The Effects of Electrolytes on the Liquid Limit of Clay

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ABSTRACT

The liquid limit of clay treated with electrolytes were investigated and examined with respect to electrolyte types and concentration, time-dependent effects, and mineralogy of clay. The findings indicated that the types and concentration of electrolytes in the pore fluid of clay have a marked effect on the liquid limit of clay. Ageing has a pronounced effect on the liquid limit, particularly for clay treated with cementing agents.

INTRODUCTION

The problems usually encountered in engineering practice is the alteration of geotechnical properties of clay arising from physical and chemical changes in the soil-water system. Physical changes may arise due to construction disturbance or field loading situations whereas chemical changes may be due to weathering, leaching or chemical pollution. The extent of modifications in the engineering properties of clay due to chemical changes is dependent upon the clay mineralogy hence, different soils react differently to these effects [1]. In soil engineering practice, where chemical problems are common, an understanding and knowledge of clay mineralogical form is an important aspect of the work which enables meaningful conclusions to be drawn from experimental results and to achieve a better understanding of the soil behaviour.

The type of clay minerals present in clay deposit depends on its geological history. The three most common clay minerals are kaolinite, illite, and montmorillonite. Information on these minerals and their respective structural configurations are well established [1,2,3]. The microstructure of the soil is largely governed by the clay minerals present and the forces acting between them. Many complex factors are responsible for the attractive and repulsive forces between clay particles. The repulsion between two clay particles is due to the interaction of diffused double layers. At present there is no reliable method of evaluating these forces quantitatively, although a number of investigators have attempted to improve the understanding of these effects on the mechanical behaviour of clays.

The microstructure formed by single clay mineral platelets may be associated with edge-to-edge, edge-to-face or face-to-face arrangements depending on interparticle balance between the forces of attraction and repulsion. Flocculated structure occurs when a soil is sedimented in an environment in which the net electrical force between adjacent particles is attraction. When the net electrical force between the adjacent particles is repulsion, a dispersed structure is formed.

Liquid limit is defined as the moisture content above which the soil behaves as a viscous fluid. In the mineralogical form it is defined as a measure of water which can be held within the clay with any substantial rigidity and without separating the particles. The structural configuration, grain size variation and ion exchange capacity of a particular clay mineral determines the liquid limit value of clay. Minerals with high ion exchange capacity are likely to show large variation in the liquid limit.

The liquid limit test has been considered as a simple measure of shear strength in past research [4,5]. Since the shear strength of clay increases with reduction in moisture content, an increase of liquid limit as a result of chemical addition to the pore water, is indicative of an increase in shear strength. Similarly, a reduction in the liquid limit implies a reduction in the shear strength. Studies on liquid limits of remoulded clays by other researchers indicated that the values were significantly affected by the mineralogical content and types of salts in the pore water [4,5].

STUDIES ON BIRTLEY CLAY

The work described herein is part of a major investigation into the effects of electrolytes on the engineering properties of clay. The influences of chloride salts on the liquid limit of Birtley Clay were studied and analysed in detailed with due consideration of the time effects, types of electrolytes and chemical concentrations.

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Explanation of the resulting soil behaviour is given with relations to its mineralogical background, chemical reactions involved, and double layer theory [6,7].

A detailed investigation was carried out to establish information on the mineralogical content of Birtley Clay. Liquid limit tests were conducted on clay samples using chlorides of various anions and concentrations for immediate effects and ageing.

MINERALOGY OF CLAY SAMPLE

The clay samples used in the investigation were clay deposits extracted from a brick factory site in Birtley, England, hence given the name Birtley Clay. The main mineralogical contents of Birtley Clay were determined by differential thermal analysis [8,9, 10].

The differential thermal curves for two samples of untreated Birtley Clay is shown in Fig. 1. The reactions below 200°C may be due to variations within the sample when subjected to heating. The small exothermic reaction occurring between 120°C - 200°C is entirely due to hygroscopicity of the inert material.

The maximum peak for both traces of untreated Birtley clay remains constant at 420°C. Previous references conclude the presence of an endotherinic reaction at this temperature range as an indication of hydrous mica i.e illite. The second endothermic peak at about 600°C is ascribed to the presence of finely divided kaolinite. The small peaks occurring above 650°C could be due to the presence of hydrous mica group such as muscovite. Thermal curves for muscovite vary accordingly to whether it is fine or course grained. Muscovite is expected to be one of the minor constituents of the clay since muscovite and kaolinite occur naturally as interstratified minerals [11].

The results of differential thermal analysis are supplemented with X-ray diffraction analysis which confirmed the main mineral content of Birtley Clay as illite and kaolinite.

TYPES OF ELECTROLYTES

The electrolytes used in the investigation were such that it gives a constant effect of anion exchange in all the tests. Chlorides solutions were selected as these are amongst the most commonly encountered in soils. The selection of electrolytes used in the investigation, arranged in a descending order of flocculating power for cation based on Hofmeister series, is as follows.

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Ferric chloride (FeCl$_3$)
Aluminium chloride (AlCl$_3$)
Ferrous Chloride (FeCl$_2$)
Calcium chloride (CaCl$_2$)
Magnesium chloride (MgCl$_2$)
Potassium chloride (KCl)
Hydrogen chloride (HCl)
Sodium chloride (NaCl)

The chemical concentration of electrolytes used in the series of tests were 0. 1N, 0.5N and 1N

The flocculating power of sodium chloride is extremely small since it is positioned at the end of the Hofmeister series. Experimental trials showed that sodium chloride behaves dominantly as dispersant. Ferric chloride and aluminium chloride flocculates suspensions readily and therefore are cementing agents. Ferrous chloride and ferric chloride have almost similar properties. After reacting with water ferrous chloride (FeCl$_2$) oxidises and convert to cementing agent, ferric chloride (FeCl$_3$).

LIQUID LIMIT TEST

Types of test

The tests conducted were:

i)   immediate test, generally in accordance to British Standard, BS 1377 [12].
ii)   ageing tests in which the samples were allowed to stand for up to 28 days prior to testing.

Sample preparation for tests

The initial steps for preparation of samples were the same for both tests. The sample was prepared for 200g of dry Birtley Clay powder mixed with required chemical solution to a moisture content of approximately 10%, and cured overnight in a sealed polythene bags. The samples were chemically treated with electrolytes for 24 hours to ensure consistency of mixture upon testing and giving time for chemical changes to take place.

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Procedures for immediate test

These tests were carried out in accordance with BS 1377, where the depth of cone penetration was measured immediately after remoulding. PVC containers, specially manufactured to British Standard internal dimensions, were used to replace the standard metal container in order to avoid other chemical contamination. The cured sample was further remoulded with additional solution of the same chemical to a moisture content approaching the liquid limit and the measured depth of cone penetration specified in BS 1377. Further chemical solution was added throughout the tests to increase moisture content as necessary, while maintaining a constant chemical concentration in the pore fluid. The value of the liquid limit was derived as that value of moisture content corresponding to 20 mm cone penetration. Tests were repeated to give consistent results and the liquid limit value interpolated graphically when necessary.

Procedures for ageing test

The complete series of electrolytes were used for investigation of 7-day ageing effect, whilst the ageing tests for 28 days restricts the type of electrolytes used to those for cementing agents only, namely ferrous, ferric and aluminium chloride. Hydrochloric acid was included because it indicated some major characteristics of a possible cementing agent.

The sample preparation procedures for ageing test are similar to immediate tests except that samples were cured in test containers for a period of 7 days to 28 days. The surface of the samples above the top of the test containers was mound up and the samples sealed in polythene bags for curing.

At the end of the curing period, the samples were carefully trimmed, to be levelled with the top of the containers, taking care to minimise sample disturbance. The cone penetration depths due the development of cementitious bonding were measured in the normal way. Chemical was further added throughout the tests to reach the liquid limit of clay.

RESULTS AND DISCUSSION

The liquid limit and plasticity index of untreated Birtley Clay determined in accordance to BS 1377 was 48 % and 25 % respectively, and therefore classified as an inorganic clay of medium plasticity, GI.

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The main constituents of clay mineralogy for the samples were kaolinites and illites therefore the expected liquid limit should be a combination of the characteristics of the two minerals. According to past research [13], the liquid limit of kaolinites vary from 30% to 75% whereas for untreated illites the range fall between 60% and 90%. The liquid limit value of untreated sample in this investigation, where the electrolyte used was distilled water, correlates with the ranges given by these researches. Although there is no specific theoretical method of determining the combined effects, nevertheless the value fits the average of the lower limits of the individual results.

The liquid limit of clay is determined by the structural configuration, grain size variation and ion exchange capacity of the main clay minerals present in the deposit. For kaolinite the nature of crystallinity of the lattice and particle size variation significantly affects the liquid limit. Liquid limit value tend to increase with decreasing grain size hence a larger value is expected for poorly crystallised fine grained samples in comparison to well crystalline types.

For kaolinite exchangeable cations are expected to show little variation in the liquid limit values due to its low cation exchange capacity. The particle size distribution of the original sample and the effects on this characteristic brought about by sample treatment prior to testing would influence the liquid limit. On the other hand, variation of exchangeable cations for illites has a tendency to split particles therefore increasing the clay mineral surfaces, and consequently hence higher liquid limit value is expected. For illites, the effect of exchangeable cations is largely on the attractive force between the particles and on the nature of the adsorbed water.

Figure 2 shows the variation of liquid limit with electrolyte concentration for immediate tests. The value of liquid limit displayed by samples treated with ferrous, ferric, aluminium and potassium chloride at low levels of concentration up to 0.5N are relatively higher than clay treated with distilled water. A general trend depicted from these tests is the increasing liquid limit for up to a certain level of concentration for samples treated with these electrolytes. On the other hand, addition of hydrochloric acid, sodium chloride, calcium chloride and magnesium chloride generally, caused a reduction in the liquid limits which deteriorates with increasing concentration. In all cases, the liquid limits of samples treated with sodium and calcium chloride lie below the value of untreated clay. To some extent, the observations imply the significant effects of cations and electrolytes concentration on the liquid limits of Birtley Clay. It would appear from these results that powerful flocculating agents, such as aluminium chloride, ferric chloride and ferrous chloride are capable of increasing the liquid limit whereas a reversal in behaviour resulted from less powerful flocculating agents. Amongst the electrolytes, sodium chloride has the least flocculant power. A detailed explanation of these cases are dealt with in the foregoing paragraphs.

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As indicated above, hydrochloric acid, sodium, calcium and magnesium chloride tends to reduce the liquid limit of clay and further reduction takes place at higher electrolyte concentration. The latter effect correlates well with the prediction of the double layer theory [6,7]. An increased in concentration increases the degree of suppression of the repulsive forces between clay particles which reduces the thickness of the diffused double layer and consequently increased in the apparent amount of free water in the system. This behaviour would result in a reduction of the liquid limit as demonstrated by these tests.

The performance of cations at higher concentration was demonstrated in these tests. Clay treated with calcium and magnesium chloride at concentration levels beyond 0.5N exhibit a lower range of liquid limit than sodium chloride (Fig. 2). This occurred because the degree of compression of the double layer is more pronounced for calcium and magnesium ions hence, causing greater reduction in the liquid limit of clay. The significance of ions valency and concentration of electrolytes in relation to the compression of double layer is explained by the Schulze-Hardy rule.

Recognising the fact that HCl has a low flocculant power therefore, it is not expected to show any significant effect on the liquid limit although test results indicated some reduction trend of liquid limit with increasing concentration of hydrochloric acid. Mixing of samples during tests showed indications of aluminium being involved in the reactions. Previous research [4] highlighted that the presence of aluminium, a cementing agent, generally caused an improvement of shear strength or liquid limit of clay. The contradiction in behaviour displayed by hydrochloric acid could possibly be explained by aluminium ions replacement with hydrogen ions whereby the introduction of hydrogen ions reduce the thickness of the diffused double layer, and consequently reducing the liquid limit.

Potassium chloride is not a powerful flocculant but appears to be the most efficient electrolyte for increasing the liquid limit of Birtley Clay instantaneously (Fig. 2). The performance of potassium chlorides could be explained by the soluble nature of the salt which act readily in the water phase, reducing the repulsive forces between the clay minerals and suppressing the electrical double layer. However, the continuous increase in the liquid limit at higher concentration is not well understood.

Theoretically, at high concentration of electrolytes the diffused double layer would be considerably supressed thereby causing reduction in the liquid limit, in accordance to Schulze-Hardy rule and Hofmeister series. The deviation of results from theoretical expectations could possibly be due to the large ionic radius of potassium ions in the lattice causing subsequent expansion of the clay and increases the liquid limit.

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In the immediate tests the trivalent ions, namely aluminum and ferric, had a greater reduction effect on the liquid limit than potassium chloride because they are only slightly soluble, and precipitated as hydroxides. In terms of the physico-chemical aspects, the compression of double layer for trivalent ion is greater causing subsequent reduction of the liquid limit, as illustrated by these tests. An increased in the shear strength resulted through cementing action, in addition to the double layer effects. As would be seen later, ageing of these samples has a more beneficial effect on the liquid limit.

Addition of amorphous cementing agents namely, aluminium chloride and ferric chloride caused the liquid limit to increase with concentration, up to 0.5N. The increased in the liquid limit value is an indication of an improvement in the shear strength due to developments of cementitious bond within the clay. The reduction of liquid limit above 0.5 N concentration for both electrolytes could be explained by their high cation valencies which markedly reduced the thickness of the diffused double layer. From the engineering point of view, the reduction in shear strength at high electrolyte concentration is probably due to the disruption of structural bonds in the lattice, possibly brought upon by high supression of repulsive forces.

The trend of continuous reduction in liquid limit with concentration for clay treated with ferrous chloride, $FeCl_2$, is not anticipated, however, this is believed to be associated with unstability in behaviour of ferrous cations after acting with water. Aged samples appear to show more reliable results as explained below.

The experimental results of samples aged for 7 and 28 days are shown in Fig. 3 and Fig. 4, respectively. A significant change in the liquid limit occurred at the end of 7 days for samples treated with ferrous, ferric and aluminium chloride but samples treated with other electrolytes remained relatively unchanged compared to results given by immediate tests.

The variations of liquid limit for cementing agents of various concentrations with time are summarised in Fig. 5. All samples treated with hydrochloric acid showed a reduction in liquid limit with time implying that aluminium does not contribute to any formation of cementitious bond within the clay. Samples treated with the cementing agents namely, ferric and aluminium chloride, caused a tremendous increase in liquid limit or shear strength at the end of 28 days. For aluminium chloride a concentration of 0.5N appears to be an optimum concentration for any development of cementitious bonds between particles within the clay during ageing whilst higher concentration tend to reduce such effect. The development of shear strength in clay produced by ferric chloride could only be achieved at chemical concentration of 1N but the effect is still comparatively less than aluminium chloride at the same concentration. For Birtley clay aluminium chloride can be concluded as the most effective electrolytes in increasing the liquid limit and shear strength.

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CONCLUSIONS

1. The liquid limit of Birtley Clay vary considerably with the type and concentration of electrolytes used. The double layer theory governs the the liquid limit value of clay at higher electrolyte concentration.

2. The liquid limit of Birtley Clay is considerably increased by the addition of electrolytes with powerful flocculating power (flocculants) whilst electrolytes with extremely small flocculating power, rather called dispersants, reduced the liquid limit.

3. The increased in liquid limit and improvement in shear strength during ageing is mainly brought about by the development of cementitious bonds within the clay.

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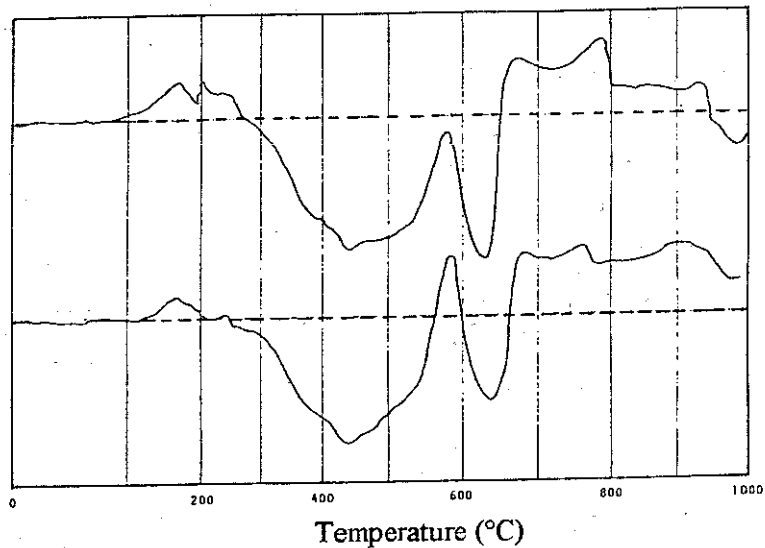
Fig. 1. Differential thermal curves for untreated Birtley Clay
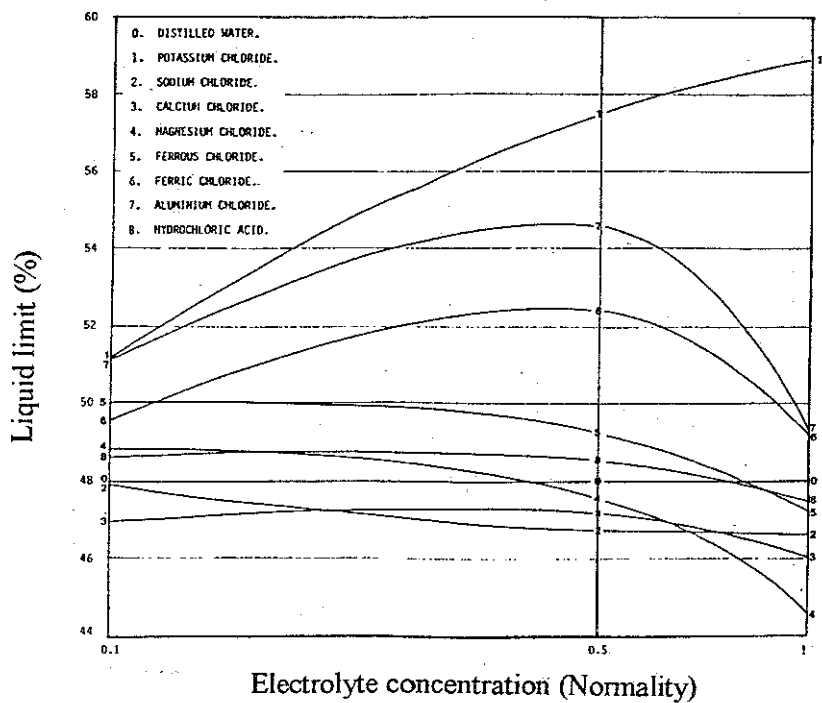
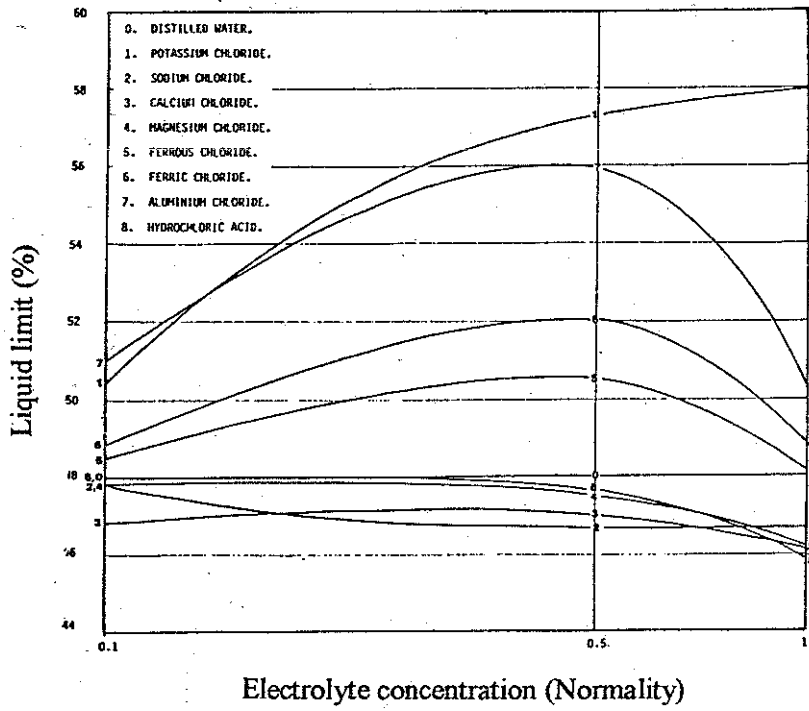Fig. 2. Liquid limit versus electrolyte concentration (Immmediate tests)

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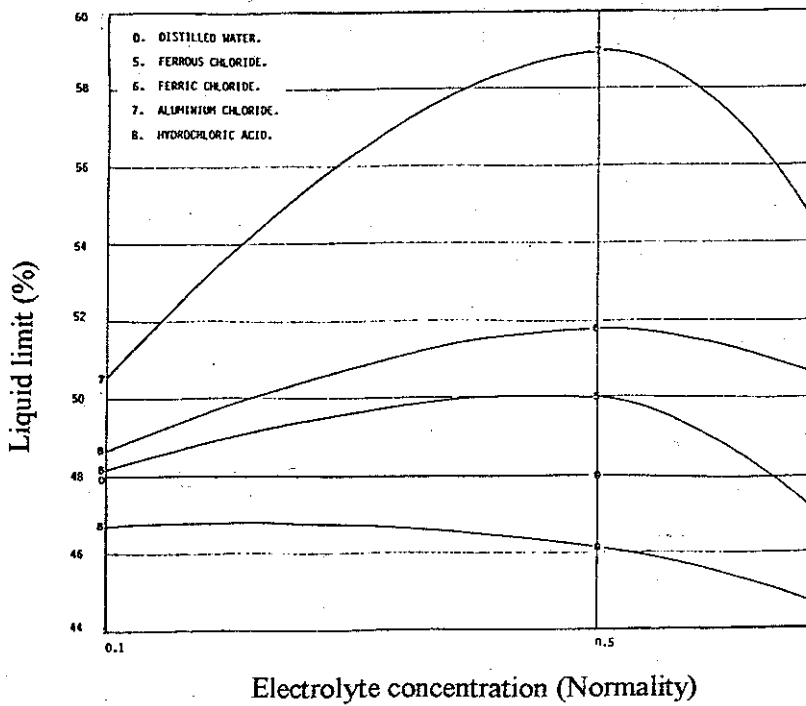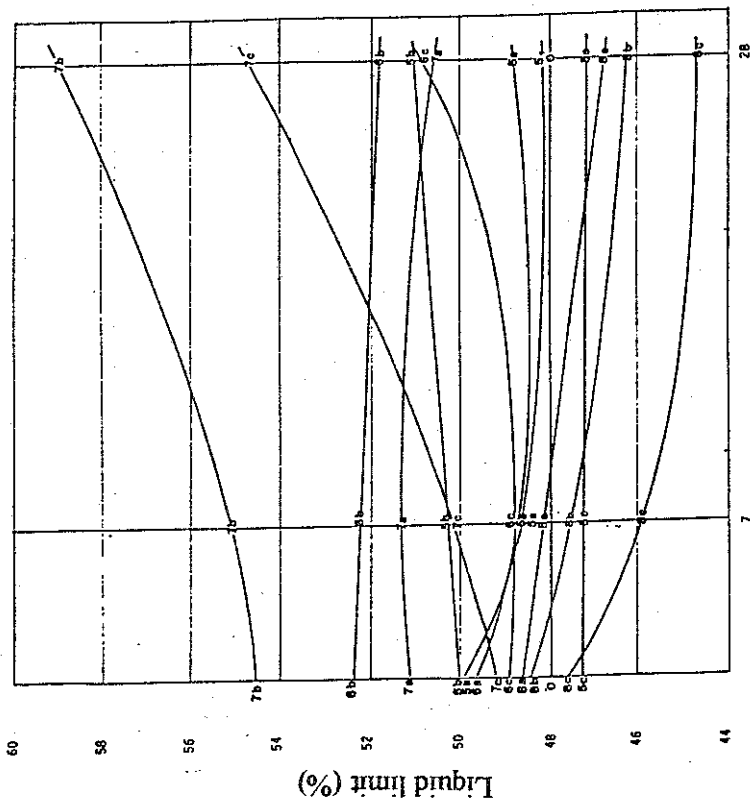Fig. 3. Liquid limit versus electrolyte concentration – aged 7 days

Fig. 4. Liquid limit versus electrolyte concentration – aged 28 days

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Fig. 5. Liquid limit versus time

0.	DISTILLED WATER.
5a.	0.1M FERROUS CHLORIDE.
5b.	0.5M FERROUS CHLORIDE.
5c.	1.0M FERROUS CHLORIDE.
6a.	0.1M FERRIC CHLORIDE.
6b.	0.5M FERRIC CHLORIDE.
6c.	1.0M FERRIC CHLORIDE.
7a.	0.1M ALUMINIUM CHLORIDE.
7b.	0.5M ALUMINIUM CHLORIDE.
7c.	1.0M ALUMINIUM CHLORIDE.
8a.	0.1M HYDROCHLORIC ACID.
8b.	0.5M HYDROCHLORIC ACID.
8c.	1.0M HYDROCHLORIC ACID.