Effects of monovalent and divalent metal sulphates on consistency and compaction of lime-stabilized kaolinite

Atul Kumar Mallik[1], Shradhanjali Moharana[2], Raushan Gupta[3,] Suchampa Bagchi[4]

[1]*Assistant Professor, Dept. of Civil Engineering, Aryan Institute of Engineering and Technology, Bhubaneswar*

[2]*Assistant Professor, Dept. of Civil Engineering, Raajdhani Engineering College, Bhubaneswar*

[3]*Assistant Professor, Dept. of Civil Engineering, Capital Engineering College (CEC), Bhubaneswar*

[4]*Assistant Professor, Dept. of Civil Engineering, NM Institute Of Engineering & Technology, Bhubaneswar*

Abstract

The factors influencing the durability of compacted lime-stabilised clay soils depend in part on the short-term material properties that emanate from the immediate changes that occur Žwithin a few hours· during the initial part of the stabilisation process. The long-term properties take a much longer period to develop and small changes are still occurring after several years. In both cases, the genesis of the properties may be directly linked to the properties of the parent soil and the cationic process that takes place as soon as the mix materials are in contact with water. Thus, the significance of the constitution of the parent material and the factors influencing the cationic exchange process cannot be over emphasised. Both these factors are affected by the presence of sulphates in the soil. This paper shows how the commonly occurring monovalent metal sulphates of sodium and potassium, and the divalent ones of calcium Žgypsum· and magnesium, affect the consistency and dynamic compaction properties of an industrial kaolinitic clay soil of high purity, to which sulphates have been artificially introduced. The results clearly illustrate that the effects of the presence of sulphate depend strongly on the sulphate cation type. Some cations $\check{z}Ca^{2q}$ and Mg^{2q}· enhance the effects of lime addition while others have the tendency to reverse these effects $\check{z}Na^{q}$ and K^{q}·.

Keywords: cation exchange; clay soils; compaction; lime; stabilisation; sulphates

1. Introduction

During the compaction of unstabilised clay soil, the dry density increases with increase in initial water content ǏCobbe, 1988; Bell and Coulthard, 1990·, due to the reduction in particle–particle frictional forces ǏGeorge et al., 1992·. The water content however reaches an optimum point, beyond which its further addition results in fewer solid particles per unit volume as more water displaces the clay particles. In the case of a lime-stabilised soil system, flocculation and agglomeration, as a result of cation exchange processes, result in material bulking. Thus as lime content is increased, lower maximum dry densities and higher optimum moisture contents are normally observed ǏCobbe, 1988; Bell and Coulthard, 1990; Abdi and Wild, 1993; Kinuthia, 1997·. The cationic exchange process stems from the fact that clay soil particle surfaces are normally negatively charged ǏGrim, 1968· due to an imbalance in ionic charge that may occur principally as a result of Ǐ1· unbalanced ionic substitution within the clay mineral crystal lattice and Ǐ2· broken bonds at particle edges. The negative charges result in particle–particle repulsive forces. The addition of lime during soil stabilisation introduces both Ca^{2q} cations and OH^{y} anions. The former are attracted to the negatively charged clay particle surfaces, resulting in a reduction of the particle–particle repulsive forces. The latter remain in the pore solution, where they are responsible for an increase in alkalinity of the system ǏGeorge et al., 1992; Smith et al., 1994 among others·. The reduction in these forces results in the adherence of clay particles to each other to form flocs, a phenomenon which is commonly referred to as 'flocculation' ǏLocat et al., 1990·. The formation of flocs results in an increase in voids volume and hence a reduction in dry density of the stabilised material. The formation of flocs and agglomerates takes place within the first few hours after lime addition ǏLocat et al., 1990; Abdi and Wild, 1993·. This compares with the much longer-term pozzolanic reactions that involve the formation of cementitious products which may take months or even years to complete ǏWild et al., 1996, 1998a,b·. Thus, material changes due to the cation exchange process such as consistency limits are unlikely to be greatly affected by prolonged mellowing beyond 24 h.

The presence of metal sulphates, which may occur either in the parent stabilisation material, in the water used for mixing andꞧor in the ground water ǏSherwood, 1962; Mitchell, 1986; Hunter, 1988; Obika and Freer-Hewish, 1990; Snedker and Temporal, 1990; Kinuthia, 1997·, present complicating effects with regard to the modified cation exchange processes andꞧor the pozzolanic reactions. The changes will obviously vary with, among other factors, the sulphate concentration, the metal cation type, the amount of available calcia and alumina Ǐand hence the amount of lime added and the type, the amount and the particle size distribution of the clay·. The presence of gypsum in lime-stabilised clay soil Ǐfor example· provides further Ca^{2q} cations in addition to those donated by the lime, as well as the introduction of SQ^{2y} anions. The extra Ca^{2q} cations lead to

an increase in the overall number of cations attracted to the clay particle surfaces. For soils contaminated with other types of metal sulphate, the Ca^{2q} cations present will be mainly provided by the added lime. In this case, the cation exchange process will be determined by the position of the sulphate metal cation in the lyotropic (or Hofmeister) series ($Li^{q} - Na^{q} - K^{q} - Mg^{2q} - Ca^{2q} - Ba^{2q} - Al^{3q} - H^{q}$) (Cobbe, 1988; George et al., 1992 among others) relative to the other cations already present in the clay–lime system. In the absence of sulphate, calcium silicate hydrate (C–S–H) gel forms along with crystalline or semi-crystalline calcium aluminate hydrates (C_4AH_{13}) and calcium alumino silicate hydrates (C_2ASH_8) (Croft, 1964; Mitchell, 1986; Abdi and Wild, 1993), after the dissolution, at high pH, of alumina and silica from the clay (George et al., 1992). Carbo-aluminate hydrates may also form depending on the availability of CO_2 or carbonates. In kaolinitic soils, when gypsum is present the formation of a colloidal product consisting of a complex calcium–sulpho–aluminate–silicate hydrate (C–A–S–S–H) is reported to form on the surface of the kaolinite plates (Wild et al., 1993). From this surface product, a compound of higher crystallinity commonly known as ettringite (C_3A3CSH_{32}) nucleates (Wild et al., 1993). Ettringite is known to impart significant strength enhancement, due to its needle-like crystalline morphology (Abdi and Wild, 1993; Wild et al., 1993, 1996, 1998a). On the other hand, the colloidal reaction products from which ettringite nucleates has the capability of imbibing large volumes of water (Mehta, 1973; Mitchell, 1986) and dramatically increases the swelling potential of the lime-stabilised soil. Wild et al. (1998b) have established that this capability of imbibing water is only present during ettringite's formative stages and is absent with fully crystallised ettringite. The rapid formation of ettringite (even during mixing; Wild et al., 1993) is likely to affect the material's immediate behaviour—including the cation exchange processes and hence the consistency, and the compaction properties of lime-stabilised clay soils. How different naturally occurring common metal sulphates influence these changes in clay soils is the principal objective of this paper. The paper reports on the changes imparted to a lime-stabilised industrial kaolinitic clay soil of high purity, by metal sulphates of calcium (gypsum), magnesium, sodium and potassium.

2. Materials

Kaolinite

Kaolinite (trade name 'Standard Porcelain') supplied by English China Clay (ECC) International St. Austell, Cornwall, UK, was used as the clay source. Table 1 shows the particle size distribution, the consistency limits and other properties of the material while Table 2 shows its chemical and mineralogical composition.

Table 1

Particle size distribution, consistency limits and other properties of 'Standard Porcelain' ŽECC International.

Sieve size	Ž%.
❭ 53 mm	0.05–1.0
❭ 10 mm	10–20
— 2 mm	28–57
Consistency limits	
Liquid limit Ž%.	61
Plastic limit Ž%.	32
Plasticity index	29
Others	
Specific gravity	2.57
Bulk density Žkg⊓m³.	1090–1170
Natural moisture content Ž%.	10–12

Lime

Hydrated lime žtrade name 'Limbux'. was supplied by Buxton Lime Industries Buxton, Derbyshire, UK. Tables 3 and 4 show its physical properties and chemical composition, respectively.

Table 2

Chemical analysis and mineralogical composition of 'Standard Porcelain' ŽECC International.

Chemical analysis	%
SiO_2	48
Al_2O_3	37
Fe_2O_3	0.65
TiO_2	0.02
CaO	0.07
MgO	0.30
K_2O	1.60
Na_2O	0.10
Loss on ignition ŽL.O.I.	12.5
Mineralogical composition	**%**
Kaolinite	84
Micaceous material	13
Feldspar	1
Other minerals	2

Table 3
Physical properties of lime (Buxton Lime Industries)·

Trade (or Product) name	'Limbux' Hydrated Lime
Chemical name	Hydrated lime or calcium hydroxide
Physical form	Dry white powder
Melting/decomposition	
Temperature	5808C
Bulk density	480 kg/m^3
Specific gravity	2.3
Specific surface	300–1500 m^2/kg
Particle size distribution	99% — 90 m
Solubility in water	1.76 g/l sat. sol. at 108C
pH	12.4 (aqueous solution approx. 2 g/l)
Vapour pressure	0 at 208C

Chemicals

The major chemicals used in the study were of reagent grade with a purity of at least 97%. They were calcium sulphate dihydrate ($CaSO_4 \cdot 2H_2O$), magnesium sulphate ($MgSO_4$), sodium sulphate (Na_2SO_4) and potassium sulphate (K_2SO_4), from either Aldrich Chemical, Gillingham, Dorset, England, UK, or from Phillip Harris and Sons, Scientific Centre, Pentwyn, Cardiff, South Wales, UK. Silica gel was used during the drying of specimens for X-ray diffraction analysis, 'Carbosob' in order to prevent carbonation, and buffer solutions for pH meter calibration.

Table 4
Chemical composition of lime (Buxton Lime Industries)·

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_2O_3	0.06
Alumina	Al_2O_3	0.10
Silica	SiO_2	0.46
Excess moisture	H_2O	0.34

3. Experimental procedure and results analysis

Atterberg limits and compaction

The Atterberg consistency limits testing and reporting was carried out in accordance with British Standard methods—BS 1377 ̌1990·. Since the materials used were either fine or water soluble, no sieving was carried out. Testing was conducted within 5 h of the introduction of water. Proctor compaction tests ̌British Standard BS 1377, 1990· were used to determine the maximum dry density ̌MDD· and the optimum moisture content ̌OMC· of various kaolinite–lime–metal sulphate systems. Mixing ̌dry and wet· was carried out in a Model SE-401 Hobart 40 Qt mixer. The first series of compaction tests was aimed at determining the compaction properties of the unstabilised kaolinite. Secondly, tests were carried out to determine the proctor compaction properties of the clay upon stabilisation with varying amounts of lime. Finally, compaction tests were performed using the kaolinite–6 wt.% lime ̌control mix· with varying additions of calcium sulphate ̌$CaSO_4$·, magnesium sulphate ̌$MgSO_4$·, sodium sulphate ̌Na_2SO_4· or potassium sulphate ̌K_2SO_4· ̌i.e., 1.0, 2.0, 3.0 and 4.0% SO_3. The use of 6 wt.% lime was arrived at during a separate test for the initial consumption of lime ̌ICL· ̌BS 1924·. Normally, the basic lime requirement ̌i.e., for modification purposes only· is in the range 1–3 wt.% of the unstabilised soil, but a little more lime is usually added for the attainment of appreciable strength development.

Effects of lime on consistency limits

Fig. 1 illustrates the changes in liquid limit ̌LL·, plastic limit ̌PL· and plasticity index ̌PI· of the kaolinite–lime mixes as the lime content increases. The liquid limit of 'pure' kaolinite increased sharply with the addition of 3 wt.% lime. Beyond this lime content, the liquid limit remained nearly constant even at high additions of lime before dropping slightly at 20 wt.% lime addition. The plastic limit also increased sharply with lime addition to a stable level at a lime content of between 3 wt.% and 14 wt.%, before increasing further at 20 wt.% lime addition. This resulted in an increase in plasticity index from 29% for 'pure' kaolinite to 33% at 3 wt.% lime. This level of plasticity index was maintained approximately, up to 14 wt.% lime addition, before dropping to 27% at 20 wt.% lime addition. Generally, between 1–3 wt.% lime is needed for modifying soil properties but between 2–8 wt.% lime is needed for stabilisation, depending on clay type and clay content. The apparently high lime content of 6 wt.% required to stabilise the plastic limit is attributed to the fact that the material used was predominantly clay.
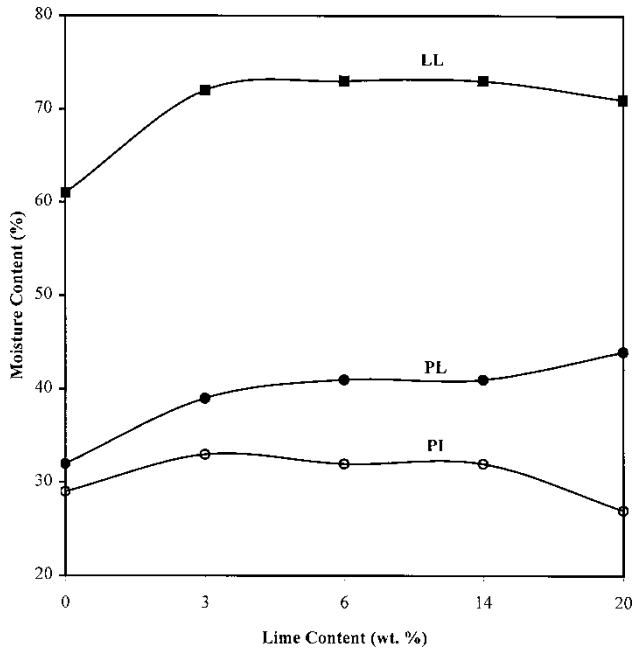
Fig. 1. Atterberg limit's moisture contents vs. lime content for kaolinite containing various amounts of added lime.

Effects of sulphates on consistency limits

Fig. 2a–d illustrate the changes in liquid limit, plastic limit and plasticity index of kaolinite–6 wt.% lime ǐcontrol‧ mix when varying amounts of different sulphate types were added. Although sulphates were added in the form of metal salts ǐi.e., $CaSO_4 P 2H_2O$, $MgSO_4$, Na_2SO_4 and K_2SO_4‧, the sulphate content is reported as weight percent SO_3 ǐexpressed as a percentage of the kaolinite‧ rather than weight percent of the metal salt, so that sulphate values are equivalent and are independent of the type of metal salt used.

The addition of gypsum lowered the liquid limit of the kaolinite–6 wt.% lime mix. On the other hand, the plastic limit decreased slightly and then increased, resulting in a gradual decrease in plasticity index as the gypsum content increased ǐFig. 2a‧. The effects of the addition of magnesium sulphate were similar to those of the addition of gypsum ǐFig. 2b‧.

The addition of a small amount of sodium sulphate ǐ1.0 wt.% SO_3 equivalent‧ lowered substantially the liquid limit of the lime-treated kaolinite from 73% to 59% ǐFig. 2c‧. Further sulphate additions had no further effect on the liquid limit. The plastic limit behaved in a similar manner, although dropping less sharply but significantly by the addition of 1.0 wt.% SO_3 and remaining at this level on further sulphate addition. Thus, the plasticity index also fell by the
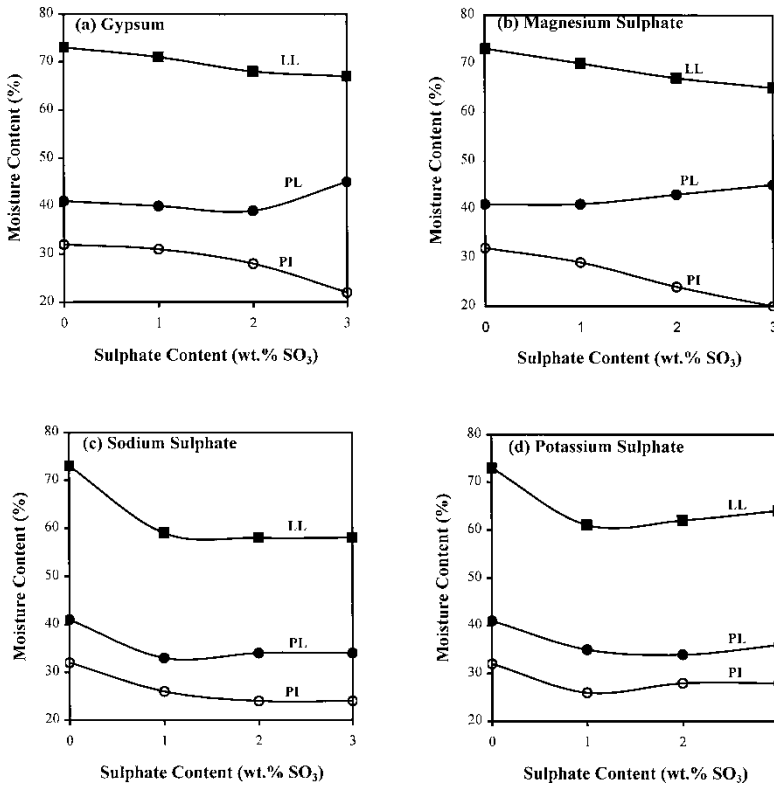
Fig. 2. Atterberg limit's moisture contents vs. sulphate content for kaolinite–6 wt.% lime mixes with varying additions of individual metal sulphates.

addition of small quantities of sodium sulphate and stayed relatively unaffected by further sulphate additions. The effects of the addition of potassium sulphate were similar to those of the addition of equivalent amounts of sodium sulphate. There was, however, a slight increase in liquid limit by further sulphate addition. The plastic limit decreased by the same magnitude as for sodium sulphate addition. The increase in liquid limit at high potassium sulphate additions retarded the decrease in the plasticity index which after its initial drop on the addition of 1.0 wt.% SO_3, increased on further sulphate addition. An outstanding feature of the four sets of curves in Figs. 2 and 3 is the marked similarity in behaviour between the two divalent metal sulphates and between the two monovalent metal sulphates.

Comparatiõe effects of the different sulphate types on the consistency limits

Fig. 3a–c emphasise the effects that different metal cations have on the three Atterberg limits, when added as metal sulphates. Increases in sulphate content
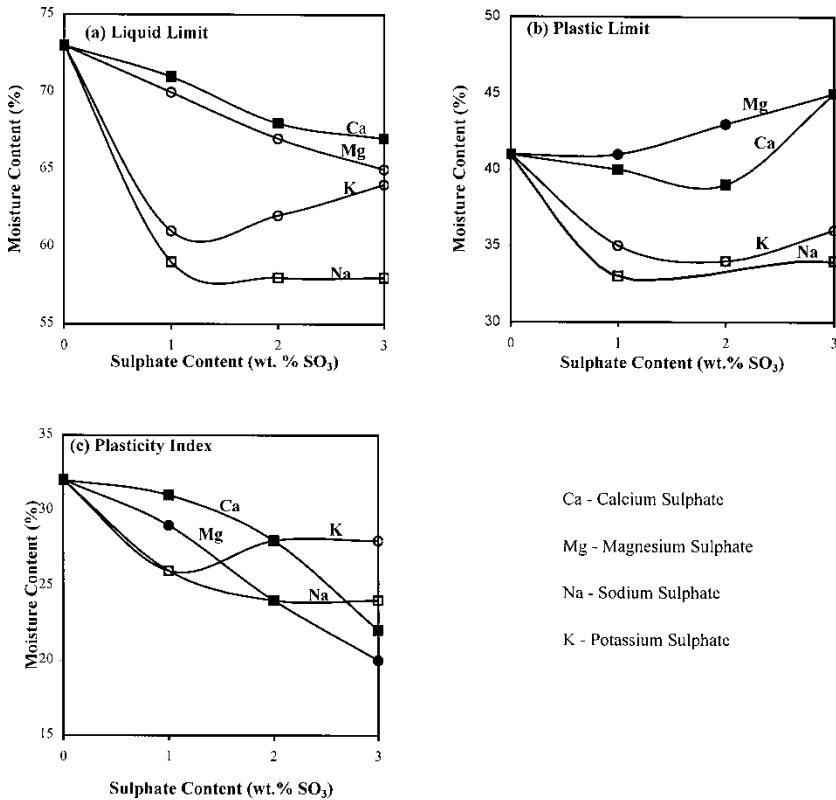
Fig. 3. Atterberg limit's moisture contents vs. sulphate content for kaolinite–6 wt.% lime mixes with varying additions of various metal sulphates.

generally lowered the liquid limit, the magnitude of the decrease increasing in the cation order Ca^{2q}— Mg^{2q}— K^q— Na^q, the sulphate containing the cation to the left decreasing the liquid limit by a smaller magnitude than the one containing the cation to the right. It should be noted that the cation order ǐi.e., Ca^{2q}— Mg^{2q}— K^q— Na^q. is the same as that in the lyotropic series ǐsee Section 1.. The sulphates containing Ca^{2q} and Mg^{2q} cations displayed similar liquid limit trends as did those containing Na^q and K^q although the trends were different in the two cases ǐFig. 3a..

The two groups of sulphates ǐthose containing monovalent and those containing divalent cations· also showed pairing trends with respect to their effects on the plastic limit ǐFig. 3b.. Ca^{2q} and Mg^{2q} cation containing sulphates recorded little or no drop in plastic limit at low sulphate contents but showed significant increases at high sulphate contents. In contrast, Na^q and K^q cation containing sulphates exhibited sharp decreases in plastic limit at low sulphate levels and subsequently showed only small increases in plastic limit at higher sulphate
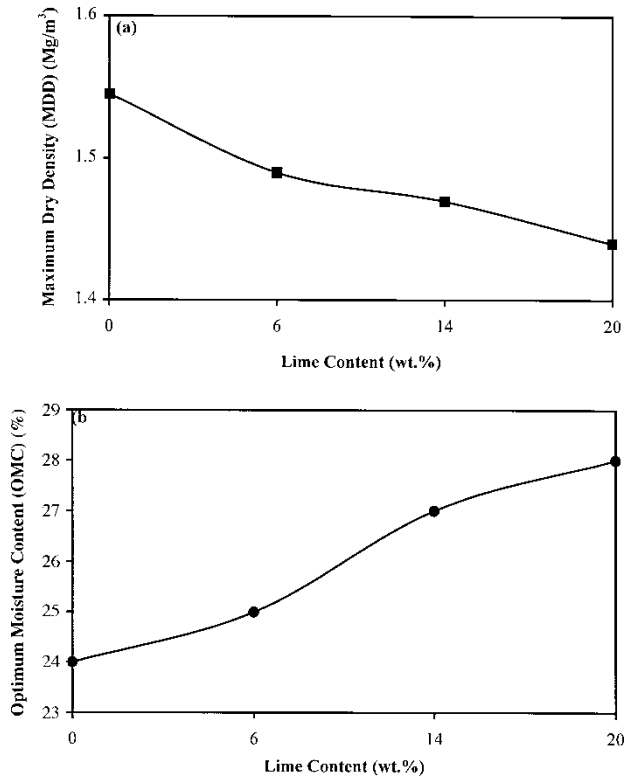
Fig. 4. Ža. Maximum dry density ŽMDD. vs. lime content and Žb. optimum moisture content ŽOMC. vs. lime content for kaolinite.

levels. The resulting changes in both liquid limit and plastic limit resulted in decreased plasticity with increasing sulphate content ŽFig. 3c.. Na^q and K^q cation containing sulphates reduced the plasticity by greater amounts than did Ca^{2q} and Mg^{2q} sulphates at low sulphate levels, but at higher sulphate levels, the plasticity index either increased ŽK^q. or showed little change ŽNa^q.. Thus up to about 1.0% SO_3 content, the effect of the cation in reducing the plasticity index was in the order Ca^{2q}— Mg^{2q}— K^{q}FNa^q, where sodium caused the largest reduction, but at high SO_3 contents Ž≠3.0%·, the order was K^q— Na^q— Ca^{2q}— Mg^{2q}.

Effects of sulphates on compaction properties

The addition of lime had the overall effect of lowering the maximum dry density ŽMDD. and raising the optimum moisture content ŽOMC. of the

unstabilised kaolinite ˇƵFig. 4a and b·. Fig. 5a and b show the effects of different metal sulphate additions on respectively the MDD and the OMC of the kaolinite–6 wt.% lime control mix. The introduction of sulphates to the kaolin-ite, in addition to lime, particularly at low sulphate concentrations ˇƵof the order of the equivalent of 1.0 wt.% SO$_3$·, further lowered the MDD for all the sulphates ˇƵFig. 5a·. However, sodium sulphate had the least effect on the MDD. Also, the sulphates further raised the OMC of the lime-stabilised kaolinite, again sodium sulphate addition having the least effect. Overall, the sulphates of calcium and magnesium, produced similar trends to those produced during the addition of lime ˇƵcompare Fig. 5a and b with Fig. 4a and b·. As with the Atterberg limits, there is a close similarity in the effects that the two divalent metal sulphates and the two monovalent sulphates have on compaction be-haviour. The behaviour of the OMC tends to be equivalent, but in the opposite sense. As sulphate content increases, the OMC increases sharply for specimens
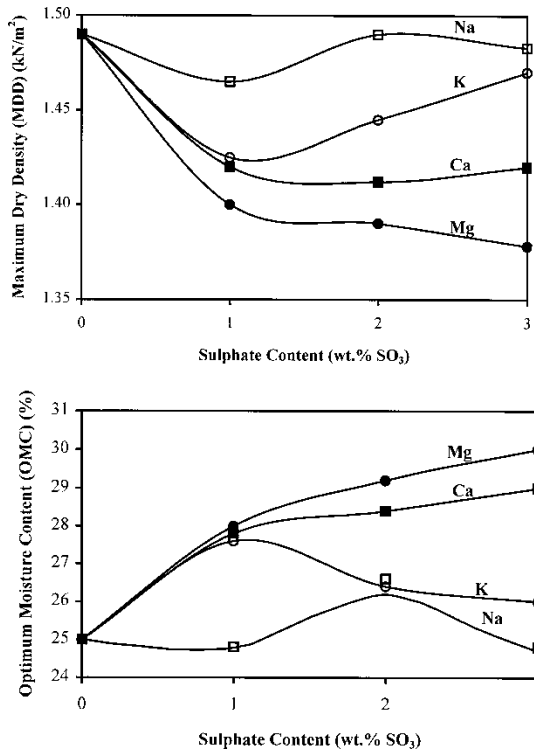

Fig. 5. Ƶa· Maximum dry density ˇƵMDD· vs. lime content and Ƶb· optimum moisture content ˇƵOMC· vs. lime content for kaolinite–6 wt.% lime mixes containing varying amounts of various sulphate types.

containing the divalent cations ˇup to 1% SO_3· and then continues to increase at a much reduced rate, whereas specimens containing the monovalent cations show ˇbelow 1 or 2% SO_3 content· a smaller initial increase in the OMC followed by a subsequent decrease. Thus, Fig. 5a is effectively an inverted mirror image of Fig. 5b, magnesium sulphate emerging as the most powerful in its influence on the compaction process.

X-ray diffraction analysis

X-ray diffraction ˇXRD· analysis was performed on all the kaolinite–lime–sulphate mixes after moist-curing for 1 week, with a view to understanding the mechanisms involved in the interaction between the clay, lime and sulphate. Samples were obtained from specimens that had already been tested for uncon-fined 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 ˇas 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 ˇECC· International using a Philips PW 1825 X-ray generator and CuK**a** radiation of a wavelength ˇ*l*· of 1.542 Å. The X-ray tube detector ˇa PW 1050 vertical goniometer· was fitted with a diffracted-beam graphite monochro-mator together with an automatic sample changer to enable a continuous scan at 90 s**r**degree. A simple calibration standard ˇnot an internal standard· was used for all minerals and each mineral was analysed at a single ˇoptimum· line. The minor minerals ˇQuartz, 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. Clearly small quantities of amorphous material could not be quantified using this method although large quantities could be estimated from the absolute drop in the kaolin and mica peaks, however this was not evident.

Table 5 gives the estimated amounts of ettringite and gypsum present at 7 days relative to the clay minerals. Quantitative measurements after a few hours of moist curing would clearly be very difficult because of the very small quantities of reaction products which will have formed at such an early stage. Thus, analysis was carried out at 1 week although this represents a considerably more advanced stage than the 1–5 h typical of the age at which compaction or consistency limits tests were carried out. The results however do give a good

Table 5

XRD analysis results for the kaolinite–6 wt.%lime–sulphate specimens containing varying amounts of different metal sulphates moist cured for 1 week at 308C and 100% relative humidity

Mix composition	Sulphate content Ž% SO$_3$.	Ettringite Ž%.	Gypsum Ž%.	Kaolinite Ž%.	Mica Ž%.	Quartz Ž%.	Feldspar Ž%.
K^{a}qL^b ŽControl.	0	– ^{c}	–	91	8	− 0.5	1
KqLqCaSO$_4$	1	1	− 0.5	89	7	− 0.5	2
	2	1	–	90	7	− 05	2
	3	1	4	87	6	− 05	2
	4	1	9	83	5	− 0.5	2
KqLqMgSO$_4$	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
KqLqNa$_2$SO$_4$	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
KqLqK$_2$SO$_4$	1	− 0.1	–	92	6	− 0.5	2
	2	− 0.1	–	92	6	− 05	2
	3	− 0.1	–	89	9	− 05	2
	4	− 0.5	–	89	8	− 0.5	2

^{a}K—kaolinite; ^{b}L—lime; ^{c}'–' means 'not detected'.

indication of the reaction products which are forming in the early stages of reaction and their probable proportions.

4. Discussion

Effects of cation exchange

Consistency limits

Figs. 1–3 illustrate the changes in the Atterberg consistency limits brought about by the presence of metal sulphates. Sulphates influence the cationic exchange process to varying degrees, depending on the type and concentration of cation. The divalent cations enhanced the effects of lime addition ˇbeyond that at the lime fixation limit· producing a reduction in liquid limit, an overall increase in plastic limit and a reduction in plasticity ˇFig. 2· as the divalent cation content increased. The cations with lower charge ˇe.g., monovalent cations· initially lowered both the liquid limit and the plastic limit very substantially, although high concentrations of these cations tended to stabilise both these parameters. This is an undesirable outcome since it prevented further significant reduction in the plasticity index ˇFig. 2·. Therefore, at high concentrations, sulphates containing divalent cations lowered the plasticity more than those containing monovalent ones.

The different effects of the different sulphates on the Atterberg limits of lime-stabilised clay may be explained in terms of the clay particle–particle interactions, which are significantly influenced by the cation exchange process. These limits may be defined in terms of the resistance to the flow, or the shear stress, of the soil ˇLeroueil and Le Bihan, 1996·. At the LL, the soil is fully saturated and it flows like a liquid. Therefore viscosity, which is the property of a liquid to resist motion of elemental particles with respect to one another, is a good indicator of the shear stress and therefore also, at or near the LL, of the LL of the material. When cations are introduced in a soil, the initial neutralisation of the clay particles negative charge during the ensuing cation exchange process results in the break up of the edge-to-face arrangement of the clay particles to a more parallel arrangement ˇYong and Warkentin, 1975; Vyalov, 1986·. This arrangement has a better flow resistance as the mutual interference of the particles' electric fields is greater. Thus, the LL initially rises ˇFig. 1·. Further increase in cation concentration results in increase in the particle–particle spacing, since the cations are normally hydrolysed ˇGrimshaw, 1971·. Consequently, resistance to flow and hence shear resistance and the LL of the mix decreases. The divalent cations, because of their higher positive charge, resulted in a higher resistance to flow than the monovalent ones. Thus, the former ˇcations· produced a soil–water mix of higher LL ˇhence, less reduction in LL· than the latter ˇFig. 3a·. Also, relatively many more of the monovalent cations

will be attracted to the clay surface because of their lower positive charge, and also the hydro-sphere on the clay particles with monovalent counter ions can be very large. Therefore, the inherent repulsion between clay particles coupled with the large hydro-sphere, gives maximum particle–particle separation and subsequent dispersion. The particle–particle interaction is therefore seriously reduced. However, excessive increase in the cation concentration leads to a compression of the electric diffuse double layer of ions surrounding the clay particles, allowing closer approach of the particles. The resulting resistance to flow again increases the shear stress, preventing further reduction in liquid limit especially by the monovalent cations which are more hydrolysed and which had not achieved adequate negative charge neutralisation compared to divalent cations ǏFig. 3a‥. Potassium has a higher replacing power than sodium and is more strongly held to the clay because it fits better into the hexagonal holes on the tetrahedral faces of the clay surface ǏYong and Warkentin, 1975‥. It is proposed that increased K^q ion concentration would then dramatically increase the particle–particle bonding, resulting in increased resistance to flow as apparently happened in the current work, where at 3.0% SO_3 concentration, the reduction in LL was very close to that due to the presence of the divalent metal cations ǏFig. 3a‥.

The smaller the size of the cation and the higher its charge, the more rigid a structure it will impose. The lower the charge, the less rigid the structure will be. The imposed structure will therefore depend on the position of the cation in the lyotropic or Hofmeister series ǏLi^q— Na^q— K^q— Mg^{2q}— Ca^{2q}— B^{2q}— Al^{3q}— H^q‥. The series was observed to correlate well with the observations in the current work where the reduction in liquid limit was greater in the cation order Ca^{2q}— Mg^{2q}— K^q— Na^q ǐsee Fig. 3a‥, the sulphate containing the cation to the right, which has a larger hydro-sphere than the one to its left depressing the liquid limit by a bigger magnitude than the cation to the left.

In contrast to LL which occurs at or near the liquid phase of the soil–water mix, the PL occurs at the plastic-solid phase where the material is at a considerably lower moisture content. In this state, the clay particles are much closer together and the capillary forces originating at the air–water interfaces, are very high ǏYong and Warkentin, 1975‥. It is suggested that varying the exchangeable cations and changing the cation concentration also changes the particle arrangement and hence the size and distribution of pores, which changes the water content at the PL. The presence of cations allows, at low concentrations, easier particle–particle movement ǐas was the case for LL‣ and thus they tend to lower the shear resistance and hence the PL, particularly the more hydrated monovalent cations ǏFig. 3b‥. At high cation concentrations, the resistance to flow becomes higher as the interference of particle–particle electric fields becomes stronger and the drop in PL ǐas for LL,‣ is arrested. Due to their higher positive charge, this arrest is more pronounced in the case of divalent

cations ˅Fig. 3b˙. For the particular kaolinite used in the study, the LL is roughly twice as sensitive to changes in cation concentration as the PL.

Compaction

In the agglomerated state, as a result of lime addition, there is increased pore volume which lowers the dry density. This state also accommodates more water during compaction, raising the optimum moisture content ˅OMC˙. The introduction of small concentrations of sulphate metal cations tends to reduce particle separation, thus enhancing flocculation and agglomeration, and further lowering the dry density and further raising the OMC of lime-stabilised clay soil. At high sulphate concentration, renewed repulsive forces reduce the flocculation effects, and there is a significant reduction in the rate of decrease in MDD. The rate of increase in the OMC is also noticeably reduced ˅Fig. 5b˙. The more hydrated monovalent cations result in deflocculation and even dispersion, causing a complete reversal in the trends for both the reduction in MDD and increase in the OMC ˅Fig. 5a and b˙. Thus, the lowering of the MDD of the control mix was least for the monovalent cations and highest for the divalent cations. The effect on reducing the MDD was in the cation order $Mg^{2q} \rangle Ca^{2q} \rangle K^{q} \rangle Na^{q}$ ˅see Fig. 5a˙, where the sulphate containing the cation to the left lowered the MDD more than the one containing the one to its right. The equivalent pattern for OMC is similar, this time the cation to the left raising the OMC by a bigger magnitude than the one to its right ˅Fig. 5b˙. These trends again emphasise the significance of the position of the sulphate metal cations in the lyotropic series, although in this case the positions of Mg^{2q} and Ca^{2q} are reversed.

Effects of sulphate reactions

A second, and perhaps less published effect of the presence of sulphate in lime-stabilised soil on the consistency and compaction properties is due to the fact that the sulphate anions combine with the calcium from the added lime and the alumina from the clay to form ettringite ˅Mitchell, 1986; Wild et al., 1993, 1996, 1998a,b˙. Thus, additional short-term material changes occur when sulphates are present in clay–lime systems. Wild et al. ˅1993˙ have shown from thermogravimetric work that ettringite forms very rapidly in hydrated kaolinite–lime–gypsum mixes and is even present immediately after mixing. The ettringite nucleates on the surfaces of the kaolinite particles, and this surface layer of reaction products imbibes water and swells. Also ettringite, like gypsum, is a fairly insoluble product. Its formation leads to a further increase in porosity, by forcing the clay particles apart, and also results in a decrease in free moisture content due to the chemical consumption of water during ettringite nucleation and subsequent growth. The removal of this water and the formation of new solid phases may influence the compaction properties of the clay. It is apparent from Table 5 that additions of calcium sulphate and magnesium

sulphate both result in strong ettringite formation whereas sodium sulphate and potassium sulphate addition lead to formation of much less ettringite. In particular, magnesium sulphate also reacts to form gypsum ž in addition to ettringite. which is an additional 'sink' for water. This may explain why the OMC values for specimens with magnesium sulphate additions continue to increase significantly with increasing sulphate content, whereas specimens containing both sodium and potassium sulphates ž which lead to less ettringite formation and no gypsum formation. show a fall in OMC at high sulphate levels. The formation, and growth of both gypsum and ettringite crystals may also contribute to the very marked fall in MDD which these specimens exhibit.

5. Conclusions

ž1. Lime addition generally increases the liquid limit, plastic limit and plasticity index of kaolinite, although at high additions the LL and PI fall.

ž2. Added sulphates lower the liquid limit of lime-stabilised kaolinite. The magnitude of lowering depends on the nature of the sulphate cation ž s., the monovalent cations lowering the liquid limit more than the divalent ones. On the other hand, different sulphates have different effects on the plastic limit of lime-stabilised kaolinite. The divalent cations increase the PL while the monova-lent ones lower it. The overall effect in both cases is that the plasticity index is lowered. At high sulphate concentrations, the divalent cations lower the PI more than the monovalent ones.

ž3. The effects of divalent metal sulphates on the compaction properties of lime-stabilised kaolinite are similar to those produced by the addition of excess lime ž beyond 6%.. They further lower the maximum dry density ž MDD. and further raise the optimum moisture content ž OMC.. The divalent metal sulphates lower the MDD and raise the OMC by a larger magnitude than those containing monovalent cations. Although low concentrations of monovalent metal sulphates do produce reductions in MDD and increases in OMC, at high concentrations these effects are reversed. The practical significance of these effects is that the presence of sulphates would result in consumption of more water during mixing operations and relatively lower field densities compared with the sulphate free material. This is particularly so for divalent metal sulphates.

ž4. The changes in Atterberg limits and in compaction characteristics result mainly from cation exchange processes. Results from the current work show that these changes are dictated both by sulphate concentration and by the relative positions of the cations in the lyotropic or Hofmesiter series. However, there is evidence particularly for divalent metal sulphates that early formation of ettringite and gypsum also influence these material properties.

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