

Effects of Some Metal Sulfates on the Strength and Swelling Properties of Lime-Stabilised Kaolinite

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The presence of sulfates during lime-stabilisation of clay soils may modify the clay – lime reaction products with undesirable consequences such as excessive expansion and reduced strength. Some failures in major highways have been attributed to formation of these expansive products. Sulfates may occur in the parent stabilisation material or in the ground water either naturally, or artificially due to industrial or non-industrial human activity. This paper reports the effects of varying sulfate type and concentration on the development of compressive strength and on the expansion behaviour of a lime-stabilised commercial kaolinitic clay, when sulfates of calcium, magnesium, sodium and potassium are artificially introduced into the clay. The results clearly illustrate that the sulfate cation type is a major factor in influencing subsequent behaviour and performance of the clay. The effects of the sulfates of sodium, magnesium and potassium are found to be different from and more deleterious than those of calcium.

Keywords: Clay soils, soil stabilisation, sulfates, lime, compressive strength, swelling

1 INTRODUCTION

Research has established that the type and morphology of the products of clay-lime pozzolanic reaction determine the physical, chemical and mechanical properties of lime-stabilised clay soil (Sloane, 1965; Mitchell, 1986; George *et al.*, 1992; Mitchell and Dermatas, 1990; Abdi & Wild, 1993; Wild *et al.*, 1993). Pozzolanic reactions which cement the soil particles together occur over long periods (i.e. years) and, depending on the curing environment, eventually cease. Deterioration may also occur depending on the chemical environment. Problems arising from clay –

lime reaction modifications associated with sulfate-bearing clays are a major concern to design engineers. The problems have been attributed to pavement failures on parts of major highways such as parts of the M40 Oxford – Birmingham Motorway (Banbury IV contract) in the UK (Snedker & Temporal, 1990; Snedker, 1996), and also parts of Stewart Avenue and Owens Street in Las Vegas, Nevada, USA (Mitchell, 1986; Hunter, 1988). In both cases, gypsum was found to be present in the lime-stabilised road layer. Sulfates may result from the oxidation of sulphide minerals, particularly pyrites. They may occur naturally either in the parent stabilisation material or in

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the ground water. They may also occur artificially due to industrial activity, as a result of man's industrial or other activities, in particular sulfates of sodium and magnesium (Sherwood, 1962, 1992, 1993; Mitchell, 1986; Hunter, 1988; Mitchell and Dermatas, 1990; Obika & Freer-Hewish, 1990; Snedker & Temporal, 1990; Snedker, 1996). In their natural state, sulfates occur as SO_4 . However, in soil testing and analysis, sulfates are normally expressed as SO_3 (BS 1377). The test for total sulfate content (BS 1047) provides a measure of the sulfates (SO_3) already in the soil plus those sulfates converted from the oxidation of sulphides. Total sulfate content is determined as the acid soluble sulfate. In addition, water soluble sulfate is determined and this helps in ascertaining the potential for migration of sulfates (BS 1377 Part 3) and also the level of sulfate present in ground water. The most commonly encountered sulfates are presented in Table 1. In the UK, sulfate salts could occur in most of the major clay formations. Of these salts, the most abundant sulfate is gypsum, known geologically as selenite, which occurs as individual crystals. It is abundant in clay formations such as Oxford Clay, Lower Lias Clay, Kimmeridge Clay and Mercia Mudstone. These clays may also contain small quantities of other sulfates including those of sodium and magnesium (Sherwood, 1962, 1992, 1993; Snedker, 1996).

When gypsum is present in the kaolinite – lime system for example, Wild *et al.*, (1993) have observed that the formation of a colloidal product consisting of a complex calcium sulpho-aluminate silicate hydrate (C-A-S-H) takes place on the surface of the kaolinite plates. From this surface product, ettringite ($\text{C}_3\text{A}_3\text{C}_3\text{H}_3_2$) was observed to nucleate and grow. It was observed to form very rapidly in the hydrated kaolinite – lime – gypsum mixtures, and may even have been present immediately after mixing, depending on the relative amounts of clay, lime and sulfate present. Its formation greatly affects the behaviour of the stabilised material including imparting significant strength enhancement, as well as expansion (if soaking of the material occurs during the early stages of moist curing before effective cementation takes place). The expansive and other deleterious reactions that can occur depend on: 1) the period of moist cur-

ing before water ingress, 2) the period of soaking, 3) the concentration of sulfate and lime, and 4) the type of cations deriving from the sulfate and ground conditions. Expansion depends also on whether ettringite nucleates within the pores or on the clay particle surfaces, a factor determined by the prevailing chemical environment, especially alkalinity (pH) of the pore solution (Mitchell, 1986; Hunter, 1988; Mitchell and Dermatas, 1990; Wild *et al.*, 1993). If it predominantly forms in the voids, there is likely to be little or no expansion until all the voids are filled. Ettringite formation is temperature dependent. At temperatures below 5–15°C, ettringite is observed to be unstable (Snedker, 1996) and in the presence of carbonate, thaumasite may form, the expansive behaviour of which is not well established to-date. Since the damage to lime-stabilised soil in all the reported cases to date has been associated with the presence of gypsum, there is very limited information available on the effects of other sulfates although these do occur in soils. The principal objective of this paper is therefore to establish the influence of other sulfates on the strength development and swelling behaviour of lime-stabilised clay soils. Solubility data shown in Table I shows that the sulfates of the monovalent metals sodium and potassium, and of the divalent metal magnesium, are all much more soluble than gypsum. The paper reports the manner in which varying concentrations of gypsum and these other sulfates influenced both the strength development and swelling behaviour when the sulfates were artificially introduced in a lime-stabilised commercial kaolinitic clay.

2 MATERIALS

Soil

'Industrial' kaolinite was used as a source of kaolinite. It was supplied by IMERYS Minerals Ltd. (former ECC International Ltd.), Cornwall, UK, under the commercial trade name "Standard Porcelain". It is a natural kaolin clay in the form of a white powder and consists of 84% kaolinite, 13% mica, 1% feldspar and

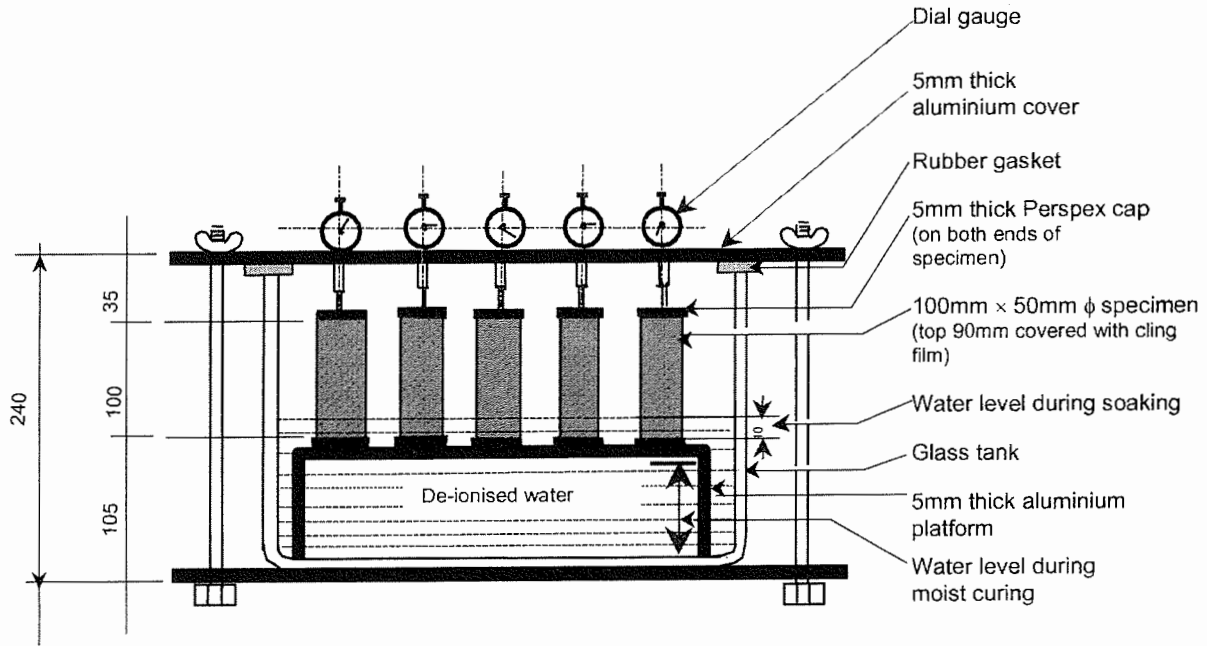


FIGURE 1 Chamber employed to monitor linear expansion at 30°C and 100% relative humidity (Not to scale; dimensions in mm)

2% other minerals. Table II shows the particle size distribution and other engineering properties, and Table III the chemical and mineralogical composition of "Standard Porcelain". The advantages of using an 'industrial' clay in analytical studies is that it is a consistent homogeneous and well characterised material and this avoids problems posed by, sampling, disturbance, inconsistent microstructure and inherent geological variability. Artificial soil batches prepared in the laboratory can therefore be made homogeneous and can give properties that do not vary with time or from one batch to another. Use of standardised kaolin-based industrial clays has traditional recognition in soil research in studies of soil behaviour, as it is easier to identify and explain some of the complex interactions that would be difficult to decipher using inhomogeneous natural soils. For example, Sloane (1965) used an ultra-fine-grained Georgia kaolinite, processed and distributed by the Georgia Kaolin Co. U.S.A. under the trade name "Hydrite UF"; Rossato *et al.*, (1992) used sand blended with pure kaolin, commercially processed and distributed as high plasticity fine china clay "Speswhite", by Whitfield and

Son Ltd., Stoke on Trent, England, UK; Abdi (1992) and Wild *et al.*, (1993, 1998 and 1999) used the fine-grained kaolinite used in the current work, while Smith and Narimatsu (1993) used a high grade kaolinite, commercially obtained from Lewiston, Montana, U.S.A. The use of artificial soil, however, has its disadvantages such as behaviour being not typical of natural clays, as a result of the artificial particle size distribution, mineral composition and soil geological history. For this reason therefore, it is desirable also to perform some work on natural soils. Thus, a brief comparison between strengths at 1 week and 4 weeks for lime-stabilised Kimmeridge Clay and equivalent ones for the industrial kaolinite (i.e. soil + 6% lime) has been indicated in Section 4. However, the main focus in the current work was to compare strength and linear expansion performance for different sulfates and for one particular clay type. A more extensive comparison of strength and swelling, between lime-stabilised Kimmeridge Clay soil and the lime-stabilised industrial kaolinite used in the current work has been reported elsewhere (Wild *et al.*, 1998, and 1999).

TABLE I Sulfate types most likely to be encountered during lime-stabilisation of soils

<i>Sulfate Type</i>	<i>Chemical formula</i>	<i>Solubility (g SO₄/l)</i>	<i>Common names</i>
Calcium sulfate	CaSO ₄ .2H ₂ O	1.44	Selenite, Gypsum
Potassium sulfate	K ₂ SO ₄	130	Arcanite
Magnesium sulfate	MgSO ₄ .7H ₂ O	225	Epsomite
Sodium sulfate	Na ₂ SO ₄ .10H ₂ O	>225	Thernadite, Mirabilite, Glauber's salt.

TABLE II Particle size distribution, consistency limits and other properties of "Standard Porcelain" (IMERY'S Minerals Ltd. - Formerly ECC International Ltd., UK)

<i>Sieve Size</i>	<i>(%)</i>
> 53 μm	0.05 - 1.0
> 10 μm	10 - 20
< 2 μm	28 - 57
Consistency Limits	
Liquid limit (%)	61
Plastic Limit (%)	32
Plasticity Index	29
Others	
Specific Gravity	2.57
Bulk density (kg/m ³)	1090 - 1170
Natural Moisture Content (%)	10 - 12

TABLE III Chemical analysis and mineralogical composition of "Standard Porcelain" (IMERY'S Minerals Ltd. - Formerly ECC International Ltd., UK)

<i>Chemical Analysis</i>	<i>%</i>
SiO ₂	48
Al ₂ O ₃	37
Fe ₂ O ₃	0.65
TO ₂	0.02
CaO	0.07
MgO	0.30
K ₂ O	1.60
Na ₂ O	0.10
Loss on ignition (L.O.I)	12.5
Mineralogical Composition	
Kaolinite	84
Micaceous material	13
Feldspar	1
Other minerals	2

Lime

Hydrated lime (Ca(OH)₂) under the trade name "Lim-bux" was supplied by Buxton Lime Industries Ltd. Buxton, Derbyshire, UK. Tables IV and V show its physical properties and chemical composition respectively. Generally between 1-3wt.% lime is needed for modifying soil properties and 2-8wt.% lime for stabilisation, depending on clay content. As the current work was carried out on clay with a very high clay mineral content (84% kaolinite (see Table III) with an initial lime consumption value of approximately 3%, a nominal value of 6wt.% lime was chosen as a generous addition (as reported by Rogers and Glendinning, 1996), in order to achieve both modification and significant stabilisation.

Chemicals

The major chemicals used in the study were of reagent grade with a purity of at least 97%. They were calcium sulfate dihydrate (CaSO₄.2H₂O), magnesium sulfate (MgSO₄), sodium sulfate anhydrite (Na₂SO₄) and potassium sulfate (K₂SO₄), all from Phillip Harris & Sons Ltd., Cardiff, South Wales, UK. Silica gel was used during the drying of specimens for X-ray diffraction analysis, in conjunction with 'Carbosorb' a CO₂-absorbing agent in order to prevent carbonation.

3 EXPERIMENTAL WORK

Proctor compaction: During sample preparation it was necessary, for the purpose of comparing performance, that samples were of approximately the same volume and density for all the material compositions

in a given system. Due to the chemical nature of pozzolanic reactions, it was also necessary to maintain the same amount of water available for reaction in all test specimens. Thus, Proctor compaction tests (British Standard (BS) 1377 (1990)) were carried out in order to establish values for the maximum dry density (MDD) and optimum moisture content (OMC) for each system. However, rather than compact each specimen at its own MDD and OMC, the mean MDD and OMC values were adopted as the target values for all specimens. Thus, although values of MDD and

OMC varied between 1.38 – 1.49 Mg/m³ and 25 – 30% respectively, a dry density value of 1.41 Mg/m³ and a moisture content value of 27% were adopted throughout. The effects of sulfate on compaction and on consistency are extensively covered elsewhere (Kinuthia *et al.*, 1999). In brief, the divalent cations were observed to result in higher flocculation and hence lower maximum dry densities, and in higher optimum moisture contents compared with the monovalent cations, which showed an opposite effect.

TABLE IV Physical properties of lime (Buxton Lime Industries Ltd., UK)

Trade (or Product) name	"Limbox" Hydrated Lime
Chemical name	Hydrated lime or calcium hydroxide
Physical form	Dry white powder
Melting/decomposition temperature	580°C
Bulk density	480 kg/m ³
Specific gravity	2.3
Specific surface	300 – 1500 m ² /kg
Particle size distribution	99% < 90µ
Solubility in water	1.76 g/l sat. sol. at 10°C
pH	12.4 (aqueous solution approx. 2g/l)
Vapour pressure	0 at 20°C

TABLE V Chemical composition of lime (Buxton Lime Industries Ltd., UK)

Compound	Chemical Formula	Composition (%)
Main (and hazardous) Ingredient		
Hydrated lime (Calcium Hydroxide)	Ca(OH) ₂	96.79
Others		
Calcite (Calcium Carbonate)	CaCO ₃	1.36
Anhydrite (Calcium Sulphate)	CaSO ₄	0.06
Magnesia	MgO	0.83
Ferric Oxide	Fe ₂ O ₃	0.06
Alumina	Al ₂ O ₃	0.10
Silica	SiO ₂	0.46
Excess Moisture	H ₂ O	0.34

Preparation of Test Specimens and Curing

Cylindrical test specimens of dimensions 50 mm diameter and 100 mm in length were prepared. They consisted of kaolinite, 6wt.% lime, and various amounts of sulfates of either calcium, magnesium, sodium or potassium. The sulfates were introduced at concentration levels equivalent to 1, 2, 3 and 4% SO₃ by weight of the dry components (clay and lime). Dry materials, enough to produce three compacted test samples were thoroughly mixed in a variable speed Kenwood Chef Excel mixer for 2 minutes before slowly adding the calculated amount of water. Intermittent hand mixing with palette knives was necessary to achieve a homogeneous mix. A steel mould fitted with a collar, so as to accommodate all the material required for one sample, was used to compress the cylinders to the target density and moisture content. The pre-fabricated mould ensured that the material was not over compressed. The cylinders were extruded using a steel plunger, trimmed, cleaned of releasing oil, weighed, measured and wrapped in several runs of cling-film. Two cylinders were to be subjected to unconfined compressive strength (UCS) tests and one to swelling tests. Those for UCS tests were labelled and placed in polythene bags before being placed on a platform in a plastic container. Water was always maintained below the platform to ensure that there was no evaporation from the samples. The sealed plastic containers were then placed in an environmental chamber capable of maintaining temperatures to $\pm 0.1^\circ\text{C}$ and humidity to $\pm 2\%$ relative humidity. Specimens for the unconfined compressive strength tests were then moist cured for various periods up to a maximum of 20 weeks at 30 °C and 100% relative humidity. A temperature slightly above ambient was chosen in order to accelerate the curing process and provide practicable curing times, without at the same time modifying the reactions significantly. The 20 weeks period of moist curing was chosen based on previous work by Abdi (1992), which showed that for specimens containing 0–8% gypsum further strength development was insignificant after 5–10 weeks (depending on the gypsum content) of moist curing.

Testing for Unconfined Compressive Strength

At the end of each of the specified moist curing periods, two samples were removed from the environmental chamber and any surface moisture on the wrapped cylinders removed with paper tissue. They were then unwrapped from the cling-film and weighed. The end surfaces of samples were gently abraded using a flat wire brush to ensure good contact with the testing rig platens. A special self levelling device was used to ensure a uniaxial load application. An M30K J J Instruments testing machine capable of loading up to 30 kN was used to apply the load at a compression rate of 1 mm/min. Two specimens were tested to failure for each mixture, and the maximum compressive loads recorded. If the two strength values obtained were within 10% of each other the average of the two was taken as the representative value of unconfined compressive strength for that mixture. This was usually achieved within the first testing, but if however the difference between the values was greater than 10%, a further two cylinders were made and tested after curing until consistency was achieved.

Testing for Linear Expansion

The first phase of linear expansion tests was carried out to evaluate the axial linear expansive effects of different metal sulfates during moist curing. Test specimens, freshly prepared as described above, were wrapped in several runs of cling-film and placed on a platform in a glass tank and covered with a lid fitted with dial gauges (Figure 1). Through a hole at the top lid, de-ionised water was siphoned and maintained below the platform so as to maintain a relative humidity (r.h.) of approximately 100%. The tank was placed in an environmental chamber set at 30°C and 100% r.h. and the specimens monitored on a daily basis until no further expansion occurred. This took approximately 2 – 8 weeks depending on the sulfate type and content. The second phase was performed in order to assess the effects of excessive water ingress after an initial 7-day moist curing period. It was carried out under the same temperature and humidity conditions

as the first phase, on specimens whose bottom 10 mm were not wrapped with cling-film in order to allow water ingress. The specimens were monitored during moist curing for 7 days as in the first phase. Thereafter, partial soaking was achieved by raising the water level in the tank to cover the unwrapped bottom 10 mm of the specimens and monitoring continued until no further significant linear expansion was observed. Specimens containing the same sulfate type were soaked together to avoid contamination by different cation types. This test method has since been modified to monitor specimens in their individual soaking environments.

For the purpose of comparing the effects of different sulfate types, the linear expansion testing method adopted in the current work has several advantages over either the laboratory Oedometer or California Bearing Ratio (CBR) tests (BS 1377 (1990) and BS 1924 Part 2 (1990) respectively):

- i. The BS tests are more suited for cases where the bulk of the swelling is achieved within 0–28 days of soaking. Testing for sulfate-induced chemical swelling requires longer periods. With various combinations of soil, stabiliser and sulfate type and content, the current work would require a continuous engagement of more than the available apparatus for long periods. Periods in excess of 50 days were sometimes necessary to achieve maximum expansion. Other systems may require even longer periods. Snedker (1996), for example, observed continued laboratory swelling for periods of the order of 25 months.
- ii. Particularly during soaking tests, the adopted method simulates much more severe soaking conditions because, except for the cling-film wrapping, there is no significant lateral restraint. This sometimes happens when soaking occurs during or immediately after construction when the soil has little restraint. On the M40 heave problems cited earlier, swell tests on soaked specimens in CBR moulds proved to be unsatisfactory in reproducing either the degree of swell or the condition of the lime-stabilised material in the field (Snedker, 1996). Snedker (1996) further reports that the
- iii. most significant tests were carried out on a sample of field material, mixed with lime and compacted into a cylindrical mould and cured. This is precisely what was carried out in the current work.

Besides enabling precise temperature and humidity controls, the current method involves closed moist curing and soaking environments, reducing the availability of carbon dioxide and thus preventing carbonation that would take place for lime exposed for such a long period. Excessive carbonation of the lime would reduce the amount of lime available for pozzolanic reaction and is therefore undesirable (Sherwood, 1962, 1992, 1993, DMRB-HA 74/00, MCHW1, 1998).

X-ray Diffraction (XRD) Analysis

X-ray diffraction (XRD) analysis was performed on all the kaolinite-lime-sulfate mixes after moist-curing for 1 week, with a view to understanding the mechanisms involved in the interaction between the clay, lime and sulfate. Samples were obtained from specimens that had already been tested for unconfined compressive strength. The tested specimens were broken to expose internal surfaces free from carbonation and small fragments were obtained. These were placed in open bottles and vacuum dried in a desiccator using silica gel in the presence of 'carbosorb' to prevent carbonation. After drying for several weeks, each fragment was ground separately into a fine powder and was further dried (as above) for an additional period of several weeks. Each powder was then analysed for relative changes in phase composition. Diffraction runs were performed using fixed settings for the X-ray equipment and a standard amount of powder specimen. The work was carried out at the R & D Centre of English China Clays (ECC) International, St Austell, Cornwall, England, using a Philips PW 1825 X-ray generator and CuK α radiation of a wavelength (λ) of 1.542Å. The X-ray tube detector (a PW 1050 vertical goniometer) was fitted with a diffracted-beam graphite monochromator together with an automatic sample changer to enable a continuous scan at 90 sec/degree. A simple calibration standard (not an internal standard) was used for all minerals

and each mineral was analysed at a single (optimum) line. The minor minerals (Quartz, Feldspar, Ettringite and Gypsum) were first analysed according to peak heights, since they are well crystalline and with narrow peaks. Kaolin and mica have more variable peak widths and were analysed according to peak area and then proportioned to 100%, minus the already analysed minor minerals. Table VII gives the estimated amounts of ettringite and gypsum present at 7 days (relative to the clay minerals). The results give a good indication of the reaction products which are forming in the early stages of reaction and their estimated proportions.

4 RESULTS

4.1 Strength Development

4.1.1 Effects of gypsum addition

Figure 2a illustrates the effects, on the strength development, of adding various amounts of gypsum in the control mix (kaolinite stabilised with 6wt.% lime), during moist curing for up to a maximum of 20 weeks. At curing periods of more than 1 week, the addition of gypsum at levels higher than that equivalent to 1% SO_3 resulted in enhanced strength development. The maximum strength was achieved after 10 weeks of moist curing at a gypsum content equivalent to 3% SO_3 . The strength maxima clearly show an optimum gypsum content shifting towards higher gypsum levels as moist curing time increases. However there are probably no further gains in strength at sulfate levels in excess of 3% even after 20 weeks of curing. This limit to the amount of sulfate which can be consumed is most likely to depend on the original lime content in the mix and the type of clay. The strength results for Kimmeridge Clay (which naturally contained 1.73% SO_3 as gypsum (as selenite crystals)) stabilised with 6% lime are also shown in Figure 2a (refer to Wild *et al.*, 1998). The results are very close to the closest equivalent ones for kaolinite (i.e. kaolinite – 6% lime – 2% SO_3). Strength enhancement due to gypsum, in clay – lime mixtures,

has been confirmed by many researchers (Croft, 1964 and Abdi & Wild, 1993 among others).

4.1.2 Effects of magnesium sulfate addition

Figure 2b shows the strength development of the control mix upon addition of various amounts of magnesium sulfate. The maximum strength enhancement after 1 week of moist curing was achieved with 4% SO_3 . In contrast to the results for specimens with gypsum addition, moist curing time beyond 1 week had little influence on strength development for specimens with sulfate contents above 2% SO_3 . However, samples containing up to 2% SO_3 continued to record appreciable strengths beyond 1 week of moist curing, but they also started to deteriorate after 10 weeks of curing. A peak in strength is identifiable at 2% SO_3 between 1 and 10 weeks of moist curing. At 20 weeks all specimens containing MgSO_4 had strengths significantly below that of the control. The results clearly indicate that magnesium sulfate is a severely deleterious sulfate with respect to its influence on strength development.

4.1.3 Effects of sodium sulfate addition

All levels of Na_2SO_4 addition resulted in enhanced strength relative to the control during the early stages of moist curing, up to a period of 5 weeks (Figure 2c). For Na_2SO_4 levels of up to 3% SO_3 , strength continued to increase with age up to 10 weeks, beyond which there was no further significant strength gain. Specimens containing 4% SO_3 showed no further strength increase after 3 weeks. Only the specimens containing 2% SO_3 had strengths significantly in excess of the control at 20 weeks. An optimum sulfate content for maximum strength of about 2–3% SO_3 is identifiable from one week of moist curing onwards. This optimum sulfate content does not appear to change significantly with curing time as was the case with gypsum addition.

4.1.4 Effects of potassium sulfate addition

As with the addition of sodium or magnesium sulfate, specimens containing potassium sulfate showed strength development during the first few weeks of

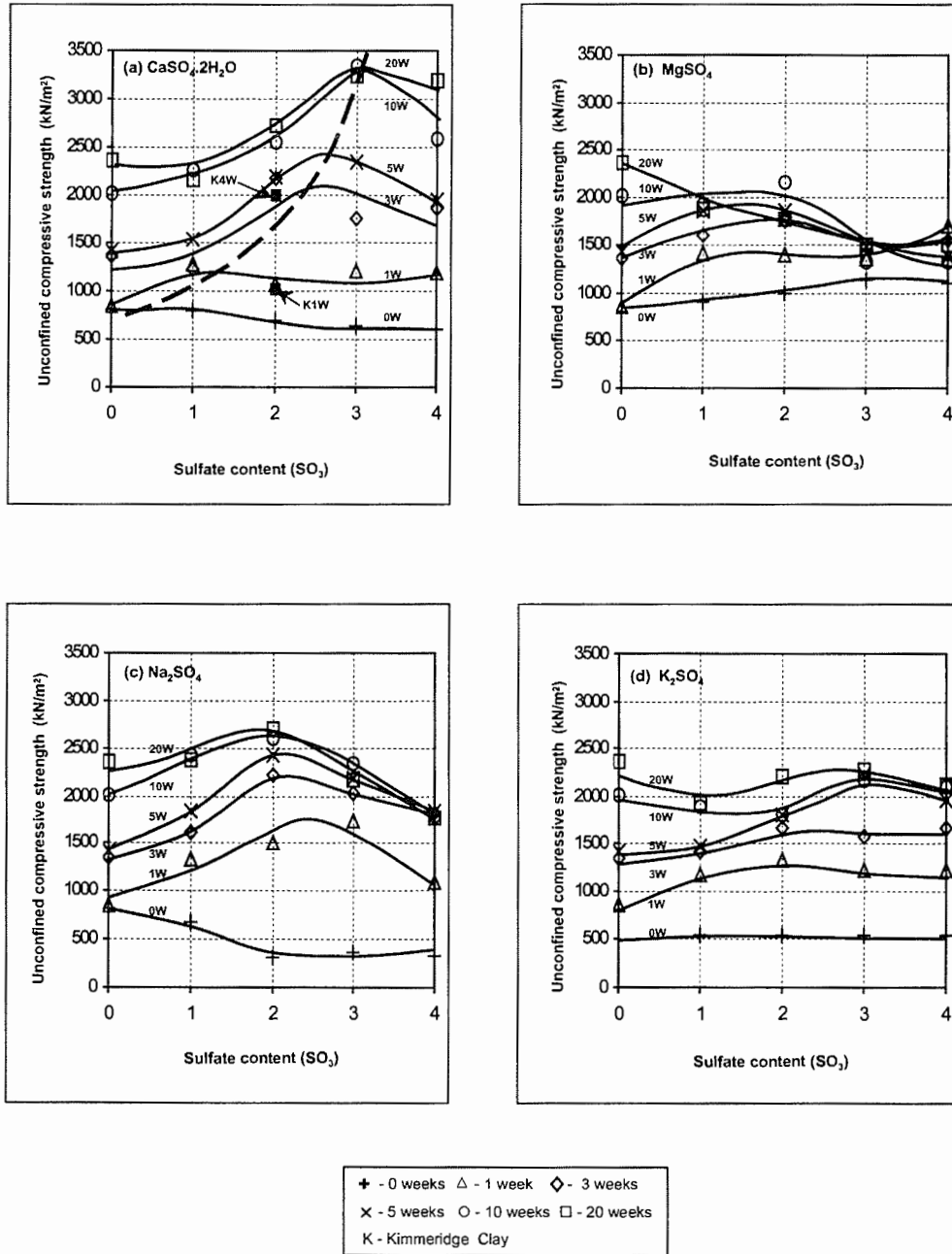


FIGURE 2 Compressive strength of cylindrical specimens of kaolinite stabilised with 6wt. % lime and containing additions of varying amounts of the sulfates of (a) calcium (b) magnesium (c) sodium and (d) potassium, during moist curing for up to 8 weeks at 30°C and 100 % relative humidity

moist curing (Figure 2d). After 5 weeks, samples containing more than 2% SO₃ showed little further

strength gain. An optimum sulfate level for maximum strength occurred at about 2-3% SO₃ from the third

week of moist curing onwards. As was the case for magnesium sulfate addition, and in contrast to calcium sulfate and sodium sulfate additions, all samples containing potassium sulfate showed strengths similar to or slightly below that of the control at 20 weeks of moist curing.

4.1.5 Comparison of the effects of the different sulfate types on strength

Figures 2a-d confirm that pozzolanic reactions can take considerable time, even beyond the 20 week test duration used in the current work. However, based on the strength data, the reactions appear to slow down considerably after 10 weeks of moist curing. In some cases the strength enhancing reactions can also cease altogether and deterioration may even occur. However, from Table VI which summarises the effects of varying concentrations of the different sulfates in samples moist cured for 1, 3 and 20 weeks, the addition of sulfates in all cases accelerated the initial rate of strength development during the first 1–3 weeks. After 1 week of moist curing, specimens containing magnesium sulfate or sodium sulfate demonstrated greater overall effect on strength enhancement compared with those containing gypsum or potassium sulfate. For curing periods between 3 and 20 weeks, there was a tendency for reduced strength, relative to the control, for samples containing additions of sulfates of Mg, Na and K. Magnesium sulfate clearly has a severe deleterious effect on strength development at 20 weeks and strength values observed were substantially below the control at all sulfate concentrations. This suggests that although magnesium sulfate may initially accelerate the cementitious reactions, the ultimate reaction products contribute to a fall in strength. Potassium sulfate is also deleterious compared to the control, but shows progressive increase in strength unlike magnesium sulfate. At high sulfate concentrations, sodium sulfate demonstrated a more deleterious effect on strength than potassium sulfate at 20 weeks, although it should be noted that at 2% SO₃, the former was quite effective in achieving strength enhancement at this extended moist curing period. Thus, at high sulfate concentrations and long curing periods, only specimens containing calcium sulfate

achieved strengths in excess of the control. It is apparent therefore that the pozzolanic reactions involved when the added sulfate provides Ca²⁺ cations are favourable for strength enhancement, and different from those when the added sulfate provides other cations (i.e. Mg²⁺, Na⁺ and K⁺).

4.2 Linear Expansion

4.2.1 Linear expansion during moist curing

Figure 3 shows the peak linear expansions observed for the control mix containing increasing amounts of the various sulfates, during moist curing for up to 8 weeks. Peak expansion magnitudes were generally lower (by between 1 and 4 times) for the monovalent sulfates (Na₂SO₄ and K₂SO₄) compared with those observed for the divalent ones (CaSO₄ and MgSO₄). All the specimens recorded reduced expansion beyond 2% SO₃, those containing sodium sulfate or gypsum showing further increases in expansion as the SO₃ concentration is increased further from 3% to 4% SO₃. Peak expansions were observed after 1–2 weeks of moist curing for the monovalent sulfates and from 1–7 weeks for the divalent ones depending on the sulfate type and content. Except for specimens where K₂SO₄ was the added sulfate where peak expansion magnitudes were observed within 2 weeks of moist curing at all sulfate levels, specimens containing 1–2% SO₃ generally attained peak expansion earlier than those with relatively higher contents of 3–4% SO₃. Dependence of peak expansion on the sulfate content appears to agree with similar observations by Snedker (1996) and Hunter (1988), where swelling for low sulfate soils was generally faster (complete with 10 days, Snedker (1996)), with swell for materials with high sulfate contents progressing at a much slower rate.

4.2.2 Linear expansion during soaking

Figure 4 illustrates the effects of the various sulfates on the maximum linear expansion of the control mix during soaking in de-ionised water for up to 8 weeks. Compared with linear expansion during moist curing where expansion magnitudes did not exceed about

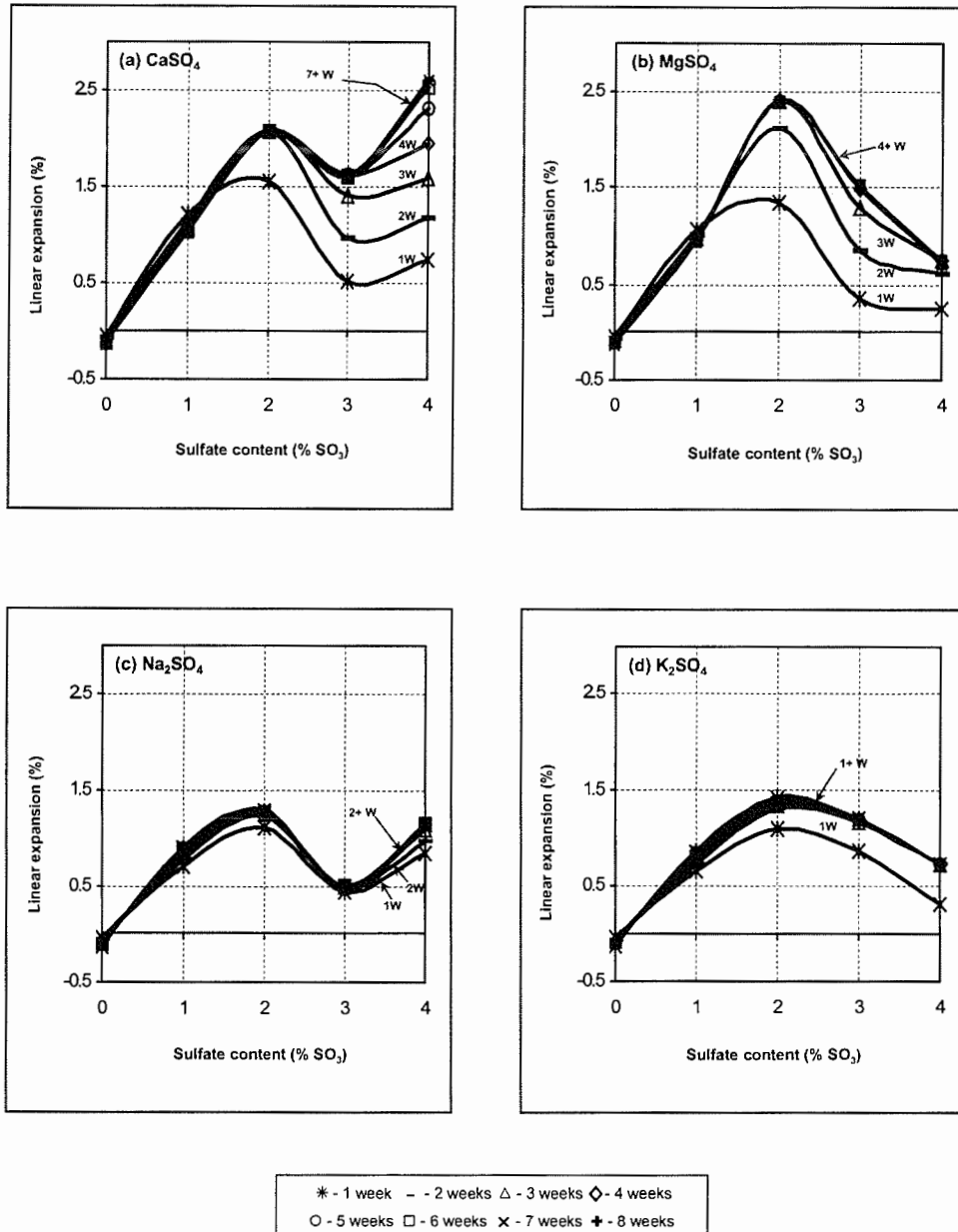


FIGURE 3 Linear expansion of cylindrical specimens of kaolinite stabilised with 6wt. % lime and containing additions of varying amounts of the sulfates of (a) calcium (b) magnesium (c) sodium and (d) potassium, during moist curing for up to 8 weeks at 30 °C and 100 % relative humidity

2.5%, the highest linear expansions during soaking were approximately 9 times higher. However as during moist curing, expansion levels at all sulfate contents were lower for the monovalent sulfates

compared with those observed for the divalent ones (by between 2 and 5 times). Significant expansion levels (above ~5%) due to the addition of monovalent sulfates were only observed beyond 2% SO₃ com-

pared with approximately 1% SO₃ for the divalent ones. As was the case during moist curing, the times of attainment of maximum expansion were also different for the two sulfate categories, specimens con-

taining monovalent sulfates recording most of the expansion within 1 week of soaking compared to up to 4 weeks of soaking for cylinders containing divalent sulfates.

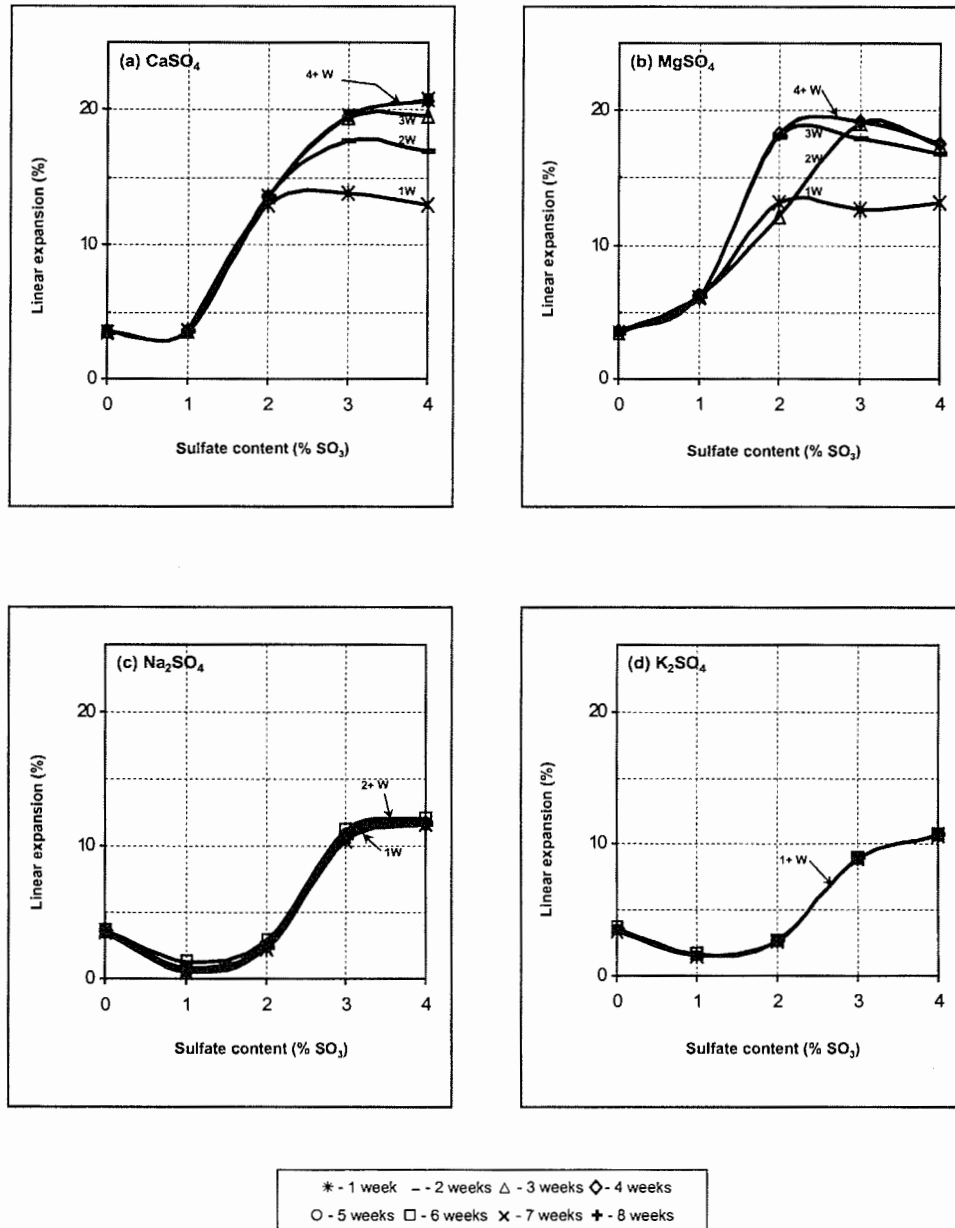


FIGURE 4 Linear Expansion of cylindrical specimens of kaolinite stabilised with 6wt. % lime and containing additions of varying amounts of the sulfates of (a) calcium (b) magnesium (c) sodium and (d) potassium, during both moist curing for the first 7 days and subsequent soaking in de-ionised water for up to 8 weeks at 30°C and 100 % relative humidity

TABLE VI Order of strength development for control^b specimens containing varying amounts of various sulfates

Sulfate content (% SO ₃)	1 Week	3 Weeks	20 Weeks
1	Mg ^a > Na > Ca > K > Con ^b	Na > Mg > K > Ca > Con.	Na > Con > Ca > K > Mg
2	Na > Mg > K > Ca > Con	Na > Ca > Mg > K > Con	Ca > Na > Con > K > Mg
3	Na > Mg > K > Ca > Con	Na > Ca > K > Mg > Con	Ca > Con > K > Na > Mg
4	Mg > K > Ca > Na > Con	Ca > Na > K > Mg > Con	Ca > Con > K > Na > Mg

^a Mg = Magnesium sulfate etc;

^b Con = Control specimens = 84% purity commercial kaolinite stabilised with 6wt. % lime.

TABLE VII XRD analysis results for the kaolinite-6wt.% lime-sulfate specimens containing varying amounts of different metal sulfates moist cured for 1 week at 30°C and 100% relative humidity

Mix composition	Sulfate content (% SO ₃)	Etringite (%)	Gypsum (%)	Kaolinite (%)	Mica (%)	Quartz (%)	Feldspar (%)
K^a + L^b (Control)	0	- ^c	-	91	8	<0.5	1
K+L+CaSO₄	1	1	<0.5	89	7	<0.5	2
	2	1	-	90	7	<0.5	2
	3	1	4	87	6	<0.5	2
	4	1	9	83	5	<0.5	2
K+L+MgSO₄	1	1	-	90	5	1.0	3
	2	1	-	92	6	<0.5	<0.5
	3	1	1	93	4	<0.5	1
	4	1	2	89	6	1.0	1
K+L+Na₂SO₄	1	1	-	91	6	1	1
	2	-	-	87	11	1	1
	3	<0.1	-	91	8	<0.5	1
	4	<0.5	-	89	8	<0.5	2
K+L+K₂SO₄	1	<0.1	-	92	6	<0.5	2
	2	<0.1	-	92	6	<0.5	2
	3	<0.1	-	89	9	<0.5	2
	4	<0.5	-	89	8	<0.5	2

a. K – Kaolinite

b. L – Lime

c. “-” means “not detected”

4.2.3 Comparison of effects of the different sulfate types on linear expansion

It is interesting to note that for specimens containing calcium sulfate or sodium sulfate, well defined maximum compressive strength (Figure 2a and 2c) and minimum linear expansion during moist curing (Figure 3a and 3c) both occur at or close to an SO₃ content of 3%. Also, gypsum-containing specimens, that achieved maximum strength during moist curing

up to 20 weeks (Figure 2a) were also the most expansive during, both moist curing and during soaking (Figures 3a and 4a), suggesting that high expansion does not necessarily imply weakness in respect of either the unsoaked or soaked moist cured material. Specimens containing magnesium sulfate tended to achieve maximum linear expansions at lower SO₃ concentrations than those containing gypsum. However during soaking, both of these systems containing divalent metal sulfates showed the largest increases in

expansion with increasing sulfate content between sulfate levels of 1% and 2% SO_3 . Similar increases in expansion during soaking occurred between sulfate levels of 2% and 3% SO_3 for the monovalent sulfates. Table VII shows the estimated percentage of ettringite and gypsum, relative to the total mineral content present, in 1 week moist-cured specimens of lime-stabilised kaolinite containing varying amounts of the different sulfate types. For the specimens containing the sulfates of calcium and magnesium (both which recorded the highest and comparable linear expansions during soaking), the level of ettringite detected remained the same for all levels of SO_3 . In both cases the amount of gypsum detected tended to increase with increase in sulfate content with little or no gypsum being detected at lower sulfate levels. Thus it would appear that gypsum is only present if sulfate was not fully consumed, most probably, in ettringite formation. The fact that the level of ettringite detected did not increase with sulfate level also suggests that for the levels of sulfate chosen the amount of ettringite formed in the early stages is determined by other factors in addition to the availability of sulfate. Figure 5 illustrates the effects of prolonged initial moist curing on expansion, upon subsequent soaking of these highly expansive compositions. Four of the most expansive compositions encountered (with 3 and 4% SO_3 as CaSO_4 and MgSO_4) were moist cured for a prolonged period of 14 weeks before soaking. The figure shows that these systems can also fully stabilise and exhibit negligible expansion during soaking. This suggests that it is the initial surface products formed during the very early stages of hydration, which are implicated in absorption of water and excessive expansion as previously suggested by Wild *et al.*, (1993). Table VII shows that for sodium sulfate and potassium sulfate additions, very little ettringite is formed. Also, no gypsum was detected in either system. More research is required before a reaction mechanism can be proposed. However, it is apparent that most of the sulfate added was neither "fixed" as ettringite or as gypsum and must have remained in the pore solution or taken up in other reactions, resulting in low strength development and in low expansion.

5 DISCUSSION

Strength increase in lime-stabilised soil is due to the interaction of calcium cations from the added lime and the silicate and aluminate ion species from the silica and alumina in the clay to form strength-enhancing calcium-based hydrated gels (Rogers and Glendinning, 1996). Thus, for lime-stabilisation, the type and particle size of the target soil are important factors for the provision of silica, compared for example to Portland cement (PC) soil stabilisation where the PC not only provides calcium but also silicate ions. The presence of gypsum in lime-stabilised clay soil provides further Ca^{2+} cations in addition to those donated by the lime. The extra Ca^{2+} cations are consumed in part by ettringite formation which contributes to strength development. The extra Ca^{2+} cations however also lead to increased swelling potential via ettringite formation particularly where abundant free water is available during the early stages of curing. For specimens where other sulfates were introduced, the Ca^{2+} cations could only be provided by the added lime, while the cations and SO_4^{2-} anions will be more readily available due to the higher solubilities of these sulfates.

In the case of magnesium sulfate addition, there are two possible explanations for the mechanism by which damaging effects on strength and expansion can occur. Firstly, MgSO_4 is known to attack both C-S-H and C-A-H gels (Heller & Ben-Yair, 1964). It decalcifies them to form gypsum and magnesium hydroxide (brucite). The magnesium hydroxide may react further to form hydrated silicates of magnesium (i.e. M-S-H). Magnesium silicates are known to be of extremely low strength (Grim, 1968). Secondly, it has been established that ettringite, a major contributor in strength enhancement, is unstable in the presence of magnesium sulfate, ultimately decomposing to gypsum and hydrated alumina (Gollop and Taylor, 1993; Chartschenko *et al.*, 1993 and Havlica & Sahu, 1992) in a reduced pH environment. Results from the current work indicate that similar detrimental reactions (on addition of MgSO_4) occur in the current work, contributing to the consistently low strength values observed, particularly at extended moist curing periods and at high SO_3 contents (see Figure 2b).

In the systems where sulfates containing monovalent cations were added, the pH is likely to increase significantly, depressing the solubility of Ca(OH)₂ (Lambe *et al.*, 1960; De Silva & Glasser, 1992; Shayan & Ivanusec, 1996). The resulting suppression of ettringite formation is in agreement with the XRD data shown in Table VII, the poor strength development in these system (Figures 2c and 2d), and the lower linear expansion magnitudes relative to the systems with sulfates containing divalent cations (Figures 3 and 4). Numerous researchers (Lees *et al.*, 1982, 1983; De Silva & Glasser, 1992; Li *et al.*, 1996; Shayan & Ivanusec, 1996) have proposed that in silicate and aluminate cementitious systems containing both Ca²⁺ and monovalent cation species, intermediate monovalent silicate and aluminate hydrates precede Ca-based silicates and aluminates.

6 PRACTICAL IMPLICATIONS

The current observations provide valuable insight into the effects of different sulfate types on lime-stabilised clay soils. This has some bearing on the current specifications and practices. This and previous works indicate that the behaviour of lime-stabilised clays is likely to be significantly influenced by the initial cation exchange process. In systems containing both monovalent and divalent cation species, the divalent cations will predominate over the cation exchange, displacing the monovalent cations in the process. Although both cation species are involved in reaction, the monovalent ones become engaged in the formation of intermediate silicates and aluminates as mentioned earlier. While such systems will generally develop relatively low strengths compared to systems predominantly containing calcium cations, there are certain sulfate levels where significant combined strength enhancement and development can occur. Strength enhancement in the presence of monovalent cations is also corroborated by Lees *et al.*, (1982, 1983) for systems containing sodium cations. Since the overall swelling in these systems, even at high sulfate levels has been shown, in the current work, to remain low despite the higher solubility of these sul-

fate types, the classification of sulfate damage in lime-stabilised cohesive soils is envisaged in future sulfate specifications, to discriminate between different sulfate types. It may be argued that a similar discrimination is in progress, upon the recognition of the significance of the total sulfur content, as opposed to total sulfate, arising from fact that the provision of sulfate in the soil may continuously be enhanced by the oxidation of sulfides. In the meantime, although there is a stipulation of the acceptable swelling magnitudes based on soaked CBR results, there is still a blanket (over)emphasis on, and specification of, total sulfate values (HDMRB-HA 74/00 and in MCHW1), irrespective of sulfate type.

7 IMPLICATIONS FOR PAVEMENT DESIGN AND PERFORMANCE

The economic, technological and environmental advantages of lime-stabilisation of soils, and the importance of capping layers as foundations and working platforms for pavement construction make the understanding of this technique, under all possible conditions, potentially useful to the pavement engineer. This understanding is likely to increase the likelihood of lime-stabilisation proposals, not only for capping layers but also for sub-bases, further enhancing the advantages. Recent research work by the authors has indicated that presence of sulfate per se need not be problematic for lime-stabilised soils (Wild *et al.*, 1999). In relation to pavement design, the current findings suggest that some materials, hitherto classified unsuitable for UK Class 7E highway construction material (Selected cohesive fill for stabilisation with lime to form capping) on the basis of integrated sulfate content levels, may otherwise be acceptable (and vice versa). Thus, in the assessment of alignment soils, sulfate tests should ideally be accompanied by detailed cationic studies. Not only should possible future sulfate migrations in sub-formation water emanating from site clearance operations, supply services, disused surface water drains and sewers, ducts, tidal, flowing and standing water, etc. be taken into account but also accompanying cationic

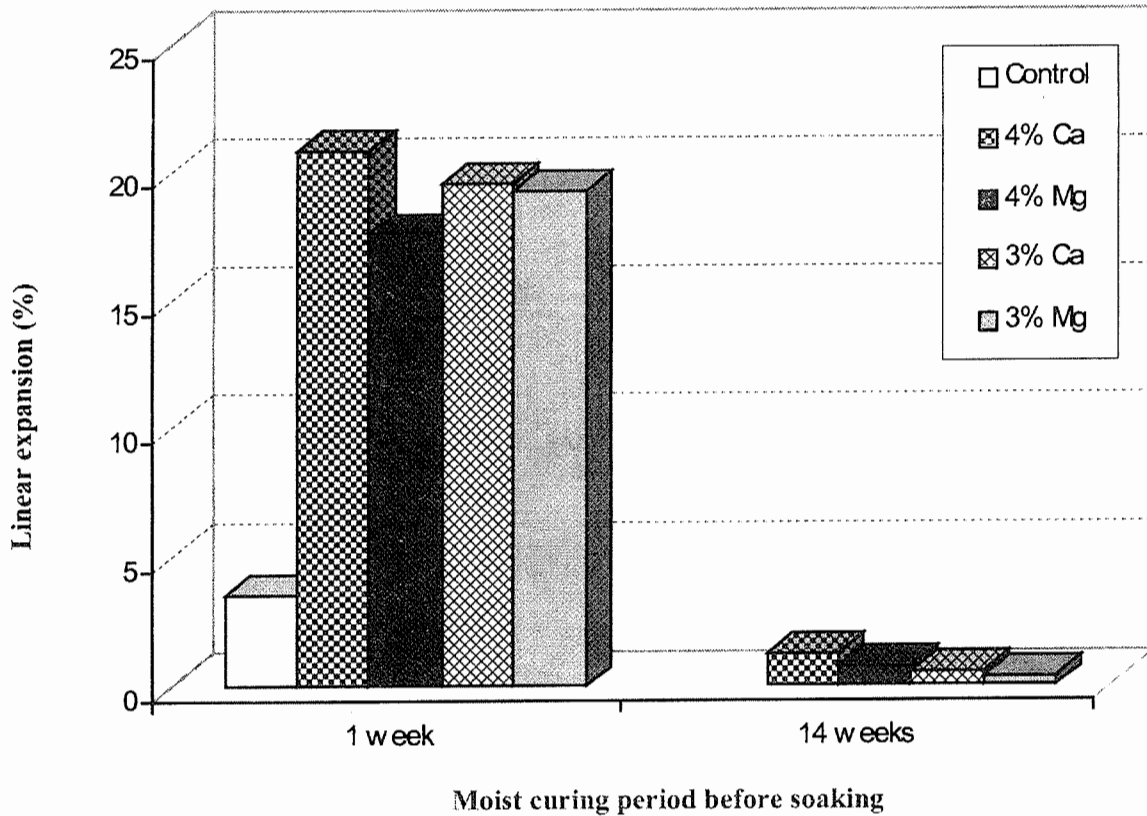


FIGURE 5 Maximum linear expansion of cylindrical specimens of kaolinite stabilised with 6wt. % lime and containing additions 3% and 4% SO_3 as calcium and magnesium sulfates, during soaking in de-ionised water after moist curing for 1 and 14 weeks at 30 °C and 100 % relative humidity for up to 8 weeks

onic ones. This is currently not explicitly implied for lime-stabilised material (DMRB-HA 74/00; MCHW1). Only sulfate, and recently sulphide, levels have previously been emphasised, pH levels being viewed only in relation to sulphide oxidation or lime addition levels. The case of the presence of Ca^{2+} -based sulfate should be treated rather differently from that of other cations. This study suggests that even in the presence of lime, the presence of some Ca^{2+} -based sulfate is likely to be beneficial even to long-term strength although, as in the current practice, the engineer may have to establish the amount which is likely to result in a high swelling potential. However, while high concentrations of K^+ -based sul-

fate are neither very detrimental or particularly beneficial, all levels of Mg^{2+} cations should be considered detrimental to both long-term strength development and to swelling. Low levels of Na^+ (equivalent to up to 2% SO_3) may be beneficial to long-term strength development without excessive swelling. As has been witnessed in the past, previously suitable UK Class 9D highway construction material (Lime-stabilised cohesive material) can deteriorate and be a precursor to pavement failures. The emphasis therefore, in relation to both pavement design and performance, should be for both integrated and individual sulfate and cation recognition, analysis and specification.

8 CONCLUSIONS

The following principal points may be deduced from the results, with regard to the influence of sulfates on strength and expansion behaviour of kaolinite when stabilised with lime.

1. Gypsum had the greatest effect in enhancing the strength of lime-stabilised kaolinite. The maximum strength enhancement occurred when the control mix contained approximately 6wt.% gypsum (equivalent to 3% SO₃). However, the enhancement appeared to decline after 10 weeks of moist curing.
2. Magnesium sulfate had the most deleterious effect on strength development after 20 weeks of moist curing. However, all sulfates including magnesium sulfate produced early strength enhancement, over and above non-sulfate kaolinite, and appeared to accelerate the initial cementitious reactions.
3. Gypsum and magnesium sulfate produced the highest overall linear expansions, both during moist curing and during soaking.
4. The sulfates containing monovalent cations displayed lower linear expansion (by up to 5 times) than those containing divalent cations, both during moist curing and on soaking. Also, higher SO₃ concentrations were required before the onset of expansion during soaking for clay containing monovalent metal sulfate cations than for clay containing divalent metal sulfates cations.
5. The observed difference in expansion produced by divalent and monovalent cations would seem to be related to initial ettringite formation. Expansion was lower in systems where this was suppressed, such as in sulfate systems containing monovalent cations.
6. Significant reduction in expansion occurs during soaking if samples are moist cured for prolonged periods before soaking. It is suggested that this is because with long curing periods all ettringite forming reactions have terminated.

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