J Appl Electrochem (2010) 40:1225–1237
DOI 10.1007/s10800-010-0096-8

ORIGINAL PAPER

Physico-chemical effects on clay due to electromigration using stainless steel electrodes

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Received: 28 August 2009 / Accepted: 25 January 2010 / Published online: 12 February 2010

Abstract The physico-chemical changes in clay soils due to the application of electrokinetics are difficult to predict with accuracy because of the very wide range of parameters interacting. The effects of the application of an electrical gradient across controlled specimens of a pure form of kaolinite using stainless steel electrodes and a deionised water feed to the electrodes, to mimic electrokinetic stabilisation without the stabiliser added, are reported. The specimens in which electrical and chemical changes were induced over different time periods (3, 7, 14 and 28 days) were subsequently tested for Atterberg limits, undrained shear strength, water content, pH, conductivity, Fe concentration and zeta potential. Changes in strength and plasticity indices were attributed to electrolysis, electro-osmosis, electrode degradation, clay mineral dissolution, ion movement due to electromigration, cation exchange reactions and precipitation of reaction products.

Keywords Electrokinetic · Electromigration · Electro-osmosis · Kaolinite · Steel electrodes

1 Introduction

Improvement of the engineering properties of soft clay soils can be achieved by water content reduction and/or the addition of stabilising chemicals. This can be done by physically intensive processes such as mass preloading and in-situ or ex-situ mixing of clay with stabilisers prior to compaction. An attractive alternative that avoids such extensive physical activity and ground disturbance is to use electrical means. Soft, wet clay dewatering can be achieved by electro-osmosis (see [1–3]). Chemical alteration of fine-grained soils *in situ* can be achieved using electrokinetic treatments, in which stabilisers are introduced at one or both of the electrodes (for example, see [4, 5]). While these treatments can undoubtedly be effective, a full understanding of the implications of the treatment for any one clay is difficult to gain as a result of the many interconnected chemical effects taking place. This complexity has spawned some interesting explanatory studies (e.g. [6, 7]) and important clues can be gained from the extensive work on electrokinetic soil remediation research (e.g. [8]). Nevertheless there is a need for a comprehensive guide to the many chemical effects taking place in the clay, and this is the aim of this paper dealing with stainless steel electrodes and its companion paper dealing with inert electrodes [9].

The research described herein relates to the movement of ions within a saturated clay under an imposed electrical gradient with the specific intention that ions from no external source other than the electrodes are introduced. By using relatively pure kaolinite, steel electrodes for the provision of an electrical gradient and consistency of the treatment, and a 'Reverse Osmosis' (RO, i.e. water that is deionised using reverse osmosis techniques) water feed at the electrodes, this study aims to demonstrate and explain the essential physico-chemical effects induced by the process. The situation imitates the treatment used to induce electro-osmotic consolidation using steel electrodes in which electrode degradation causes iron ions to be

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introduced into the clay thereby bringing about "soil hardening" as an added benefit (e.g. see [10]), but with the important difference that a water feed at the anode is introduced. It therefore can be considered to replicate electrokinetic stabilisation yet without the addition of aqueous stabiliser solutions. Only once such results have been reported can the effects of the introduction of stabilisers be accurately inferred. This paper is thus a companion paper to Liaki et al. [9], which reports a study identical in every aspect other than the use of 'inert' (pressed carbon-coated) electrodes and therefore provides a baseline understanding of physico-chemical changes from which the effects of iron ions can be accurately determined.

It has been suggested that the costs of "electrical treatment" of soil can prove practically prohibitive. However, there are important practical advantages of electrokinetic stabilisation that counteract such arguments, such as the ability to bring about improvements in the ground between two points without physical disturbance of the ground (e.g. to reduce or remove shrink-swell potential) beneath building foundations, thereby avoiding underpinning (piling or groundbeams). Similarly the ground beneath or surrounding elements of the surface or buried infrastructure could be strengthened and/or stiffened without disruption, such as soft spots beneath roads, railways or pipelines. A permanent improvement in the ground due to electro-osmotic (over)consolidation in cases where no stabilisers are added is an alternative benefit. This level of improvement must be offset against the costs of the electricity, the stabilisers (where used) and replacement of electrodes as they degrade. A further cost comparison is possible by comparing the additional benefit of iron ions (i.e. above those reported by Liaki et al. [9]) with the cost of electrode replacement. Finally, an improvement in the basic understanding of the processes allows treatments to be accurately designed and targeted, making their application potentially far more efficient.

The literature reports that application of an electrical gradient across a clay soil results in changes in soil pH due to the decomposition of water via reduction and oxidation reactions at the electrodes, water flow between the electrodes, and migration of ions towards the electrode of the opposite sign. The ions referred to in the last of these include ions existing in the clay soil, ions introduced via hydrated solutions added to the anode or cathode, and ions released from the electrodes as they degrade. The underlying effects from the application of an electrical gradient to a soil mass have been extensively reported (e.g. [11–15]) and have been summarised by Liaki et al. [9] to provide a context for this paper, which aims to quantify such effects in a controlled environment with a relatively pure clay. The paper thus aims to provide a solid fundamental understanding of all of the relevant corrosion effects, in addition to the electrical effects reported by Liaki et al. [9] occurring in a relatively pure clay, from which the effects in other types of clay soil can be predicted by extrapolation.

2 Experimental methodology

2.1 Materials

The soil used in this study was a refined form of kaolinite deriving from china clay quarries in South-West England (Puraflo 50 supplied by WBB Devon Clays Ltd, Devon, UK). The Liquid Limit (LL) and Plastic Limit (PL) for the untreated soil (i.e. the control sample) were 55.6 and 23.6% respectively. The control sample, which was consolidated from a slurry in precisely the same manner as the test specimens (see below), was tested for water content (51.1%), undrained shear strength (8.2 kPa), pH (5.68), conductivity (37.6 μS/cm), Fe ion concentration (398.3 ppm) and zeta potential (−25.2 mV), again using the methods described later. In addition, a series of slurry samples of 90% water content were consolidated in a California Bearing Ratio (CBR) mould to different final water contents and hand vane tests were performed to provide a control relationship between water content and undrained shear strength.

RO water, having a conductivity of 7.5 μS/cm at 25 °C, was used for the slurry preparation and all the physical and chemical tests with the exception of the preparation and the atomic absorption analysis of the acid digested samples, where "Ultra High Quality" (UHQ) water with a conductivity of 0.06 μS/cm was used. The material used for the electrodes was welded stainless steel mesh (12.7 × 12.7 mm × 16 gauge). The electrodes were cut to a length of approximately 400 mm and width of 200 mm.

2.2 Equipment and specimen creation

2.2.1 *Tanks configuration and development*

The tank used for the electromigration tests consisted of three chambers (Fig. 1), which were separated with perforated walls and had two different detachable bases (one solid and one perforated), as described by Liaki et al. [9]. The experimental arrangement was identical to that described by Liaki et al. [9] with the exception of the electrode material.

2.2.2 *Specimen creation*

The tank was fitted with the perforated base and its main compartment was filled with a clay slurry (with a water content of 90%), which was then incrementally

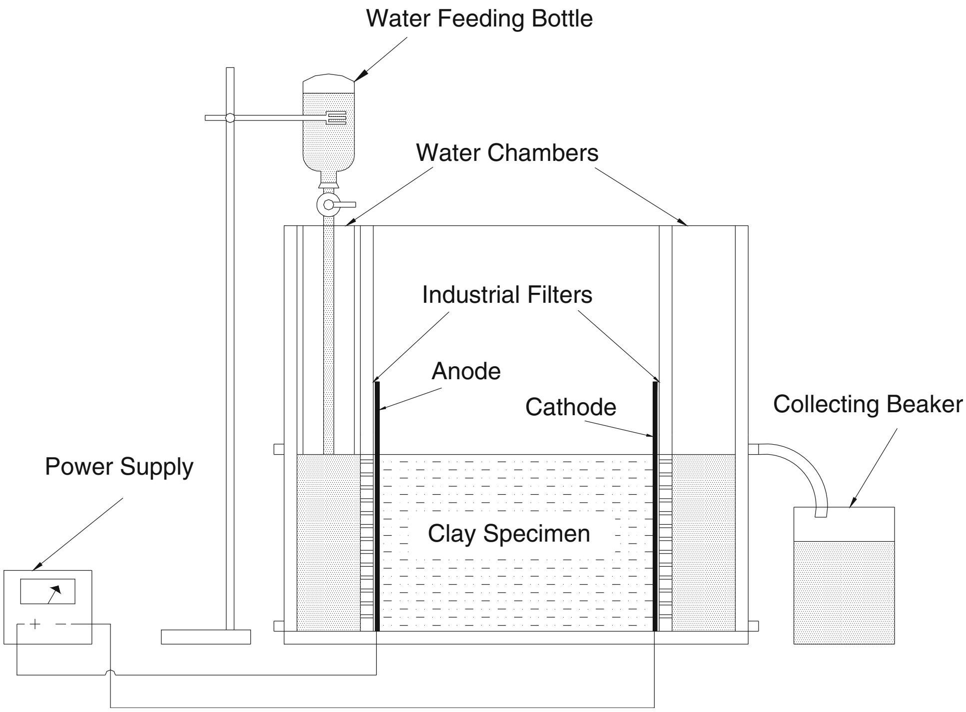

Fig. 1 Electrokinetic treatment arrangement with the consolidated clay specimen formed and the solid tank base in position

consolidated using a hydraulic jack arrangement over a period of 7 days, as described by Liaki et al. [9]. The main requirement for the consolidation process was to produce clay samples in a repeatable way by normal consolidation. Homogeneity of the samples was achieved by measuring and ensuring that the final height of all specimens was the same. Once consolidation was complete the perforated base was removed, the solid base was then attached and the electrodes were placed adjacent to, and brought into intimate contact with, the soil specimen from the inside of the main compartment.

2.3 Treatment using electromigration

The two side chambers were filled with 2,600 ml of water to reach the same level as the clay specimen. An inverted water bottle, with a flexible plastic tube attached, was installed above the 'anode chamber' to feed it with water such that, when water was transported towards the cathode due to the electromigration treatment, the water level remained the same at both ends of the tank and no hydraulic gradient was formed at any point during the test. This ensured that flow was not caused by a hydraulic driver. A water collecting beaker was connected to the cathode chamber to receive the overflow water.

Power distribution cables were attached to the electrodes and connected to the power supply, which provided a constant voltage gradient between the electrodes equivalent to 0.5 V/cm length. The different clay specimens were treated for 3, 7, 14 and 28 day periods.

2.4 Post-treatment testing

2.4.1 Sample extraction and standard geotechnical testing

Once electromigration treatment was terminated, hand vane tests were carried out to determine the undrained shear strength distribution while the solid treated specimen was still inside its tank. Duplicate readings were taken in each of the 8 zones between the anode and the cathode, as described by Liaki et al. [9], and, due to their similarity in each case, the first measured values, which were at larger spacings and certainly not affected by adjacent testing, are reported here in. The core samples extracted from the hand vane test were used for water content determination.

The solid base of the tank was then detached from the walls, the electrodes were removed and the walls were then carefully removed upwards in order not to cause any disturbance to the treated specimen. The upper 60 mm, was removed to ensure that any surface drying/wetting or disturbance effects were avoided. A core sample was then trimmed from the remaining lower portion of each treated specimen and was cut transversally into 8 smaller samples (annotated as Samples 1–8 from anode to cathode, respectively) with an approximate width of 45 mm, as described by Liaki et al. [9]. These 8 samples were placed into airtight plastic bags and stored in a controlled-temperature room at 3.9 ± 0.1 °C until further testing.

Each of the eight samples was tested for Plastic Limit (PL) and Liquid Limit (LL) according to BS 1377: Part 2 [16] with the exception that the samples were brought directly to the correct water contents for testing by either air drying or wetting with RO water so as to avoid any physico-chemical changes resulting from drying back fully prior to rehydration.

A small sample of wet soil deriving from each of the eight samples was mixed with RO water to achieve a dry solid to water ratio of 1:5 and subjected to both pH and conductivity tests. It is recognised that the addition of water has an effect on the measured pH, however it was necessary at this time because the amount of extractable pore fluid was not sufficient to measure pH with the pH probes available. Further details of these tests are reported by Liaki [17] and Liaki et al. [9].

2.4.2 *Iron concentration measurements*

Atomic absorption (AA) spectrometry analysis was carried out on the eight samples from each specimen, which had been previously acid digested with a mixture of HCl and HNO_3. Small soil samples (either 1.0000 or 1.2000 g) derived from each of the eight electrokinetically treated samples, which had been dried at 105 °C and sieved to pass through a 425 μm filter, were placed into 150 ml Pyrex glass beakers with 2.7 ml of concentrated HCl and 1.3 ml of concentrated HNO_3. UHQ water was then added to the mixture to reach a total volume of 50 ml. The mixtures were then brought to boil on a hot plate surface, evaporated to reach approximately 5 ml volume and left to cool at room temperature for approximately 10 min. Concentrated HCl, HNO_3 and UHQ water were once again added in the same quantities as before and the evaporation process was repeated.

The samples were then were filtered through a Whatman 540 filter paper into volumetric flasks. Ultra High Quality (i.e. UHQ) water was then added to reach a volume of 100 ml and a second filtration took place using a Whatman 0.20 μm membrane filter. The samples were then stored in a controlled-temperature room at 3.9 ± 0.1 °C. The acid digested samples were then analysed for their Fe ion contents using atomic absorption spectrometry using the Solar System-ATI Unicam 939 model, the data presented herein being the average of two values.

2.4.3 *Zeta potential measurements*

Zeta potential analysis took place on selected electrokinetically treated soil samples extracted from the eight locations on the core sample mentioned earlier, the five representative samples analysed being Samples 1, 2, 4, 7 and 8 (working from the anode to the cathode). The already wet samples were mixed with water to achieve 9.93% of soil:(soil and water) ratio in a 200 g diluted sample and analysed for their zeta potential using an AcoustoSizer II v3.037 provided by Colloidal Dynamics [17].

2.4.4 *Accuracy and repeatability*

Precautions were taken to optimise the accuracy of the measured Atterberg limits (an additional penetration was used in the LL tests, while a single operator using standardised procedures yielded PL results consistently within 0.5%), water content and undrained shear strength data (duplicate readings in each case). The zeta potential readings reported herein are an average of 10 values taken for each sample during the analysis.

Accuracy and repeatability were ensured during the Fe ion analysis by testing two acid digested samples, of 1.0 and 1.2 g dry soil content, from each of the 8 locations along the anode-cathode axis of the treated sample. The general trends in the analysed data between the two samples were consistent for each experiment, and the average values are reported herein. All the samples were analysed by the AA spectrometer at the same time, ensuring that that the height of the flame was always the same; three readings were taken from each sample and the average of these three values is presented herein. UHQ water was passed through the aspirator probe between each measurement to ensure no contamination between samples was taking place.

All glassware, plastic ware and equipment used throughout the preparation of the acid digested samples and their analysis was acid-washed prior to use.

3 Results

3.1 Undrained shear strength

3.1.1 *Relationship with water content*

The undrained shear strength data (Fig. 2) were split in three zones for analysis: between 0–110, 110–280 and 280–360 mm from the anode. The undrained shear strength showed a general correlation with the water content of the soil (i.e. strength reducing as water content rose, and vice versa), as might be expected. The undrained shear strength in the vicinity of the anode increased with treatment time, even though the water content generally increased. Interestingly there was a marked fall in strength at the anode after 3 days, although no increase in water content at this time. In the second zone the undrained shear strength was generally marginally lower than the control value, while the water content was markedly higher than the control. The undrained shear strength in the third zone decreased while the water content increased, in accordance with classical soil mechanics theory. Nevertheless there was sufficient evidence in this graph to indicate that the water content was not the only factor influencing the undrained shear strength of the electrokinetically treated soil.

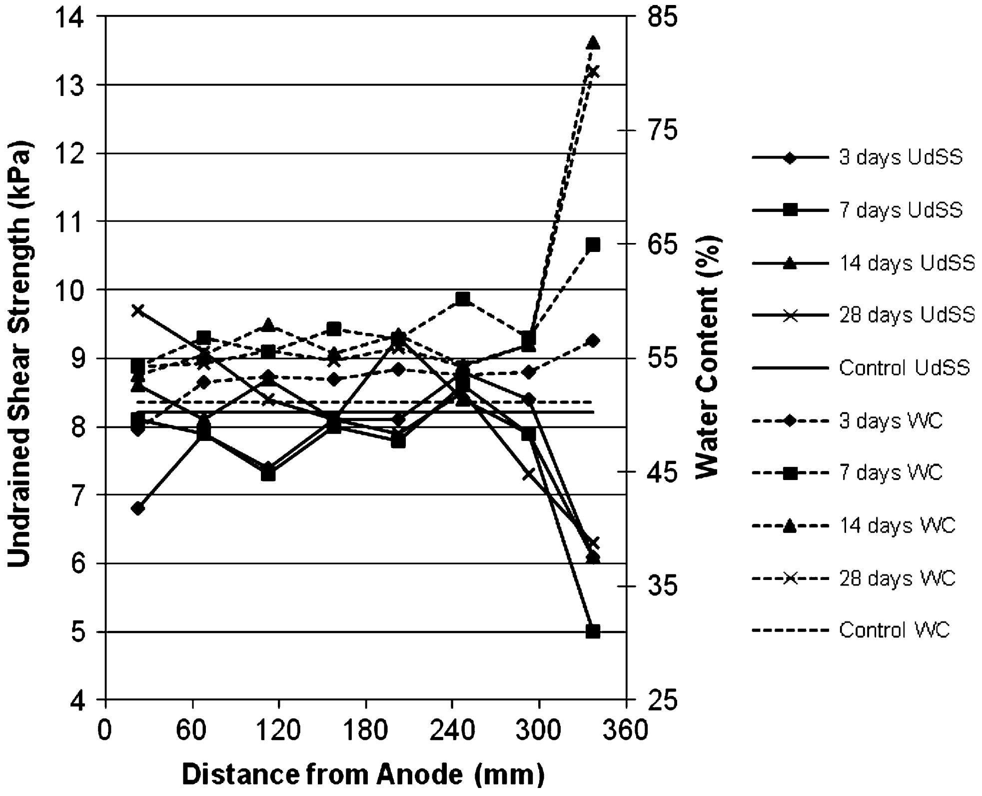

Fig. 2 Relationship between clay undrained shear strength and water content with distance from the anode

Figure 3 illustrates the relationship between the undrained shear strength and water content. The control line refers to the undrained shear strength measurements from the control specimen and those from the untreated soil consolidated to different water contents, and hence provides an indication of experimental variability that might be expected. It also illustrates the variation in undrained shear strength with water content which enables the identification of potential changes in undrained shear strength caused by other processes. All data that lie above and/or are shifted to the right of the control line indicate soil strengthening, while the data below and/or shifted to the left of the control relationship suggest weakening (i.e. the broken arrows signify chemical improvement, while the full arrows signify the opposite, as proposed by Rogers et al. [18]). Data points that lie a small distance away from the control line may be attributed to chemical changes occurring on the surface of the clay particles, for example due to changes in the diffuse double layer, while those showing large improvements in strength may be attributed to chemical reactions occurring in the clay, such as compound precipitation since the apparent strength increases, particularly at the cathode relative to the control line illustrated in Fig. 3, are accompanied by high pH illustrated in Fig. 4. Where the pH is greatly raised classic soil stabilisation cementitious reactions could be occurring [19]. The squared points in Fig. 3 denote the points in the vicinity of the anodes, while the circled points denote those closest to the cathode. All points corresponding to the cathode were markedly weaker than the soil elsewhere in the tanks (i.e. had a smaller ordinate in the graph, consistent with the increases in water content here); however all lie above the control line. The points corresponding to the anode for the 7, 14 and 28-day experiments show improvement, while the 3-day data exhibit notable soil weakening.

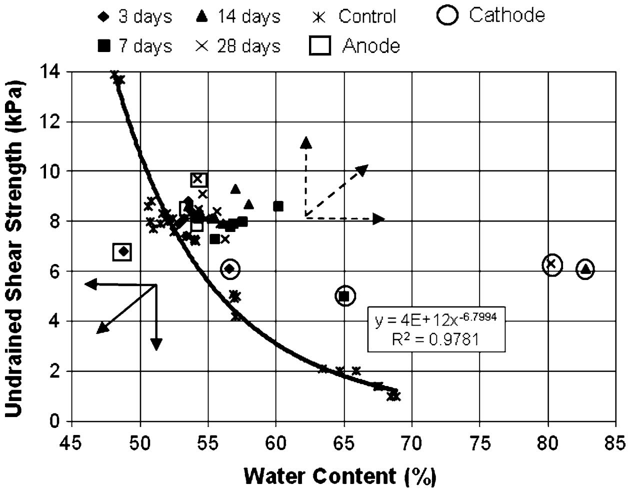

Fig. 3 Relationship between clay undrained shear strength and water content

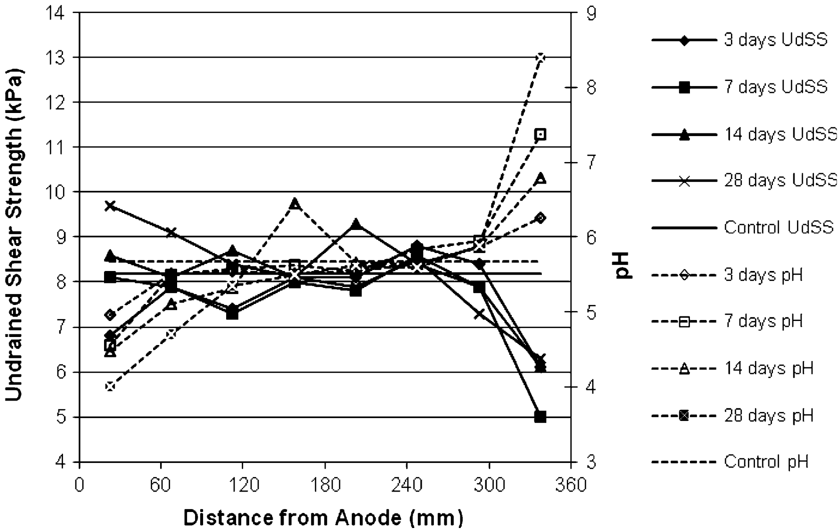

Fig. 4 Relationship between clay undrained shear strength and pH with distance from the anode

The clay in the vicinity of the cathode (circled) exhibits progressive relative strengthening above the control trendline, with two extreme points (corresponding to the two longest treatments) lying at high water content values yet maintaining significant (and in relative terms very high) strengths. In contrast, the majority of the points for the anode lie much closer to the control line. The data in the zone adjacent to that containing the cathode (i.e. 280–360 mm from the anode, Sample 7) generally indicated soil strengthening with respect to the control. Between the electrodes (at 110–280 mm, Samples 4–6) the values showed marginal soil strengthening (i.e. in relation to the control line, in Fig. 3, but in absolute terms there is a weakening as shown in Fig. 2; this shows the value of removing the influence of water content). Weakening around the anode was observed for the 3-day tests and might superficially be attributed to cation movements within the soil away from this area and flushing with RO water, particularly given that anode degradation was only *observed* to occur *after* 3 days. However evidence for such a supposition is lacking, particularly given the measured increase in Fe ion concentrations reported later, and a different mechanism will be proposed later in the paper.

3.1.2 Relationship with pH

Figure 4 illustrates the relationship between undrained shear strength, pH and distance from the anode. The data in zone three (280–360 mm) are of a particular interest. While the pH generally increased, the undrained shear strength reduced towards the cathode, indicating an inverse relationship between the two parameters, with the control lines acting as the inflection axes. However, there is not a strong correspondence between pH and shear strength. For example, the 7-day strength (with a pH > 7.0) is markedly lower, while the 14 and 28-day strengths (both with pH > 6.5) and, importantly, very greatly raised water contents (Fig. 2) are the same as the 3-day value.

A distinct relationship between pH and undrained shear strength also appeared in the first zone (0–110 mm). However, in this case the pH reduced towards the anode and reached progressively lower values over the 28-day period while the undrained shear strength increased, with the lowest pH observed for the 28-day experiment and corresponding to the highest undrained shear strength. Figure 4, when allied to the observation during the experiment of anode degradation after 3 days and greatly increased degradation in the longer tests, also suggests that the longer the treatment time, and consequently more Fe ions released in the vicinity of the anode, the higher the undrained shear strength and the stronger the acid front. This reflects a notable difference between steel and inert electrodes, the strengths for steel electrodes at the anode after 3 days being markedly greater for pH values that are 0.5–1.0 point higher for steel than those for inert electrodes [9].

In the second zone (110–280 mm), a transition between the two extremes was observed (Fig. 4). This may be attributed to the fact that the acid and alkali fronts are moving towards each other and meet somewhere in the second zone, although at different points depending on the length of the treatment.

The differences in pH at the anode between the two types of electrodes are influenced both by the acid front forming due to water decomposition and the Fe release due to electrode degradation (the lack of Fe ions in the case of inert electrodes resulting in greater H ion production). However, the results of both the pH and the undrained shear strength measurements at the cathode do not exhibit major differences between steel and the inert electrodes reported by Liaki et al. [9]. This indicates that the alkali front is what causes the changes from the control values here, and perhaps that it is the absolute value of pH in the vicinity of the cathode, regardless of electrode type, that is important.

3.1.3 Relationship with conductivity

Figure 5 illustrates the relationship between undrained shear strength and conductivity with distance from the anode. The first and the third zones indicated raised conductivity values, excepting the 3-day data close to the cathode for which the conductivity fell. In the first zone (Samples 1–3, 0–110 mm) the undrained shear strength initially decreased from the control value, whereafter there was a progressive strength gain with time while at the same time the conductivity also rose markedly. It should be noted that although there is strength gain with little change in conductivity moving from 7 to 14 days, there is a large change from 14 to 28 days, which demonstrated that undrained shear strength changes were not directly proportional to those of conductivity. Conductivity is affected by pH change. High conductivity values can be due to high concentration of H or OH ions, which is observed in the first and third zones (Fig. 4).

In the second zone (110–280 mm) in Fig. 5, there is an indication of a general plateau for both the undrained shear strength and conductivity plots. Close scrutiny of the conductivity data shows an interesting and well defined pattern of reduction from a consistent higher level to a consistent lower level with time away from the cathode with both levels being below the control. This is presumably the result of progressive developments of the acid and alkali fronts, although there is no apparent correlation to the variation in the strength data in this zone.

Zone three (280–360 mm) also illustrates a general decrease in the undrained shear strength, while the conductivity is increasing, albeit to a much smaller degree than is exhibited at the anode. A more detailed study of the decrease in undrained shear strength showed no apparent correlation between the two parameters. The strength at 7 days lies (markedly) lower than the other three values, while the conductivity at 7 days is high being intermediate between the 14 day and 28 day values.

3.1.4 Relationship with iron concentration

Figure 6 illustrates the relationship between the undrained shear strength and the acid soluble Fe concentration (Fe^{2+} might be expected in pore water rather than Fe^{3+} due to its greater solubility). The acid soluble Fe concentration in all cases was markedly higher than that for the control sample. The soil was strengthened in the vicinity of the anode when more Fe ions were present, i.e. when the treatment time was longer, via a linear relationship, and yet a large rise in Fe ions at 3 days resulted in an absolute strength reduction (Fig. 6) and relative strength reduction (Fig. 3). This implies that there is an alternative explanation. In addition, there was no apparent relationship between Fe ion concentration and undrained shear strength measurements at the cathode.

An alternative explanation is that Fe ions caused a detrimental effect in the vicinity of the anode at the pH of ~5 (though not elsewhere where the pH remained close to the control value), such an effect, even though contra-intuitive, being reported by Boardman et al. [20]. After 3 days, the pH reduced to a value below 5 and aluminium oxide (Al_2O_3) dissolved, thereby releasing Al^{3+} ions into the system [21]. This high valency ion substitutes preferentially onto the clay mineral exchange sites (as a result of

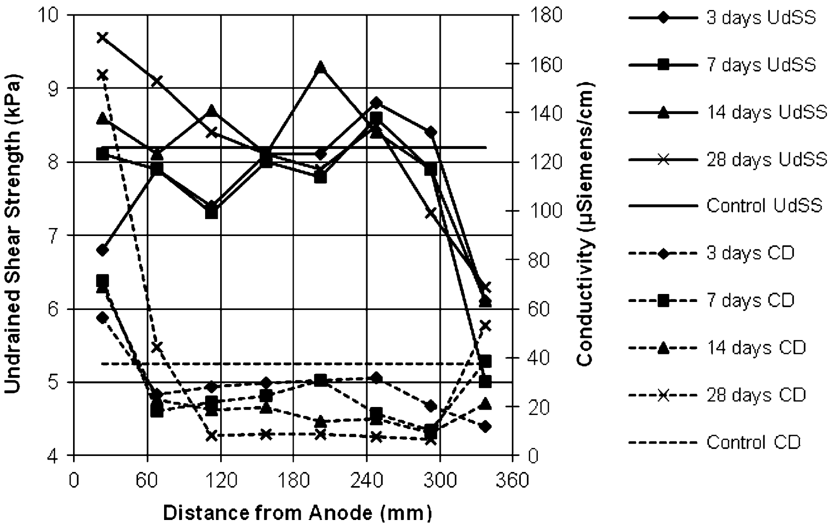

Fig. 5 Relationship between clay undrained shear strength and conductivity with distance from the anode

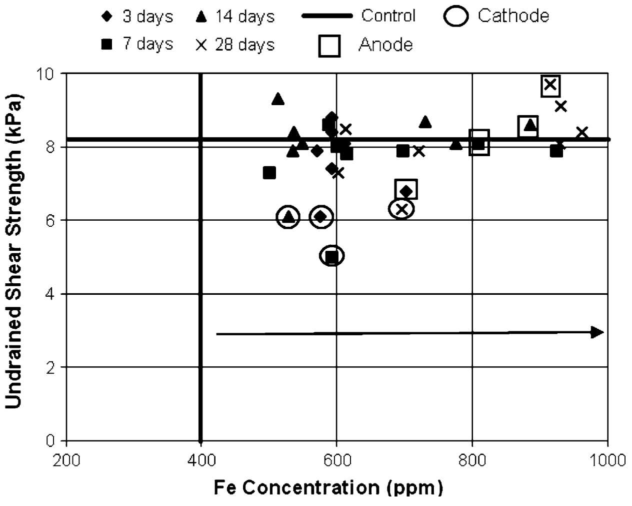

Fig. 6 Relationship between clay undrained shear strength and acid soluble Fe concentration

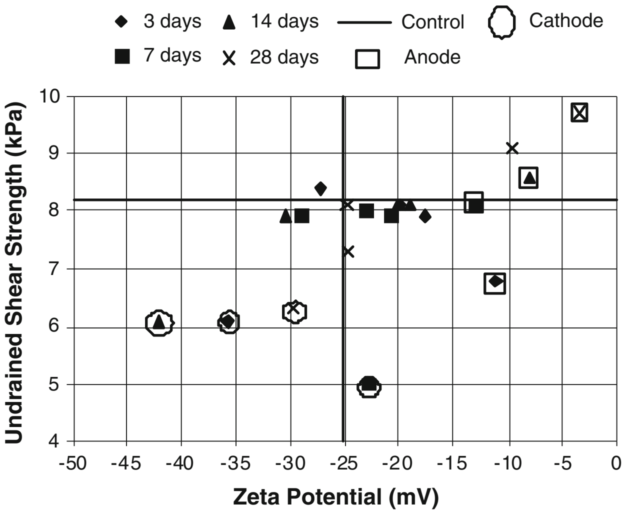

Fig. 7 Relationship between clay undrained shear strength and zeta potential

its high valency), thus causing a thinning of the diffuse double layer, flocculation of the clay particles and an increase in undrained shear strength.

These cations (Fe^{2+} and Al^{3+}) are equally transported across the system from the anode to the cathode under the electrical gradient. When these amphoteric ions reach the vicinity of the cathode, iron and/or aluminium compounds such as hydroxides—$Fe(OH)_2$ and $Al(OH)_3$—precipitate at raised values of pH (>6.5), and in so doing they use up OH^- ions.

3.1.5 Relationship with zeta potential

Figure 7 presents the relationship between the undrained shear strength and the zeta potential. The plot shows that only the values close to the electrodes tend to deviate greatly from the control values, while the overall trend is of higher undrained shear strength values for generally less negative zeta potential. At the anode there is a strong trend of increasing strength with time as the zeta potential becomes less negative, which can be attributed to the combined effects of pH and (after 3 days) perhaps Al^{3+} causes an effect on the system together with Fe ion release into the system from the electrodes, and may be associated with thinning of the adsorbed water layer. The points in the vicinity of the cathode generally exhibit a more negative zeta potential.

3.2 Liquid limit

3.2.1 Relationship with pH

Figure 8 shows the variation of LL and pH with distance from the anode and clearly illustrates that the LL for an electrokinetically treated kaolinite is pH dependent. In the first zone (0–110 mm), as the pH increased, the LL decreased away from the anode. Zone three (280–360 mm) illustrates a large decrease in the LL as the pH obtains its highest values. Zone two (110–280 mm) acts as a ‘transition zone’, where the changeover between the two different states takes place.

There are strong inverse relationships in the first and third zones, though the relationship at the anode is strongest since the points are ordered in terms of time at each point up to 120 mm away from the anode. Interestingly, the LL at the anode in the ‘inert’ electrode tests [9] rose from 57.8 after 3 days to a consistent value of approximately 58.5 thereafter, for pH values that reached lower values than those reported here for steel electrodes, while Fig. 8 shows a steadily increasing trend of LL above this level that can be attributed to the influence of the electrodes. Increases in LL near the anode in the presence of an acidic environment may be attributed to flocculation occurring due to compression of the diffuse double layer, as there are more positive ions such as H^+ ions present by implication from the pH values, which reduce the negativity of the zeta potential. In the case of the steel electrode tests, there is a further rise in the LL due to the additional higher valency positive ions (i.e. Fe ions) coming into the system from the anode and further thinning of the diffuse double layer via cation exchange of higher for lower valency ions. This can be seen in the shortest test, with 3-day values away from the electrodes generally being raised to a level between 56.5 and 57.2%. However, it is postulated that there is a third effect taking place. Given the chemical constitution of the clay and the solubility of these chemical components (see [21]), alumina (Al_2O_3) would be expected to go into solution as the pH falls below 5.0 and this could cause Al^{3+}

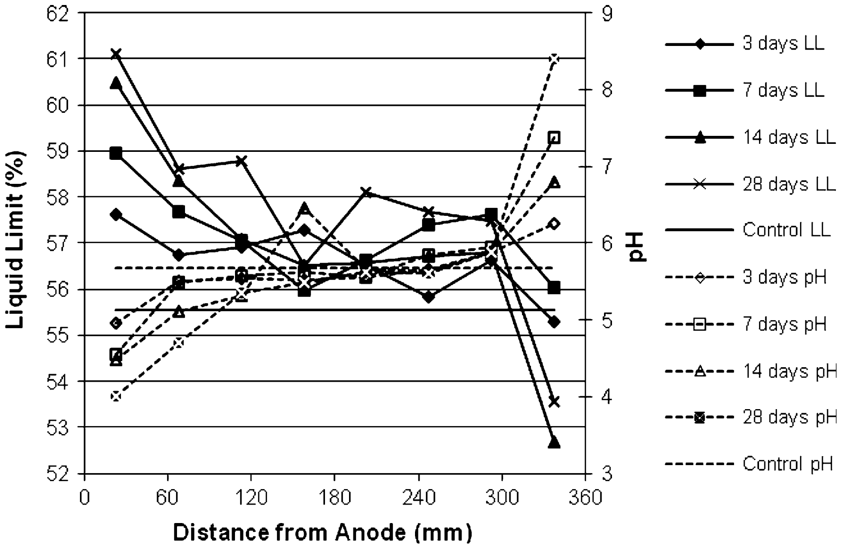

Fig. 8 Relationship between Liquid limit and pH with distance from the anode

ions to be transported from the area close to the anode throughout the clay mass under the electrical gradient. Since Al^{3+} has a smaller ionic radius than Fe ions, it could substitute more readily on the cation exchange sites of the kaolinite and depress the diffuse double layer (DDL) further, thereby causing a further increase in LL. Although by no means a consistent pattern, it might explain the LL values above 57.0 in Fig. 8, while also explaining the strength increases and markedly depressed LL values after 14 and 28 days at the cathode due to aluminium hydroxide ($Al(OH)_3$) precipitation.

Low LL is observed at the cathode for both types of tests due to the opposite phenomenon occurring, i.e. raised pH causing the zeta potential to become more negative and a thickening of the diffuse double layer. However, while the inverse pattern of LL falling as pH rises is excellent for the inert electrodes [9], the data for steel electrodes tests show the highest LL for the 7-day test while the pH is second highest. Following the arguments for the behaviour at the anode, this might reflect the contradictory influences of pH increase (lower zeta potential, thicker DDL) and Fe ion substitution (higher zeta potential, thinning of the DDL) at 3 days causing a small fall in LL; introduction of Al^{3+} ions at 7 days causing enhanced cation exchange effects and a small rise in LL; and then domination of the effects of $Al(OH)_3$ precipitation causing the LL to fall markedly, and the undrained shear strength to rise. This could be the result of clay mineral dissolution prior to gel crystallisation.

Figure 9 shows the variation of LL with pH. A ‘transition zone’ is observed between pH 5.0 and 6.0 and LL 56 and 58%. The majority of the more acidic values correspond to points in the vicinity of the anode. The plot illustrates higher LL values for lower pH (4.0–5.0) in the ‘acidic zone’. The points at high pH values correspond to those in the vicinity of the cathode, indicating that the LL

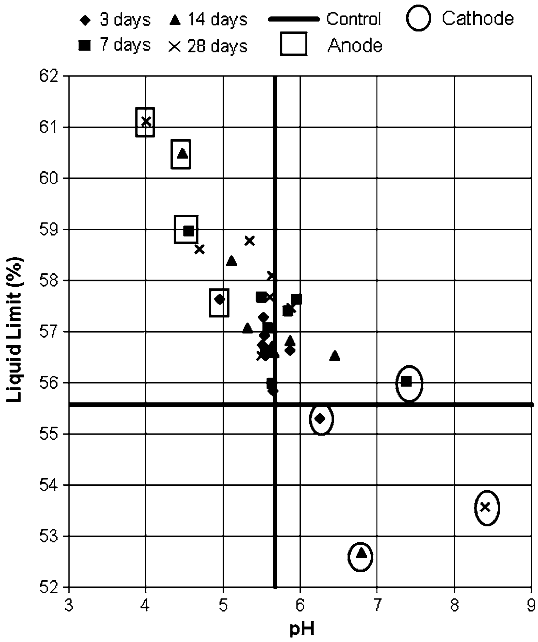

Fig. 9 Relationship between liquid limit and pH

decreases in a high pH environment and that the LL is sensitive to pH change. The LL has generally increased from the value of the untreated soil with the exception of the longer-term LL values close to the cathode.

English China Clay is known to have a highly pH sensitive surface charge [22]. Hence there is a greater exchange capacity in a higher pH environment resulting in a thicker diffuse double layer close to the cathode and a lower LL. In contrast, the acidic environment around the anode results in a thinner diffuse double layer and an increased LL up to a maximum of 3.0%, any greater reduction in thickness of the adsorbed water layer being attributed to Fe and Al^{3+} ion substitution and resulting in further increases in LL. The generally raised LL between the electrodes can be attributed to a combination of a marginally lowered pH, a general increase in Fe ion concentration and an introduction of Al^{3+} ions after 3 days, as discussed above.

3.2.2 Relationship with iron content

Figure 10 illustrates the effect of acid soluble Fe content on the LL of the treated soil. The data show that the Fe content of the soil is higher than that for the control sample. The Fe concentration increases with treatment time and this causes a progressive increase in the LL data closest to the anode. No general conclusions can be derived for the data around the cathode, as the LL tends to much lower values than the rest of the data, but with variable Fe contents. The data between the electrodes form a cluster for both types of experiments lying between LL values of 56–58% and Fe concentrations generally between 500–600 ppm. The LL reduces with distance from the anode as the Fe concentration reduces.

3.2.3 Relationship with zeta potential

Figure 11 shows the effects of zeta potential on the LL of the treated soil. The LL rises as the zeta potential becomes less negative (or from cathode to anode), which is also time dependent for the points in the vicinity of the anode. It should be noted that the acid soluble metal analysis revealed generally increased levels in the concentration of Fe and especially in the vicinity of the anode. This suggests that the higher the Fe concentration in the soil, the less negative the zeta potential becomes (i.e. the more positive the ionic concentration within the diffuse double layer is) and the more compressed the diffuse double layer becomes, and this causes flocculation of the particles and consequently an increase in the LL. The points in the vicinity of the cathode where high pH values are observed (implying high OH^- ion concentrations) generally illustrate more negative zeta potential and consequently thickening of the diffuse double layer, which results in the low LL values observed.

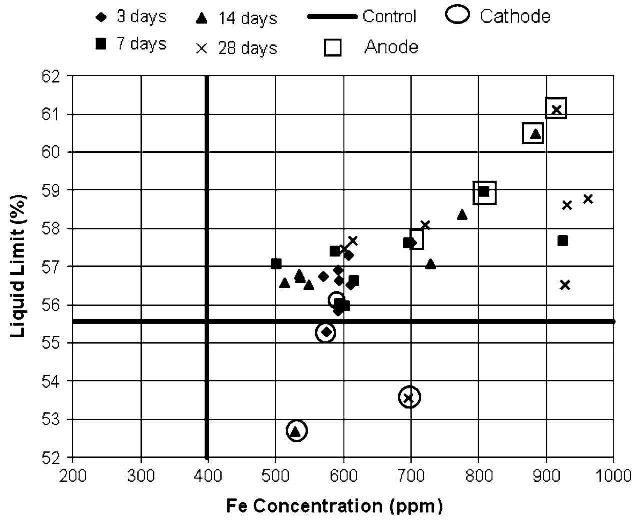

Fig. 10 Relationship between liquid limit and acid soluble Fe concentration

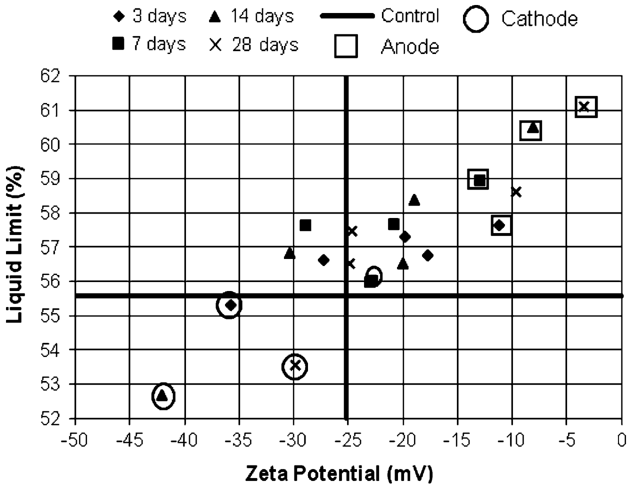

Fig. 11 Relationship between liquid limit and zeta potential

3.3 Plastic limit

3.3.1 Relationship with water content

Figure 12 presents the variation of PL with clay water content. There is a variation in the PL values of 33.8–

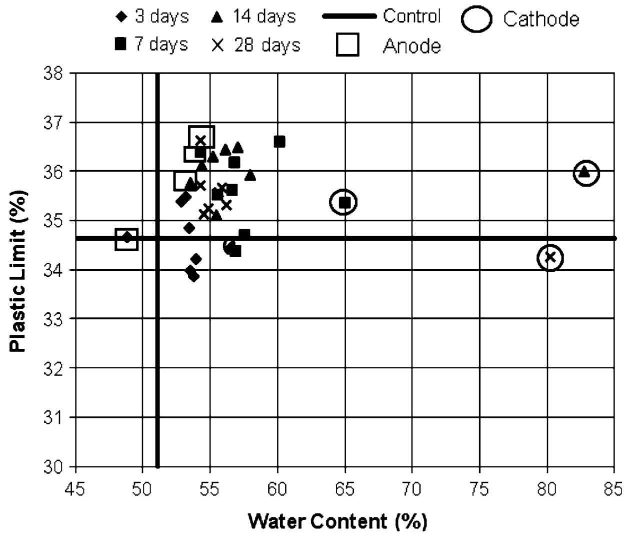

Fig. 12 Relationship between plastic limit and water content

36.4%, while the water content has a range (neglecting the data at the electrodes) between ~52–60% and there is a general tendency for PL to rise with treatment time. The general higher PL range (away from the electrodes) may be attributed to flocculation taking place, and there is a possible tendency for this flocculation being associated with a marginally raised water content suggesting a change in free and adsorbed water.

There are two additional observations from Fig. 12. While the electro-osmotic effect causes water to flow from the anode to the cathode and progressive swelling of the clay close to the cathode might be expected (the clay was overconsolidated during preparation), the reduction in water content at the anode at 3 days, but not thereafter, is less easy to explain in these terms. There is a water feed at the anode and thus any water driven through the clay specimen is replenished; the water content reduction at three days is thus likely to be a chemically induced effect related to the release of bound water at 105 °C. The second point is that the lowest Plastic Limit measurement at 28 days occurs in the vicinity of the cathode and this confirms the contention of chemical alteration, in this case expected to be a chemical reaction, indicated by other results.

3.3.2 Relationship with pH

Figure 13 shows the variation of PL with pH. The PL generally increases in the vicinity of the anode when the pH environment becomes more acidic, while around the cathode the PL varies.

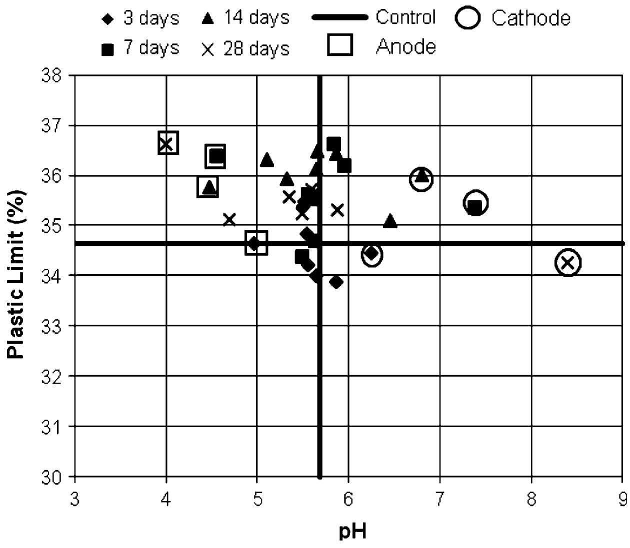

Fig. 13 Relationship between plastic limit and pH

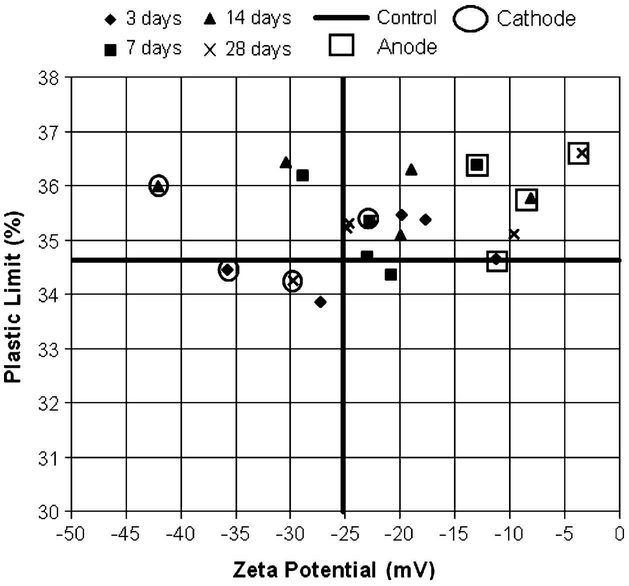

Fig. 14 Relationship between plastic limit and zeta potential

3.3.3 Relationship with zeta potential

The relationship between PL and zeta potential (Fig. 14) shows a marginal increase in the PL as the zeta potential becomes less negative. However, this relationship is weak and no firm conclusions can be drawn.

4 Discussion of results

The water content has a large influence on the undrained shear strength, as expected, but there is clear evidence that chemical alteration of the clay and/or chemical reactions influence the undrained shear strength also at every point in the test specimens, and in some cases markedly (the marked changes in strength are attributed to chemical reactions). The control line approach used in Fig. 3 is a most effective indicator of such chemical effects; without this, the complex combination of conflicting responses to the electrokinetic process mask the chemical influences on the system. The dominance of the water content on undrained shear strength measurements is a clear case in point here. Some improvement in clay strength has been brought about generally by an alteration of the chemistry of the system, yet the most profound changes in undrained shear strength occur after 14 and 28 days close to the cathode, and this is thought to be the result of chemical reactions, probably the precipitation of Al^{3+} and Fe^{2+} reaction products at high pH.

In general, the undrained shear strength increases due to a combination of pH changes and the release of Fe ions into the system. The one exception was for the shortest

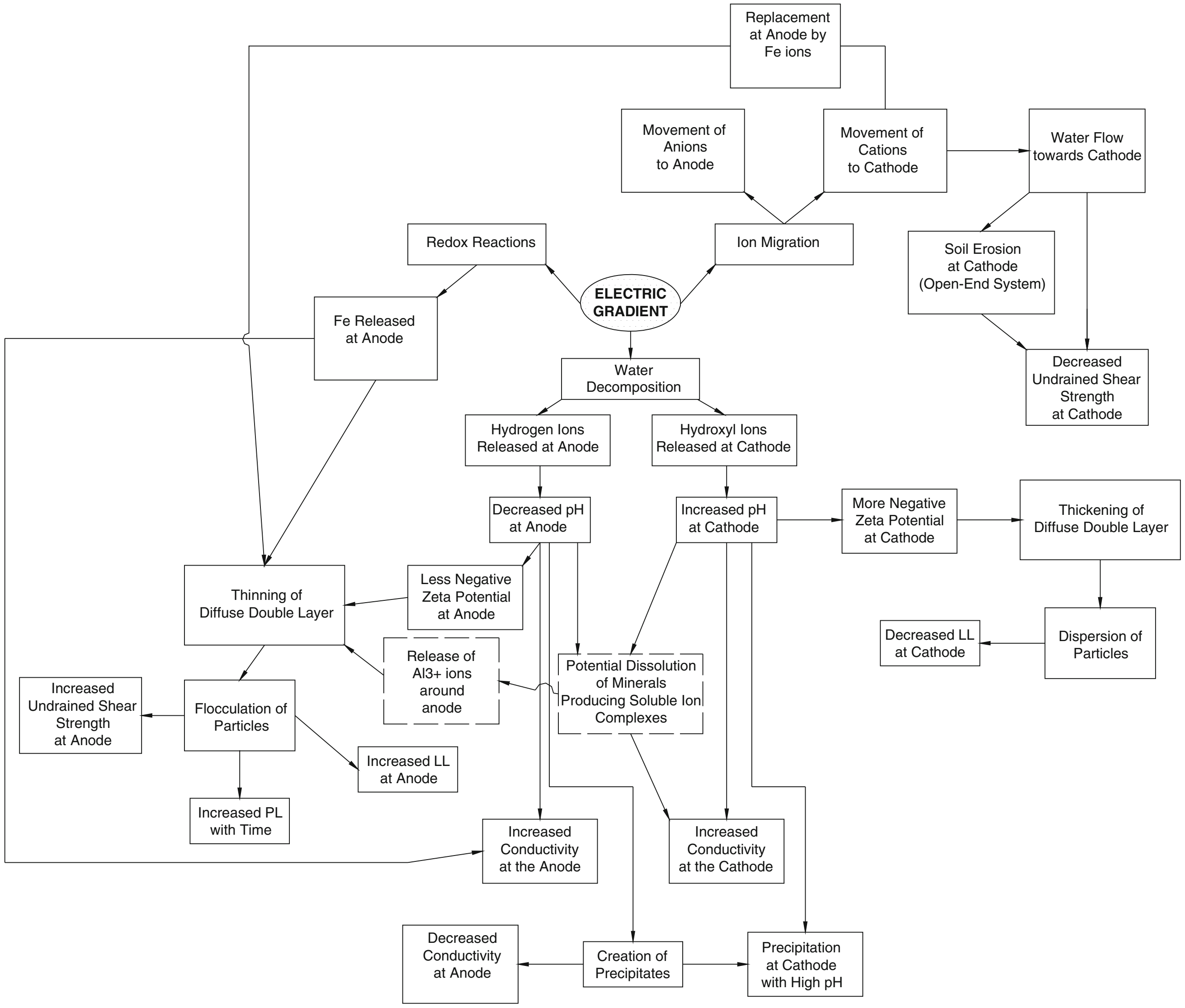

Fig. 15 Mechanisms acting

measurement period (3 days) close to the anode where the pH was lowered (to ∼5), but not lowered enough for Al^{3+} dissolution from the clay (this occurred at and beyond 7 days). Interestingly this was the only point at which a marked (or indeed any) reduction in Plastic Limit was observed. It could be hypothesised that Al^{3+} release from the clay close to the anode and the subsequent transport of Al^{3+} ions through the system, and precipitation of its reaction products close to the cathode when the pH increased high enough, have a very important influence on the outcomes of the experiments.

The contention that chemical effects have occurred in the vicinity of the anode is borne out by the large Liquid Limit values, which are the highest of all of the measured points at 3 days, and increase progressively at 7, 14 and 28 days. Similarly the chemical effects at the cathode are well described by the Liquid Limit measurements; the two lowest Liquid Limit measurements by far were for 14 and 28 days at the cathode when and where precipitation of reaction products has been postulated. Liquid Limit would thus appear to be an appropriate, and duly sensitive, parameter to measure to determine whether chemical changes have been induced in electrokinetically treated clays. The Plastic Limit is much less effective in this respect.

The strong relationships between Liquid Limit and pH, and Liquid Limit and zeta potential show revealing trends, particularly for the clay close to the electrodes, which show extremes of behaviour for all three of these indicators.

In an attempt to illustrate the various effects on a clay soil brought about by electrokinetic treatment using steel electrodes, but avoiding the addition of chemical stabilisers, the flow diagram in Fig. 15 has been produced. This succinctly summarises the chemical changes in the clay that are in turn manifested in an alteration of the physical characteristics of strength and plasticity. It therefore provides a basis for further research in which chemical stabilising solutions are added to the anode and/or cathode. Only from the foundation presented herein and by Liaki et al. [9] can the efficacy of chemical stabilisation using electrokinetics can be judged.

5 Conclusions

When electrokinetic treatment is applied to clay soils a number of chemical influences combine to bring about physical changes. This paper has explored the case of electrokinetic treatment of a pure form of kaolinite using stainless steel electrodes and pure water feeds at the electrodes while keeping the system free from a hydraulic gradient.

The first, and most obvious, of the expected effects was electro-osmotic flow, and this caused the clay in the vicinity of the cathode to swell and weaken as a result of the increased water content. No associated drying out at the anode occurred due to the continuous water feed here. However, the strength of the clay throughout the test specimen was influenced by chemical changes, and these can be explored by plotting measurements of undrained shear strength against water content and relating them to a control line for the untreated clay. This procedure demonstrated that the kaolinite in general increased in strength as a result of ion movements, and particularly once the pH adjacent to the anode was lowered below ~ 5 such that Al^{3+} ions were dissolved from the clay and transported through the system. The only case in which the strength was lowered relative to the control was the one in which it is hypothesised that Fe ions released from the anode combined with a pure water feed caused an adverse chemical ion substitution effect. Precipitation of reaction products once a high pH around the cathode had formed appeared to have the greatest relative effect on clay strength.

Liquid Limit appears to be an appropriate, duly sensitive parameter with which to determine whether chemical changes have occurred in the clay. An understanding of the chemistry of the system, such as type of clay and its mineralogy, pore water chemistry, type of electrodes and type of solutions fed to the electrodes, and the change in pH brought about by the electrokinetic process, will enable an interpretation of the likely chemical changes (cation exchange, clay mineral dissolution, precipitation of reaction products) on the basis of Liquid Limit measurements. A simple graph of Liquid Limit against pH is likely to prove illuminating. Plastic Limit measurement would appear to be far less effective in this respect.

A flow diagram summarising the various chemical effects brought about by electrokinetic stabilisation using steel electrodes in the absence of stabilising solutions provides a fundamental basis for interpreting and monitoring data available from practical applications of the technique. It equally provides a sound basis for designing such a treatment process. However some prior laboratory testing should be carried out when the treatment is proposed, in which case the flow diagram and the data presented herein will prove valuable, if not essential, for comparison.

Acknowledgements This research project was funded jointly by the Engineering and Physical Sciences Research Council and University of Birmingham via a Post-Graduate Teaching Assistant studentship, this support being gratefully acknowledged. The research and technical staff of the School of Civil Engineering are thanked for their assistance.

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