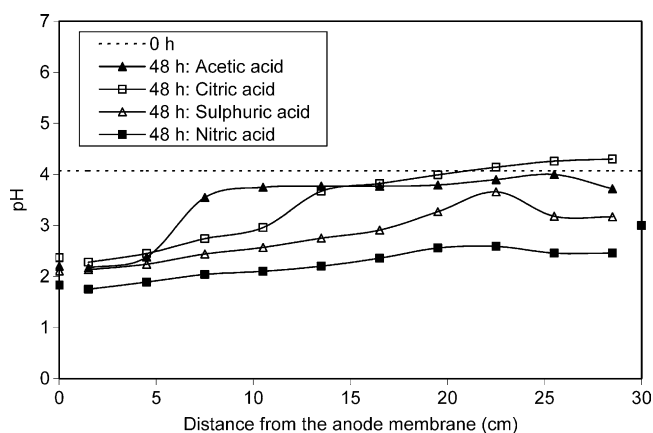
Fig. 7. In situ pH profiles as a function of the distance from the anode membrane when different acids were used to control the catholyte pH. Values of pH at 0 and 30 cm indicate the electrolyte pH. Operating conditions: treatment time = 48 h, $C_0 = 450$ mg Cs kg^{-1} dry kaolin, catholyte pH = 3.0, $E = 1$ V cm^{-1}.

pH throughout the cell corresponding to a higher caesium removal.

Since the pH of the catholyte was controlled at a value of 3.0 in all cases, it is not immediately clear how the type of acid used effects the pH distribution in the soil. The explanation is probably that the associated anion added with the acid migrated in the electric field into the soil, thus modifying the speciation in the pore fluid. In particular, for the weak acids, the citrate and acetate ions will buffer the acid front migrating from the anode. In addition, these ions will interact with other adsorbed and dissolved species, so that the overall effect is complex and difficult to predict. The weaker and more mobile acetate would be expected to have a stronger buffering effect than the citrate, consistent with the results shown in Fig. 7. The citrate and acetate might be expected to complex with caesium ions reducing the amount of adsorbed caesium [19]. However, the resulting complex, although mobile, will be uncharged and will not be subject to electromigration. Overall, the weaker acids are less effective than the stronger nitric and sulphuric acids.

The observed higher soil pH with sulphuric acid compared to nitric acid is difficult to interpret. One possibility is that some nitrate is reduced at the cathode, reducing both the amount of alkali generated at the electrode and the amount of nitrate in the catholyte. Any complexation of cations in the pore fluid will tend to increase the buffering effect of the kaolin and thus increase the soil pH. A low nitrate concentration in the pore fluid may have led to very little change in the buffering effect of the kaolin, and thus a lower soil pH.

3.3. Current flow

The lower pHs observed with nitric and sulphuric acid led to reduced resistivity and higher currents. Fig. 8 shows the variation of current as a function of time (with a constant applied voltage) when different acids were used to control the catholyte pH. At the start of each experiment, the current was around 1–3.6 mA (the variation may be attributed to the degree of wetting of the membranes separating the kaolin from the electrolytes). In all cases, the current increased rapidly to above 4 mA after 1–2 h. This rapid increase was probably associated with the generation of acid at the anode (increasing the conductivity of the anolyte) and the wetting of the membrane. When nitric acid and sulphuric acid were used as catholyte conditioners, the current gradually increased after the initial rapid rise. Conversely when acetic and citric acids
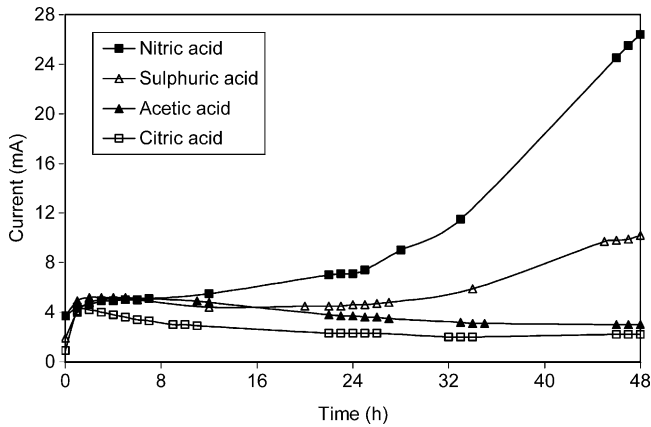
Fig. 8. Current as a function of time for electrokinetic treatment of kaolin contaminated with caesium. Operating conditions: treatment time = 48 h, $C_0 = 450$ mg Cs kg^{-1} dry kaolin, catholyte pH = 3.0, $E = 1$ V cm^{-1}.

were used, the current decreased steadily after the initial rapid increase. Generally, the low currents observed are due to the low ion concentration in the sludge. The results show that although the strong acids give higher removal rates, they also lead to much higher power consumption, especially when long treatment times are required.

Fig. 9 shows the pore fluid conductivity throughout the cell when direct current was applied for 48 h using four different acids to control the catholyte pH. The acidic conditions generated at the anode led to an increase in the pore fluid conductivity in this region. Conversely, the conductivity in the region close to the cathode decreased due to the lower concentration of H$^+$ ions compared to the area close to the anode, and the depletion of ions due to electromigration [5,16].

Pore fluid conductivity was used to estimate the resistance to the current flow using the following equation:

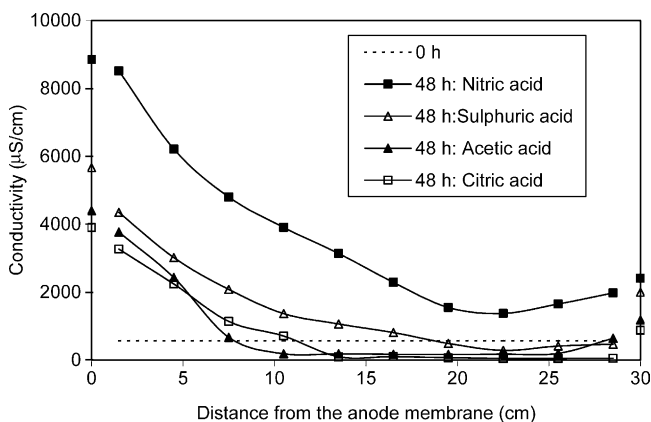$$R = \frac{1}{A} \int_0^L \frac{dx}{K^*} \tag{2}$$

Fig. 9. Pore fluid conductivity profiles as a function of distance from the anode membrane when different acids are used to control catholyte pH. Data at 0 and 30 cm indicate the electrolyte conductivities. Operating conditions: treatment time = 48 h, $C_0 = 450$ mg Cs kg^{-1} dry kaolin, catholyte pH = 3.0, $E = 1$ V cm^{-1}.

Table 4
Resistance calculated using pore fluid conductivity (assuming $\varepsilon = 0.81$ and $\tau = 0.55$) compared to the resistance across the cell estimated from the current flow

Catholyte conditioner	R based on pore fluid (kΩ)	R based on current flow (kΩ)
Nitric acid	0.84	1.1
Sulphuric acid	2.9	2.9
Citric acid	20	14
Acetic acid	7.9	10

where R is the electrical resistance of the sludge sample, L the cell length, A the cross-sectional area of the specimen and K^* the effective conductivity which can be estimated by the following correlation [16]:

$$K^* = \varepsilon \tau K \tag{3}$$

where K is the measured conductivity of the pore fluid (in the absence of the solid phase), ε the kaolin porosity, and τ the tortuosity. The porosity and tortuosity are assumed to be constant and equal to the values measured for the fresh kaolin sludge ($\varepsilon = 0.81$, $\tau = 0.545$).

The calculated resistance can be compared with the resistance across the cell calculated from the applied potential and the current flow:

$$R = \frac{\Phi}{I} \tag{4}$$

where Φ is the applied voltage across the cell and I the current passing through the cell at the end of each experiment. This calculation assumes that the electrode potentials and the potential drop in the membranes and the electrolytes are negligible.

The resistance calculated using the measured pore fluid conductivity and the measured kaolin porosity (Eqs. (2) and (3)) was found to be in relatively good agreement with the resistance calculated from the current flow (Eq. (4)), as shown in Table 4. The differences in the resistances estimated by these two methods may be due to variations in porosity (and/or tortuosity) throughout the cell. The results thus suggest that there was no significant decrease in the porosity of the sludge in spite of the consolidation observed in Fig. 5(b).

3.4. Removal kinetics

A series of experiments were carried out where the duration of treatment was varied between 48 and 240 h. Fig. 10 shows that the average caesium concentration in the cell decreased with treatment time. The results suggest that the process is limited by the strong adsorption of the caesium on the kaolin. The concentration of caesium decreased gradually throughout the cell, suggesting that most of the caesium was adsorbed on the kaolin. As the free caesium ions migrated in the electric field, the adsorbed caesium gradually desorbed to maintain equilibrium. The shape of the caesium concentration profile would depend on a number of factors,
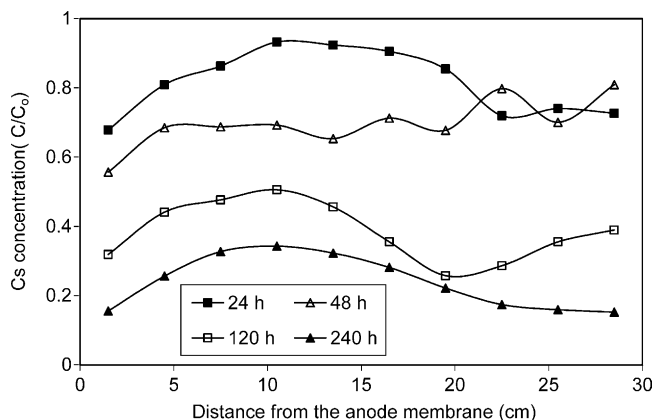
Fig. 10. Distribution of final caesium concentration across the soil specimen for a range of electrokinetic treatment times. Operating conditions: $C_0 = 450$ mg Cs kg^{-1} dry kaolin, catholyte pH = 3.0 (controlled by addition of sulphuric acid), $E = 1$ V cm^{-1}.

in particular the pH and conductivity distribution. Regions with low pH (close to the anode) would be expected to show higher rates of extraction, as the caesium is more readily desorbed into the pore fluid. In addition regions with lower conductivity (towards the cathode) would be expected to have higher rates of electromigration, as the potential gradient will be higher. This may explain the 'humped' shape observed in Fig. 10. Measurements of the potential distribution are shown in Fig. 11. Initially, a uniform potential gradient was observed across the sample, but as the treatment progressed, the potential gradient increased in the region close to the cathode and decreased in the acidified region close to the anode.

The caesium extraction process was found to be a relatively slow process, with 79% caesium removal after 240 h as shown in Fig. 12. The required treatment time can be estimated by considering the flux of caesium through the membrane into the catholyte due to electromigration:

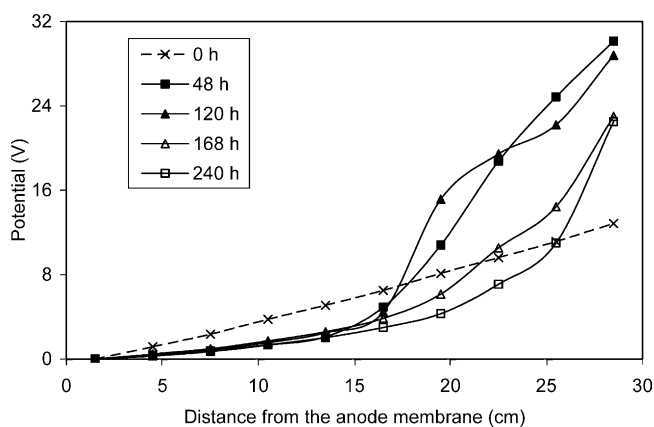$$N = z_{Cs} u_{Cs}^* Fc\nabla\Phi \tag{5}$$

Fig. 11. Potential difference profiles as a function of distance from the anode membrane for the electrokinetic treatment of kaolin contaminated with caesium. Operating conditions: $C_0 = 450$ mg Cs kg^{-1} dry kaolin, catholyte pH = 3.0, $E = 1$ V cm^{-1}.
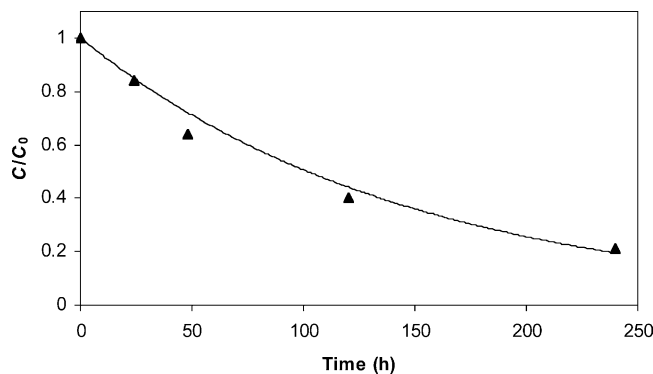

Fig. 12. Removal of caesium as a function of time for the electrokinetic treatment of kaolin contaminated with caesium. Operating conditions: $C_0 = 450$ mg Cs kg^{-1} dry kaolin, catholyte pH = 3.0, $E = 1$ V cm^{-1}. The triangles show the average concentration of caesium in the cell determined from the experimental results while the line is the prediction calculated using Eq. (6).

where z_{Cs} is the charge of the caesium ion ($z_{Cs} = 1$), u_{Cs}^* is the effective ionic mobility of the caesium ions, F is Faraday's constant, c is the concentration of caesium in the pore fluid in the soil adjacent to the membrane and $\nabla\Phi$ is the gradient of the electric potential. The pore fluid concentration can be estimated from the adsorption data (Fig. 2) which is approximately linear for concentrations below 500 mg Cs kg^{-1}. Assuming a soil pH of 3.0, approximately 13% of the caesium present in the kaolin sludge will be in the pore fluid, with the remaining 87% adsorbed on the kaolin. Assuming that this equilibrium was maintained and that the concentration of caesium was approximately uniform, carrying out a mass balance for the total caesium in the soil using Eq. (5) indicates that the average caesium concentration will decay exponentially as follows:

$$\ln\left(\frac{C}{C_0}\right) = \frac{-0.13 z_{Cs} u_{Cs}^* F\nabla\Phi t}{\varepsilon L} \tag{6}$$

Eq. (6) is plotted in Fig. 12 for the experimental conditions described above. This very simple model shows remarkable agreement with the experimental data. The time constant for the exponential decay described by Eq. (6) is 144 h, compared to 147 h obtained from a least squares fit of the experimental data. The agreement with the experimental data suggests that this simple model is representative of the experimental behaviour.

3.5. Soil type

In this section electrokinetic treatment of kaolin and a soil sample from an industrial site (an uncontaminated soil sample from the Sellafield nuclear facility, supplied by BNFL) are compared. A 15 cm sample vessel was used (i.e. using five compartments), with 15 V applied across the electrodes. The results were compared with a similar experiment carried out using kaolin in the same 15 cm cell. These two experiments were conducted on kaolin or soil contaminated with
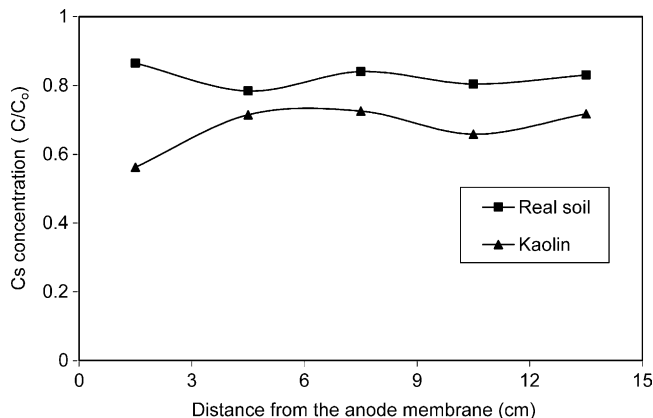
Fig. 13. Distribution of final caesium concentration across the specimen as a function of distance from the anode membrane for a soil sample and kaolin. Operating conditions: time = 24 h, $C_0 = 450$ mg Cs kg^{-1} dry kaolin or soil, catholyte pH = 3.0, $E = 1$ V cm^{-1}.

caesium nitrate to give an initial caesium concentration of 450 mg kg^{-1} of dry kaolin or soil. As described in Sections 2.2 and 2.3, the soil sample was dried and water was added to give a water content of 33.3 wt.% (compared to 64 wt.% for the kaolin). Each experiment was conducted for 24 h, and sulphuric acid was used to control the catholyte pH at a value of 3.0.

Fig. 13 shows a comparison of the caesium concentration distribution after electrokinetic treatment of both kaolin and the soil sample. Electrokinetic treatment of the soil successfully moved some of the caesium in the cell into the catholyte. The amount of caesium removed from the kaolin was 32% compared to 13% removed from the soil sample. Clearly the electrokinetic treatment process is significantly slower for the soil sample than for the kaolin.

The distribution of the in situ pH in the cell is shown in Fig. 14. As expected, the in situ pH of kaolin decreased throughout most of the sample, except in the area close to the cathode. The soil sample had a much higher initial pH,
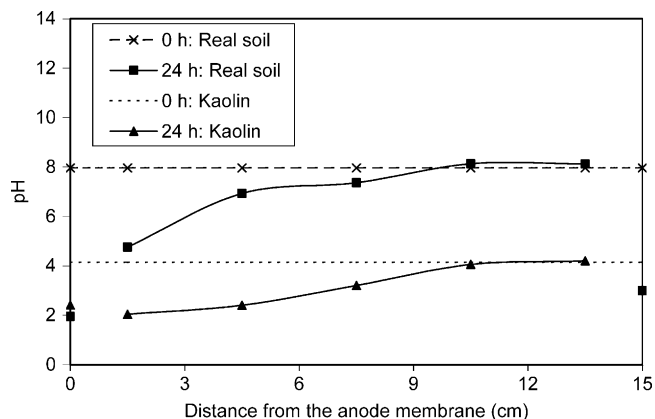

Fig. 14. In situ pH as a function of distance from the anode membrane for a soil sample and kaolin. Values of pH at 0 and 15 cm indicate the electrolyte pH. Operating conditions: $C_0 = 450$ mg Cs kg^{-1} dry kaolin or soil, $E = 1$ V cm^{-1}, treatment time = 48 h, catholyte pH = 3.0 using acetic acid.
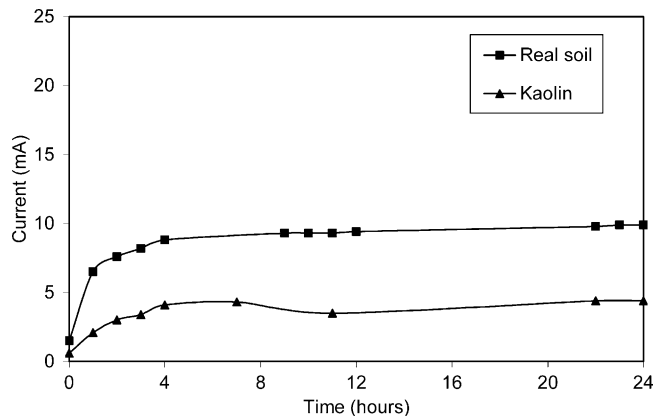

Fig. 15. Current profiles as a function of time for a soil sample and kaolin. Operating conditions: $C_0 = 450$ mg Cs kg^{-1} dry kaolin or soil, $E = 1$ V cm^{-1}, catholyte pH = 3.0 using acetic acid.

and a decrease in pH was observed only in the area close to the anode. These results are consistent with the high cation exchange capacity of the soil compared to the kaolin. The soil acted as a buffer slowing the advance of the pH front from the anode and thus reducing the rate of extraction. This, combined with the higher initial pH of the soil, may explain the relatively low caesium removal rate obtained for the soil sample. Unfortunately, the clay content of the soil has not been determined and in the absence of absorption data any further interpretation of the relatively slow caesium removal rate observed with the real soil is not possible.

Fig. 15 shows the current profiles of these electrokinetic treatment experiments. In the case of kaolin, the current increased initially, before steadying off at 3–4 mA after 4 h of operation. In the case of the soil sample, the current increased rapidly to 6.5 mA after 1 h before slowly increasing to reach 10 mA after 24 h. Clearly the soil sample had significantly higher conductivity than the kaolin indicating a higher ionic concentration. The catholyte and anolyte also developed a higher conductivity during treatment of the soil sample, due to the migration of ions from the soil into the electrolytes. In general, the higher current and the slower treatment rate obtained in the case of the soil sample indicates that more electrical energy (thus a higher cost) would be required for electrokinetic treatment of this soil compared to the low-conductivity, low-buffering kaolin.

4. Summary and conclusion

The electrokinetic treatment of kaolin contaminated with caesium is strongly effected by catholyte pH control. When the catholyte pH was not controlled caesium removal was hindered, probably due to the formation of precipitates in the area close to the cathode. By controlling the catholyte pH, a low pH environment was obtained across the sample, and the removal of caesium was promoted. The investigation

of the caesium extraction process using different acids to control the catholyte pH indicated that the type of acid used affects the rate of removal. In particular, the use of strong acids such as nitric and sulphuric acid was found to be more effective than weaker acids such as citric and acetic acid. However, the use of such strong acids for in situ remediation is questionable.

Due to strong caesium adsorption, the removal process was relatively slow, with 79% of caesium removed from the kaolin sample after 10 days of operation. The results suggest that around 87% of the caesium is adsorbed on the kaolin, and the caesium ions in the pore fluid are free to migrate in the electric field. A very simple model, which assumed that the adsorption equilibrium was maintained, that there was a uniform caesium concentration distribution throughout, and that electromigration of the caesium in the pore fluid was the only mechanism for transport of caesium ions into the catholyte, gave remarkably good agreement with the experimental data. For systems that exhibit strong adsorption, the results suggest that this model, with experimental adsorption data, may be used to obtain a good estimate of the required treatment time.

Electrokinetic treatment of a soil sample from an industrial site indicated that the required treatment time can vary significantly, depending on the properties of the soil. Further work is needed to determine whether data on the adsorption behaviour and/or the cation exchange capacity can be used to give an accurate prediction of the required treatment time for a range of soil types. In addition, the presence of high ionic concentrations in the soil led to higher power consumption, as energy was wasted in transporting these other ions rather than the caesium contaminant.

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