PROPERTY CHANGES AND MECHANISMS IN LIME-STABILISED KAOLINITE IN THE PRESENCE OF METAL SULPHATES

by

J. M. KINUTHIA *B.Sc.(Hons), M.Sc.*

School of the Built Environment
University of Glamorgan

Sponsoring Establishment:	- The University of Glamorgan
Collaborating Establishment:	- Cementitious Slag Makers Association - Buxton Lime Industry
Grant support :	- Overseas Development Administration - Cementitious Slag Makers Association

A thesis presented in fulfilment of the requirement for the degree of Doctor of Philosophy
of the University of Glamorgan

September 1997

CERTIFICATE OF RESEARCH

This is to certify that, except where specific assistance and reference is made, the work described in this thesis is the result of the candidate. Neither this thesis, nor any part of it, has been presented, or is currently submitted, in candidature for any degree at any other University.

J.M. Kinuthia

(Candidate)

24/6/98

(Date)

S. Wild

Prof. S. Wild

(Director of Studies)

24/06/98

(Date)

ACKNOWLEDGEMENT OF ASSISTANCE GIVEN TO THE AUTHOR DURING THE PROJECT

Two final year undergraduate students - Mr Peter Lewis and Ms Gabriele Veith carried out experimental works directed by the author, as part of their final year degree projects. Some of the most significant results of their experimental work are those shown in Figures 7.1-8, 7.2-2 and 7.2-5, and some of those data incorporated in Figures 7.1-7 and 8.1-22.

All other data, other than those data attributed in the text were obtained by the author from experiments carried out and designed by the author.

S. Wild

Prof. S. Wild

(Director of Studies)

24/06/98

(Date)

DEDICATION

I wish to dedicate this thesis to the entire house of Kariuki *(Nyûmba ya Kariûki)* whence I trace my roots, and to my immediate family Liz, Sarah and Sam (alias Junior).

LIST OF CONTENTS

Acknowledgements

I would like to thank all those with whom discussions have been held over the last three and a half years whilst the investigations summarised in this document have been carried out. In particular :-

the head of the School of the Built Environment, Professor Richard Neale for availing all the resources within the school to facilitate my work.

the technical staff in the school of the built environment, viz.: those in the concrete laboratory where tests on weight upon soaking were carried out, structural laboratory where all the UCS tests were performed and those from the soils laboratory where all the soils testing was carried out.

Dr. Higgins of Cementitious Slag Makers Association and Mr. Hedley Grieves of Buxton Lime Industries for their constructive comments which helped in giving the investigations carried out effectiveness and direction towards industrial applications.

final year students Ian Humphrey, Peter Lewis and Gabriele Veith whose camaraderie and co-operation during their final year projects in the soils laboratory was invaluable.

my wife Liz, daughter Sarah and son Sam, whose tremendous encouragement, especially during the final preparation of the document kept me motivated and inspired at a time when I needed it most.

finally, I would like to thank my supervisors Dr Jamal Khatib, Mr. G. I. Jones and Prof. Stanley Wild (also Director of Studies) all who have made time available to give guidance during the laboratory testing and the preparation of this thesis.

John Mûngai Kînûthia

SUMMARY

In recent times, environmental issues concerning mineral extraction and disposal of waste material have arisen world-wide. Thus the advantages of employing soil stabilisation as opposed to granular material in highway construction and foundations (i.e. cost effectiveness, material savings, and waste disposal management) have become more apparent. In soil lime-stabilisation, however, there has been increased concern over the enormous heaving that can occur when sulphate bearing soils are encountered and, to a lesser degree, the relatively slow strength development which is produced.

Thus, the major objective of this work has been first to establish the fundamental material property changes which occur when clay soils are stabilised with lime in the presence of the most commonly encountered sulphates in the soil (i.e. sulphates of calcium (gypsum), magnesium, sodium and potassium), and then in addition, establish whether inclusion of ground granulated blastfurnace slag (GGBS), which is used with Portland Cement (PC) and PC-blends to combat sulphate attack in concrete, would impart similar sulphate resistance when included with lime in the stabilisation of clay soils.

In order to achieve these objectives, carefully controlled laboratory investigations have been carried out on compacted cylinders of lime-stabilised industrial kaolinite of high purity (84% kaolinite) containing various levels of the four sulphates. The cylinders were all moist cured at 30°C and 100% relative humidity for periods of up to 20 weeks and their strength gain monitored. In addition, expansion of the cylinders has been monitored both during moist curing and during soaking. For one of the sulphates (gypsum), cylinders have been produced in which the lime was systematically replaced with GGBS and the effect of this replacement on both strength and swelling has been established. In order also to establish the effectiveness of the findings to real soils, a natural sulphate bearing clay soil, Kimmeridge Clay, was included in the investigations.

The investigations have confirmed the detrimental swelling and beneficial strength effects of gypsum addition, and also established the adverse effects, in terms of strength development and swelling, of the presence of the sulphates of magnesium, sodium and potassium. More importantly, enhancement of strength development and dimensional stability has been achieved by incorporating GGBS in clay-lime mixes, especially in the presence of gypsum. For example, the 7-day unconfined compressive strength (UCS) of kaolinite-6wt.% lime-gypsum mixes was increased by as much as 1.5-3 times (50-200% increase) depending on the gypsum content, by the substitution of approximately 80% of the lime with slag. Meanwhile, the linear expansion during soaking of the most expansive 7 day moist cured cylinders (27%) was reduced to less than 5% by a similar lime substitution. Similar, but slightly lower strength and swelling improvements were achieved with Kimmeridge Clay - 6wt.% lime mixes (i.e. 1.5-2.5 times (50-100% increase)) by the substitution of between 40% and 80% of the lime with slag, confirming the successful application of the findings to lime-stabilisation of natural sulphate bearing clay soils. In both cases, the improvement is even more significant at 28 days and at higher total stabiliser (lime + slag) contents. The findings have produced considerable industrial interest and there are on-going pilot trials currently taking place.

Recommendations for further investigations include the establishment of long term trends, so as to eliminate any possibility of potential long-term adverse effects, particularly when the apparently beneficial GGBS is present.

LIST OF FIGURES

LIST OF TABLES

LIST OF PLATES

LIST OF SYMBOLS AND ABBREVIATIONS

Å	Angstrom (10^{-10}m)
°C	degree Celcius
c	centi (10^{-2})
g	gramme
kg	kilogram
J	joule
k	kilo (10^{3})
l	litre
λ	(lambda) wavelength
m	milli (10^{-3}) ; metre
mm	millimetre
μ	micro (10^{-6})
μm	micron or micrometre (10^{-6}m)
N	Newton
n	nano (10^{-9}) ; integer 1, 2, 3...etc.
Pa	Pascal
ppm.	parts per million.
psi	pounds per square inch
r	radius (a - internal radius; b - outer radius)
s.g	specific gravity
s	second
σ_r	radial stress
σ_θ	cicumferential stress
t	time in seconds
θ	(theta) (°) plane angle
u_r	radial displacement
V	volt (electric potential, electromotive force).
A; Al	Al_2O_3; aluminium (Al^{3+} - aluminium cation)
AAS	Alkali-activated slag
AASHO	American Association of State Highway Officials
ACI	American Concrete Institute

AFm	A metastable phase (mainly monosulphate), in a hydrating system
AFt	A metastable phase (mainly ettringite), in a hydrating system
ASTM	American Society of Testing of Materials
ASR	Alkali-silica reaction
BSI	British Standard Institution
C; Ca	CaO; calcium (Ca^{2+} - calcium cation)
$\overline{C}$	CO_3
C-A-H	(CAH) calcium aluminate hydrate
C-A-S-H	(CASH) calcium alumino-silicate hydrate
C-A-S-$\overline{S}$-H	(CAS$\overline{S}$H) calcium sulpho-aluminate silicate hydrate
C-S-H	(CSH) calcium silicate hydrate
C-N-S-H	(CNSH) calcium silicate hydrate gel with sodium structurally incorporated.
C-"N"-S-H	(C"N"SH) calcium silicate hydrate gel with sodium bound in it.
CBR	California Bearing Ratio
DC	Direct Current
DTG	Derivative Thermo-Gravimetry
DTp.	Department of Transport (U.K).
EPMA	Electron Probe-Microscopic Analysis
ECCI	English China Clays (International)
EELS	Electron Energy Loss Spectroscopy
G	Gypsum ($CaSO_4.2H_2O$)
ICL	Initial Consumption of Lime
I_p	Internal hydration product
K	potassium (K^+ - potassium cation)
L	Lime as $Ca(OH)_2$
LL	Liquid Limit
L.O.I	Loss On Ignition
M; Mg	MgO; magnesium (Mg^{2+} - magnesium cation)
MAS	Magic Angle Spectroscopy
MDD	Maximum Dry Density
(M-A-H)	(MAH) Magnesium Aluminate Hydrate
(M-S-H)	(MSH) Magnesium Silicate Hydrate

N; Na	Na_2O; sodium (Na^+ - sodium cation)
NMR	Nuclear Magnetic Resonance
O_p	Outer hydration product
OPC	Ordinary Portland Cement
OMC	Optimum Moisture Content
PBFC	Portland Blast Furnace Cement
PL	Plastic Limit
PI	Plasticity Index
P_i	Pressure acting on inner cylinder wall
P_o	Pressure acting on outer cylinder wall
pH	$\log_{10}(H^+$ concentration)
RPM	Revolutions Per Minute
S	Slag (ggbs) (Only when used in the 3L5S4G notation)
S; Si	SiO_2; silicon
$\overline{S}$	SO_3 (sulphite)
SO_4	sulphate
SEM	Scanning Electron Microscopy
SFM	Scanning Force Microscopy
T	Temperature
TEM	Transmission Electron Microscopy
UCS	Unconfined Compressive Strength
wt.%	percent by mass
XPS	X-ray Photo-electron Spectroscopy

CHAPTER 1 - INTRODUCTION

The gradual depletion of global conventional construction materials has made construction engineers consider the use of materials often regarded as unsuitable for modern construction. By virtue of its great variability in origin as well as in its weathering and transportation processes, soil poses severe problems not ordinarily encountered for other construction materials, such as low strength and volume instability. Because in situ soils do not possess the desired engineering properties, the processing of land for highways and foundations normally involves the removal and dumping of large quantities of waste material and inputs of equivalent quantities of suitable material. This procedure is expensive and environmentally damaging and could be avoided. In this regard, stabilised soil has gained popularity as an economical substitute to concrete, asphalt, stone and other construction materials such as gravel. Initially, cement stabilisation was adopted with or without other additives such as lime. Gradually, use of lime alone (as a binder) in highway layers and in foundations has become popular. France, is one of the foremost lime users in the world (Buxton Lime Industries, 1993). In 1993 alone, France used 400,000 tonnes of lime in earthworks and pavements, nearly 100 times the U.K utilisation. Other users include USA, South Africa, Australia, New Zealand, Germany and Sweden. The growth in the use of lime to stabilise soil has been due to its enormous potential since soil, irrespective of type, is abundant in all areas.

Used in Asia as long as 5000 years ago, lime converts in-situ material which may be weak, moisture susceptible and difficult to handle into friable material which is easily placed and compacted to form a strong stable platform. It has the advantage of being capable of being supplied in a range of grades to meet individual project requirements and for varying candidate material suitability. As such, it contributes cost savings of up to 50% in areas of highway construction and similar applications by stabilising otherwise unsuitable or marginal soils, thereby reducing the use of imported fill materials. Stone importation, for unbound capping layers for example, can be cut by as much as 100% where lime stabilised material can be wholly adopted. Other parallel economies are made by avoiding the need to excavate, remove and dispose of large volumes of previously unsuitable material and by allowing work to proceed in wet conditions by rapidly drying out waterlogged sites. This helps in avoiding penalty payments due to completion delays and idle hired plant and labour. Thus, lime stabilisation has been adopted in many applications such as :-

- stabilisation of sub-bases and subgrades in pavement construction,
- drying out of wet soils for construction as well as agricultural purposes,
- stabilisation of embankments and canal linings,
- improvement of foundation soils beneath strip or raft foundations; lime piles (or pile columns), and
- reduction of frost heave.

In tropical countries especially, lime stabilisation has been found to be more economical than cement stabilisation due to the abundance of gravels with high clay contents, ambient temperatures and the relatively relaxed application procedures. High clay contents (at least 10 % below 2μm) and adequate temperatures (at least 15°C) are prerequisites to good strength development (Bell, 1988). In these tropical regions, slaked lime ($Ca(OH)_2$) has been preferred to quicklime (CaO). The latter is preferred in the temperate climates such as in Britain where wet soils and low temperatures predominate. Quicklime, on addition of water, undergoes an exothermic slaking to slaked lime. The heat generated is beneficial to the initial chemical reactions and assists the drying process of the soil. The total moisture loss can in practice be as high as twice the percentage addition of quicklime which is typically in a proportion of 1-4% of the dry mass of the soil. The heat generated also raises the reaction temperatures to levels adequate, or at least marginally adequate, for strength development under winter conditions.

Unlike in concrete research, the use of additional pozzolanic or latently hydraulic materials (besides lime and/or cement) in soil stabilisation has not been fully investigated. However, recent research by Wild *et al.,* (1996) using hydrated lime with additions of ground granulated blastfurnace slag (GGBS) appears promising. Soil stabilisation using these additional pozzolanic materials is unlikely to be as successful when they are used on their own, as a highly alkaline environment is required for them to react. Therefore, their use will likely be as additives and/or partial substitutes to either cement and/or lime or other alkaline compounds.

Certain soils have so far been regarded as unsuitable for construction either on their own and/or stabilised with lime, because various problems have been encountered. It has been established that soils that;

- lack in fines (at least 10 % finer than 2μm),
- have excess organic matter (more than 2 wt.%), or
- contain sulphates, especially gypsum (Calcium Sulphate ($CaSO_4.2H_2O$)), pose various problems.

It has been established that when stabilised with lime, soils that are lacking in fines and/or contain excess organic matter do not develop adequate strength, while those that contain excess sulphates and do develop strength have other problems. Sulphate bearing soils are susceptible to heaving as a result of excessive swelling upon inundation (Sherwood, 1962; Mitchell, 1986; Snedker and Temporal, 1990; Abdi, 1992). Sulphate-bearing soils may also disintegrate due to dissolution of unreacted salt leading to salt migration (Sherwood, 1992).

One of the issues that researchers have not yet settled has been the establishment of the maximum acceptable level of sulphate for allowable heave. Also, although water has been identified as an essential ingredient for heave to occur, research has identified other variables such as temperature, curing time and type of sulphate (Mitchell, 1986; Abdi, 1992) as further critical factors. These sulphates include sulphates of magnesium, sodium and potassium (Sherwood, 1962; Obika and Freer Hewish, 1990; Fanning *et al.,* 1993). The fact that these sulphates are present in the soil, at least in identifiable quantities, [and exacerbated by the fact that all these sulphates are far more soluble than gypsum (see Table 2.1 in Chapter 2) and also that the strength of some of the silicates formed by these salts are extremely weak e.g. the silicates of magnesium (Grim, 1968)], has raised questions as to the relative effects of these sulphates in lime stabilised clays. It is the intention of this research to establish answers to these questions. Thus, the principal objectives of the research are:-

A. In the absence of ground granulated blastfurnace slag (GGBS),

(i) establish the relative effects of different metal sulphates on the consistency, compaction, strength development and swelling behaviour of lime-stabilised kaolinite,

(ii) determine relationships between sulphate level, sulphate type and unconfined compressive strength for lime-stabilised kaolinite which has been moist cured.

(iii) determine relationships between sulphate level, sulphate type and swelling for lime-stabilised kaolinite which has been moist cured and then water saturated.

(iv) establish the magnitude of swelling pressure generated for lime-stabilised kaolinite specimens, when those specimens are confined.

(v) propose a mechanism by which sulphates cause swelling in lime-stabilised clay soils.

B. In the presence of ground granulated blastfurnace slag (GGBS),

(i) establish the relative effects of gypsum on the consistency and compaction behaviour of lime-stabilised kaolinite (gypsum was selected for its abundance and larger existing database),

(ii) determine the degree by which replacement of lime with ground granulated blastfurnace slag influences strength development and swelling of lime stabilised kaolinite which contains various levels of gypsum,

(iii) assess the influence of substitution of lime by slag on the strength and swelling behaviour of a naturally occurring sulphate bearing clay soil (Kimmeridge Clay) which has been stabilised with lime,

(iv) assess the influence of varying compaction moisture content on the swelling behaviour of kaolinite which has been stabilised with lime,

(v) propose a mechanism by which lime activated slag stabilises clay soils, and suppresses their swelling potential.

(vi) evaluate commercial implications the inclusion of GGBS in lime-stabilisation of clay soils, including cost analysis and possible design nomographs.

Kaolinitic clay soils have been used during previous investigations (Barshard, 1955; Croft, 1964; Abdi, 1992; Rossato, 1992). Thus, industrial kaolinite is popular as control material due to the existence of a large database on tests on kaolinitic soils in general (Rossato, 1992) and also due to its good strength development upon stabilisation (Abdi, 1992). In the current work, kaolinite under the trade name "Standard Porcelain" is used for laboratory testing. Swelling behaviour is monitored both during moist curing and during soaking. Additionally, the relative effects of different sulphates on the generation of swelling pressure in 'stabilised' kaolinite is determined. Here, a method is adopted that does not allow volume change and is of sufficient accuracy to establish swelling pressures to within 0.2 kN/m^2. The method is used to monitor the generation of swelling pressure with time during saturation of sulphate containing lime-stabilised clay. The development of mechanical strength during curing of the lime stabilised clay and the manner in which this is influenced by different sulphates is also determined. Having established the range and degree to which properties and performance of the lime-stabilised clay are modified by the presence of the different sulphates, a method is developed to reduce or eliminate the undesirable changes. This involves partial replacement of lime with ground granulated blastfurnace slag in clay containing calcium sulphate. Unfortunately, investigation into the effects of GGBS on the swelling behaviour and strength development of lime stabilised clays in the presence of the other sulphates is beyond the scope of this current work. Calcium sulphate dihydrate, or gypsum, is however the most common sulphate found in most soils. In British soils, it often occurs as the mineral selenite. Kimmeridge Clay is a typical example of this. Therefore, in addition to investigation of the changes in artificial laboratory produced 'soils' made up from kaolinite clay and gypsum when stabilised with lime/GGBS, studies are also made on the changes in natural Kimmeridge Clay when stabilised with lime/GGBS. The object of this is to determine whether the property changes in the artificial 'soil' are reproduced in the natural soil and would therefore be expected to be reproduced in the field.

The work starts by describing the mineralogy of clays in general in Chapter 2, with an emphasis on kaolinite. Clay-lime reactions are discussed in Chapter 3 both in the absence and in the presence of sulphates. Chapter 4 opens with the discussion of GGBS soil stabilisation in general. Thereafter, and in the rest of the research, work is confined to investigations into the effects of GGBS and sulphates on lime stabilised kaolinite and Kimmeridge Clay. In Chapter 5 the materials used in the research are discussed while Chapter 6 contains a discussion of the procedures, equipment and experimental techniques used in the research. Chapters 7 and 8 report the results, Chapter 9 discusses them while Chapter 10 gives the conclusions drawn from the work together with recommendations for future research.

For practical reasons, the entire investigation was organised within interrelated but self contained modules which include kaolinite - lime - sulphate; kaolinite - lime - GGBS, kaolinite - lime - GGBS - gypsum and/or Kimmeridge Clay - lime - GGBS systems. For each system, the specimens would ideally be compacted at their individual maximum dry densities (MDD) and optimum moisture contents (OMC) but it was, however, necessary to limit the range of samples evaluated and therefore representative proctor tests were conducted on only three systems viz.: kaolinite - 6wt.%lime - sulphate (with sulphates of calcium, magnesium, sodium and potassium); kaolinite - lime - GGBS - gypsum and Kimmeridge Clay - lime - GGBS systems. Therefore due to small variations in MDD and OMC, some common mixes such as the kaolinite - 6wt.% lime mix produced small variations in observed unconfined compression strength and linear expansion in the different systems. Trends should therefore be compared only within the system under which they were conducted and for the purpose for which that system was designed for. These variations were however minor and did not influence the individual trends. Where large discrepancies arose, the author has drawn attention to these instances whenever appropriate. Also, for each system, the appropriate MDD and OMC have been indicated.

It was deliberately intended that the scope of the current work would not be tailored to any specific civil engineering application but to fall within the realm of material properties for general application in construction. Thus, the choice of tests conducted combined those more generally associated with concrete materials with those employed in soil mechanics. Thus, unconfined compression strength (UCS) test was for example preferred to the California Bearing Ratio (CBR) or shear strength test. However, some of the traditional tests in soil mechanics such as the Atterberg limits and BS compaction were retained. It was established that inclusion of GGBS did solve some of the problems relating to the undesirable behaviour of lime-stabilised gypsum-containing kaolinite and of natural sulphate bearing clay (Kimmeridge Clay), such as high swelling potential and poor early strength development. It is recommended that further work be done on lime - slag stabilisation of clays in the presence of the other sulphates which are found in soils, as the results of this work suggests that including GGBS in lime-stabilisation may overcome the problem of swelling in sulphate-containing soils in general. In the meantime, the starting point of the current work will be a review of the mineralogy and general properties of clay soils, in the next chapter.

CHAPTER 2 - CLAY : MINERALOGY AND PROPERTIES

2.1 INTRODUCTION

To the civil engineer, soil substantially refers to any loose material at the earth's crust, regardless of particle-size distribution, composition, or organic content. Terzaghi and Peck defined soil as "natural aggregate of mineral grains that can be separated by such gentle means as agitation in water" (Grim, 1968).

2.1.1 CLAY MINERALS

In general terms, clay refers to soil material finer than 2µm. Clay minerals on the other hand specifically refer to a limited number of crystalline components of the clay materials. They are essentially hydrous aluminium silicates with magnesium or iron substituting wholly or in part for aluminium in some minerals and with alkalies or alkaline earths also present as essential constituents in some of them.

The most important characteristic of a soil next to its grading is recognition of the **clay-mineral** type (Grim, 1968). This is because many effects, especially reactivity, volume stability and cohesiveness depend directly on it. Mineral type is therefore a more powerful diagnostic property than say plasticity for the engineering behaviour of a soil. Also, the degree of crystallinity of the clay mineral, has a significant influence on certain properties such as plasticity. Also, certain clay minerals which may be present only in very small amounts may exert a tremendous influence on the attributes of a clay material. It is therefore not adequate to determine only the major clay-mineral compounds, as the small amounts of minor clay minerals must also be characterised.

Certain **nonclay-mineral** materials may be contained in clays. These materials include quartz, calcite, dolomite, large flakes of mica, pyrite, selenite and feldspar. These may often be separated and identified by a particle-size separation analysis, as the non clay minerals in clay material tend generally to occur as particles coarser than 2μm.

Clay mineral particles sometimes also contain **organic material**. The organic material occurs in clay material in several ways: It may be present as discrete particles of wood, leaf matter, spores etc.; it may be present as organic molecules adsorbed on the surface of the clay-mineral particles; or it may be adsorbed in between the silicate layers. The discrete particles may be present in any size from large chunks easily visible to the naked eye, to particles of colloidal size which act as a pigment in the clay-mineral materials, giving a dark-grey or black colour to a clay material. However, there is no direct relationship between the colour and organic content. A very small amount of organic material may have a very large pigmenting effect.

Determination of the kind of organic matter is a difficult task but the total amount may be determined adequately, though not precisely, by differential thermal analysis. X-ray diffraction techniques can determine the presence of organic molecules adsorbed in between the silicate layers. More sophisticated procedures applying infra-red adsorption and diffraction procedures may provide more information on the kind of organic molecules, the way in which they are tied to the clay-mineral surfaces as well as the manner in which they are oriented on these surfaces.

Some clay materials contain water soluble **salts** as a consequence of weathering or salt migration (Sherwood, 1962 and 1992; Obika and Freer Hewish, 1990; Fanning, 1993). Common water soluble salts found in clay are chlorides, sulphates and carbonates of alkalies, alkaline earths, aluminium and iron. The occurrence of sulphates and their effects on lime-stabilised clay soils is dealt with in greater detail in Chapter 3.

Soil Mineralogy can be characterised accurately and rapidly by X-ray diffraction analysis. For most soils, mineralogy can be inferred by field observations. To characterise a clay material completely and to provide adequate data to understand physical properties, clay mineral analyses must be thorough and complete. The procedures must not alter the clay mineral. For example some clays such as those composed of halloysite have different physical properties, depending on whether the mineral is in the $4H_2O$ form, the $2H_2O$ form or an intermediate state (Grim, 1968). Therefore, several lines of approach are necessary e.g. diffraction, electron microscopy and chemical methods. At times, even with a combination of methods, it is difficult to obtain complete characterisation.

It is generally recognised that the small size of the particles in clay is one of the reasons for their special attributes (Grim, 1968; Brown, 1984). Early work suggested that particle size is indeed the major factor and clays can be composed of almost any minerals if they are fine enough, about 1μm as the upper limit. Research has however indicated that certain minerals i.e. the clay minerals, must be present in appreciable amounts if a material is to have the characteristics associated with clay. In addition, the shape of such particles, their adsorptive and surface properties, in addition to their small size, are also essential if a material is to have the characteristics of clay.

In the classification of clay-minerals, factors that include textural features such as particle shape, particle size distribution and orientation of the particles and the forces binding the particles together, have to be established first. In this regard, certain procedures that affect the clay-mineral determination have to be employed with caution. For example, it is generally essential to determine the exchangeable ions on the "as received" material, since any mixing with water or washing is likely to cause a significant change to the clay. The water may produce a hydration state different from that of the original material. In this regard, it is recommended that air-drying, and not oven-drying is adopted. The latter is more likely to change the hydration state of the original material than the former. Also in wet sieving, the use of chemical dispersing agents almost certainly will alter the base-exchange composition of the material. Such agents must be used with great caution if exchangeable ions are to be determined. Also, such chemicals are likely to introduce or form salts, further complicating the identification of the clay minerals.

The actual shape of clay particles can be determined by electron microscope studies. These may for example show the hexagonal outline of the flake-shaped units of kaolinite, or the elongated tubular shape of halloysite minerals. Information on thickness and surface area can also be obtained from electron micrographs. The lower limit for the study of the shape of the particles is by optical microscopy. The aggregation of clay particles may be obtained by diffraction techniques which provide data on the microscopic structure of the clay minerals. However, the forces that bind these particles together can merely be enumerated as their actual interplay is unknown in detail. The forces that bind the clay particles together include:-

1. forces due to the inter particle mass attraction of clay minerals,
2. electrostatic forces due to charges on the lattice resulting from :-
    (i) unbalanced substitution within the lattice,
    (ii) broken bonds on edges of the lattice, and
    (iii) attractive forces of adsorbed ions for example forces due to K^+ cations between mica layers, and
3. the bonding action of adsorbed polar molecules such as the H-O-H water molecule. Similarly adsorbed polar organic molecules could serve as a bond between clay-mineral particles.

All these bonding forces in clay materials are of particular importance since they largely determine the sensitivity and strength of soil materials. The prediction of these forces in soils during construction from empirical and laboratory testing data cannot be overemphasised as the prediction of safe applied loads when the water table is altered or when other conditions are changed is of paramount importance in avoiding construction failures. In the field, these forces are inferred mainly from one engineering parameter - soil cohesion (Grim, 1960).

2.2 STRUCTURE OF CLAY MINERALS

2.2.1 GENERAL

The earliest X-ray diffraction analyses of clay materials were done in the early 1920's (Grim, 1968). The presence of crystalline material is well revealed by X-ray diffraction methods. Although the presence of poorly crystalline material is also indicated by X-ray diffraction data, the presence of fully amorphous material is usually hard to establish. Its presence is usually inferred when the analytical data do not indicate the crystalline constituents to be present in sufficient quantities to add up to 100%.

It has been established that two structural units are involved in the atomic lattices of most of the clay minerals viz.: the tetrahedral unit and the octahedral unit. In the tetrahedral unit (Figure 2.2-1 (a)), a silicon atom is equidistant from four oxygens. There is evidence that the silicon atoms may be substituted by aluminium to form tetrahedral alumina (Wang et al, 1996; Barr, 1995). Silica tetrahedral groups are normally arranged to form a hexagonal network (Brown, 1984), which is repeated indefinitely to form a sheet of composition $Si_4O_6(OH)_4$ (See Figure 2.2-1 (b)). The tetrahedra are arranged so that their apices all point in the same direction, and their bases are in the same plane. The O - O distance in the tetrahedral unit is 2.55Å and thickness of the undistorted unit is 4.65Å. The undistorted thickness of the units is theoretical as substantial distortion of the units in clay mineral structures must occur for them to be compatible with the calculated unit cells of the minerals. In the non-crystalline allophane group of minerals, the silica tetrahedra are continuous in only one direction, forming chains in which some oxygen atoms such as the oxygen atoms at the edges in Figure 2.2-3 have only one link to a silicon atom. The chains, are bound together in pairs by atoms of aluminium and/or magnesium.

The octahedral unit consists of two sheets of closely packed hydroxyls in which aluminium, iron or magnesium atoms are embedded in octahedral co-ordination, so that they are equidistant from six hydroxyls (Figure 2.2-1 (a) and (b)). Other cations such as Li, Ca, Mn, Ni, Cu and Zn occupy these octahedral sites in some species (Brown, 1984). When aluminium is present, only two thirds of the possible positions are filled to provide charge balance. This is the basis of the gibbsite structure of unit formula $Al_2(OH)_6$. The partially filled octahedra are referred to as a dioctahedra. When magnesium is present, all the possible positions are filled in order to provide charge balance. In this case the arrangement is as in the brucite structure which has the unit formula $Mg_3(OH)_6$, forming a trioctahedral layer. In the octahedral layer, the normal O - O distance is 2.60Å unlike that of 2.55Å in the tetrahedral unit. The OH - OH bond length is 3Å, with the undistorted unit height being 5.05Å, which is 0.40Å higher than in the tetrahedral unit. Structures commonly exist, in which the layers are not electrically neutral. Charge balance is maintained in such structures by interlayer material which may be individual cations, hydrated cations or hydroxyl groups. When the layer charge is small (as in Montmorillonite), the attractive forces between the layers and the interlayer cation (if any is present) are small (Brown, 1984). The hydration energy of the interlayer cation may then be sufficient to overcome the attractive forces of the layer to cations and hence allow water to hydrate the interlayer cations which causes swelling normal to the plane of the layers. This ability to swell in water allows cation exchange between interlayer cations and cations in the external solution.

Crystalline clay comprises layers of silica tetrahedra and alumina octahedra. The layering is such that a single tetrahedral sheet and a single alumina octahedral sheet combine in a unit such that the apices of the silica tetrahedra and one of the layers of the octahedral sheet form a common layer (See Figure 2.2-2). In the junction plane common to both octahedral and tetrahedral groups, two thirds of the atoms are shared by both silicon and aluminium atoms. These shared atoms are the oxygens and not the hydroxyls. The tetrahedra therefore retain all of their oxygen atoms (Si-O tetrahedrons) while the octahedra lose some of their hydrogens to satisfy the bonding requirements. The octahedra therefore have both oxygen and hydroxyl ions (Al-O (OH) octahedra), with the hydroxyl ions lying in projection at the centre of the hexagonal ring of tetrahedra (Barr, 1995; Grim, 1968). Also, the ionicity of the oxide bonds (Si - O and Al - O) depend on their strength which in turn depends on the ions' binding energy. The higher the energy required to bind together the atoms the less the chance of their staying bound together hence the higher the ionicity of the two atoms or group of atoms involved. Barr et al (1995) in their X-ray photoelectron spectroscopy studies of kaolinite observed that the binding energies (hence strength) of the Si - O and Al - O bonds depended on the Si/Al ratio. Also, the ratio of aluminium atoms in the tetrahedral layer to those in the octahedral layer (Al_{tet}/Al_{oct}) had a similar effects on bond strength. Al_{tet} occurs when aluminium substitutes for silicon in the tetrahedral unit. Barr further observed that the increase in aluminium content in various forms of kaolinite (lowering Si/Al ratio,) made the Al - O bond much more ionic, suggesting increased binding energy of Al in the Al - O bond. At the same time, the Si binding energy increased, making the Si - O more covalent (less ionic), reducing the population of Si - O bonds.

There are two-layer (or 1:1) clay types such as the kaolinite and halloysite groups where one layer of silica tetrahedra and one layer of alumina octahedra combine to form a repeat unit (Grim, 1968). There are also three-layer (2:1) types such as the montmorillonite and illite groups composed of two layers of silica tetrahedra with a central octahedral alumina layer. Each of these clay layered types may be equidimensional e.g. kaolinites and some groups of montmorillonite, or elongate as in halloysites and some other types of montmorillonite. All types of montmorillonite possess expandable lattices while illites and kaolinites have non expandable ones.

In addition to the 1:1 and 2:1 layer types, there are other layer arrangements such as in interstratified minerals. Here, structural units of different kinds occur in the stacking sequence either as a result of sorbing of organic or inorganic material between the layers or stacking of layers with different internal arrangements. There may be regular mixed layer types in which ordered stacking of alternate layers or groups of layers of different types takes place, or the stacking may be a chain-structure type where chains of silica tetrahedra are linked together by octahedral groups of oxygen and hydroxyls containing aluminium and/or magnesium atoms. The regular interstratification may be random further complicating the classification and nomenclature of these clay minerals. Their description is based on the identity and abundance of the component layers. There are no specific names and their names can only be designated from or as mixtures of the layers involved.

If the Si-O hexagonal network is referred to a rectangular cell with sides a and b (rectangle ABCD in Figure 2.2-3 (a)), measurements done by various researchers give a b-dimension ranging from 8.95Å for kaolinite to 9.2 - 9.3Å for micas and chlorites (Grim, 1968). An increase in b-dimension may arise from substitution of aluminium for silicon as in micas while a decrease may be due to deformation of the Si-O network or of the individual tetrahedra or both of these. Usually this deformation ends up with larger tetrahedral layers. Also, the dimensions of the octahedral sheets can change. One cause for such change is cation repulsion (Brown, 1984). Unoccupied octahedral structures are larger while those containing cations are smaller. To accommodate this deformation of the layer-silicate structures, alternate tetrahedra in the normally hexagonal network are rotated laterally to varying degrees (up to a maximum 30°, (Grim, 1968; Brown, 1984)) in order to allow a proper fit between the laterally larger tetrahedral layer onto the laterally smaller octahedral one. Further adjustments of the tetrahedral sheet can be made by tilting of tetrahedra. By means of these distortions from ideal geometry, tetrahedral and octahedral sheets of a wide range of compositions can link together and form 1:1 and 2:1 layers.

2.2.2 KAOLINITE

Kaolinite minerals refer to a group of clay minerals that characterise most kaolins. Kaolins are essentially clay material with the composition $2SiO_2.Al_2O_3.2H_2O$ or ($Al_2Si_2O_5(OH)_4$), (Si:Al = 1). Other oxides if present represent impurities or adsorbed materials. Replacement of Si by Al is not feasible. In comparison, montmorillonite which has a 2:1 arrangement is higher in silicon with slight replacement of Al^{3+} by Mg^{2+} and very limited Si^{4+} replacement by Al^{3+}. It has the composition $4SiO_2.Al_2O_3.H_2O$ (Si:Al = 2), with magnesium present in relatively small amounts but in many cases apparently as an essential ingredient. Non-clay minerals (allophanes) have lower Si:Al ratios (0.82 - 1.55) and contain extremely low amounts of alkalies and alkaline earths (below 0.05%).

Early work on kaolinite and halloysite was pioneered by Ross and Kerr in the late 1920's (Grim, 1968). This work did much to establish fundamental data on the properties of these clay minerals essential to their determination in clay materials. Later contributions from researchers mainly from the USA, Britain, France, Germany, and the Netherlands and to a lesser extent from Australia, Italy, India and Spain among other countries provided the basic ideas enabling further elaboration of the structure and detailed study of these clay minerals such as the nature of adsorption of organic ions on the clay minerals.

According to Grim (1968), the structure of kaolinite was first suggested by Pauling in 1930. Grim further reports that Guner, in 1932, worked out the structure in detail while Brindley and colleagues further revised the proposed structure during the period 1946 - 1951. They studied the kaolinite minerals in detail and showed the possible variations in their degree of crystallinity from disordered kaolinite, poorly crystalline kaolinite to well-crystallised kaolinite. It has now been widely established that there is considerable variation in the stacking of layers in kaolinite as well as the precise position and population of the aluminium atoms in the octahedral layer. Only two thirds of the possible positions for aluminium in the octahedral sheet are filled. The charges within the structural unit are however balanced. This big variation in stacking and location of atoms explains, perhaps, why it is possible to reconstitute kaolinite from dissolution products in kaolinite-hydrated lime systems as observed by Sloane (1965).

Work by many researchers has shown that the variation in crystallinity is caused by departure in the arrangement of atoms in the unit layers of kaolin minerals from the discussed ideal geometrical arrangement shown in Figures 2.2-1 and 2.2-2 (Grim, 1968). Ideally, the layers should be stacked with respect to one another so that the O - OH distances between adjacent layers are equal or at least approximately equal. However, this is not the case in practice. The departure takes the form of distortions in both the tetrahedral and octahedral layers. In the tetrahedral layers, the distortions are mainly of a rotational nature. The Si-O tetrahedra are alternately rotated in clockwise and anticlockwise directions as shown by curved arrows in Figure 2.2-3 (a). In the octahedral layer, the distortions are caused by a shortening of the shared edges of the Al-O (OH) octahedra (line AB in Figure 2.2-2). As a result, the octahedra are as a whole flattened, displacing the aluminium atoms towards the lower OH bases and the silicon atoms towards the upper O bases of the tetrahedra. The atoms at the bases of the polyhedra are also displaced out of their original planes by as much as 0.17Å forming a corrugated structure. Successive layers are grouped such that the oxygens of one layer pair with OH from the other. Due to the corrugations, the O - OH bond lengths of adjacent layers vary, with a mean of 2.93Å. If an oxygen atom belongs to a water molecule, it can adopt a reasonably good tetrahedral environment by forming hydrogen bonds to other oxygen atoms in the inter-layer and to hydroxyl groups (Taylor, 1973) (see Δ CDE in Figure 2.2-2).

There are finer details to the position of all the atoms involved in the kaolinite structure whose discussion here would be beyond the scope of the current work. Those discussed here are merely intended to give a fair description of the kaolinite clay mineral structure and a view of the complexity and diversity in possible structural interpretation of clay-mineral crystal lattice diffraction data. However, the electron diffraction and X-ray diffraction analyses are in agreement on the resultant kaolinite clay-mineral unit-cell parameters as a = 5.13Å, b = 8.89Å, and c = 7.25Å.

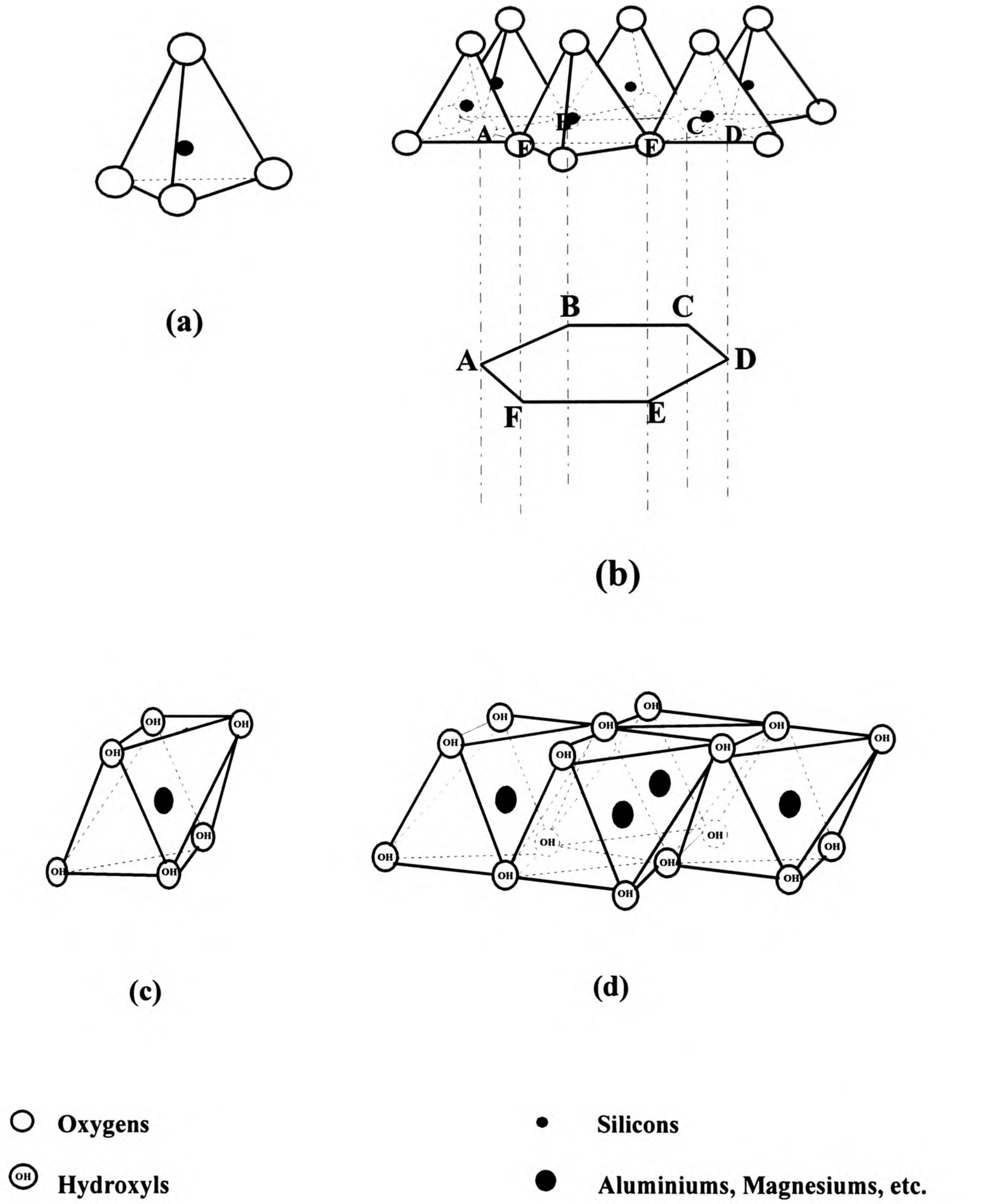


Figure 2.2-1 - Diagramatic sketch showing (a) a single silica tetrahedron (b) the sheet structure of silica tetrahedrons arranged in a hexagonal network (c) single octahedral unit and (d) the sheet structure of the octahedral units (Grim, 1968).

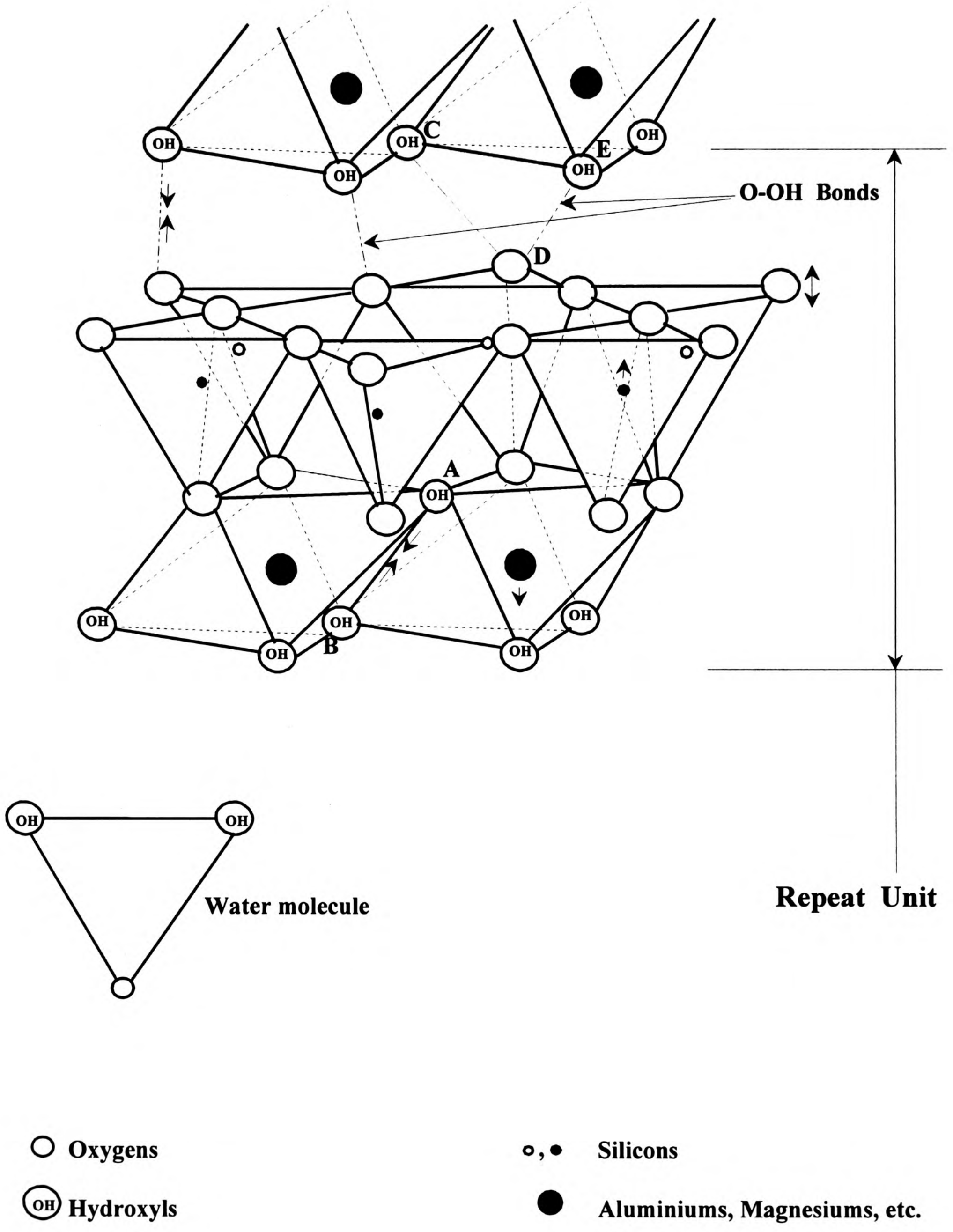


Figure 2.2-2 - Diagramatic sketch of the structure of the kaolinite layer (Grim, 1968).

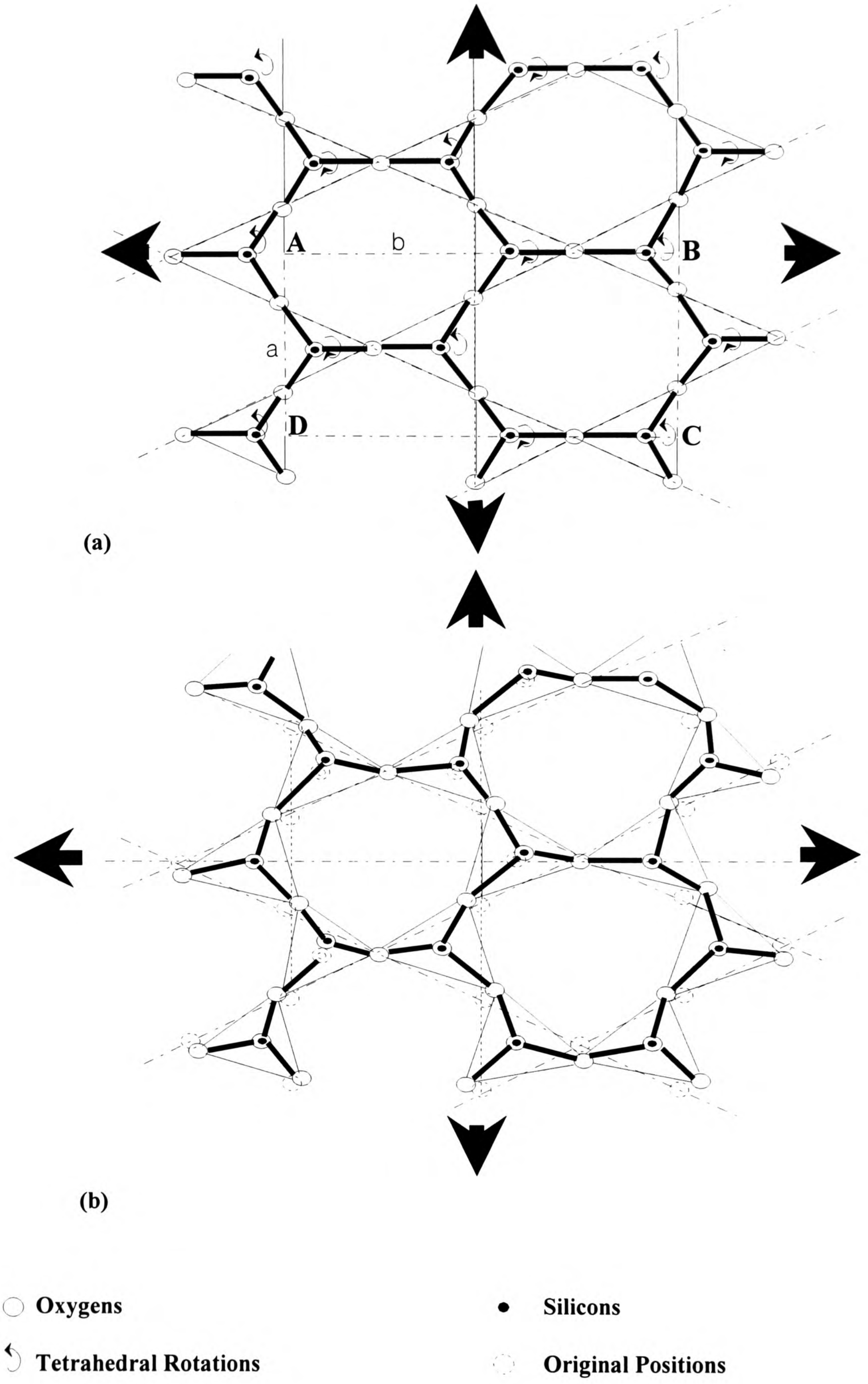


Figure 2.2-3 - Tetrahedral configuration in kaolin minerals (Grim, 1968).

2.3 CHARACTERISTICS OF CLAY MINERALS

The characteristics of clay minerals are to a great extent determined by their crystal structure. Due to their crystallinity, methods using X-ray diffraction (XRD) and X-ray photo electron spectroscopy (XPS) procedures can be used to give crystal lattice data and hence an indication of the clay-mineral crystallinity. This is because the spectral changes in peaks and other shapes relate to changes in chemistry and structural integrity of the clay minerals (Barr et al, 1995). This helps to establish details such as the nature of bonding between atoms or group of atoms. The clay-mineral characteristics may be inferred from this and other known data.

Use of X-rays in the identification of clay minerals started in the early 1930's by Pauling, Ross and Kerr et al (Grim, 1968). and the procedures are discussed in greater detail in Chapter 6. X-ray diffraction methods rely on the principle that each crystalline substance has its own characteristic atomic structure which diffracts X-rays in a characteristic pattern. Recognition of this pattern establishes the diffracting substance. Other modern methods such as Scanning (or atomic) Force Microscopy (SFM) are now available, giving more mineral surface information such as crystal growth processes (Hall and Cullen, 1996).

The shape and size of the crystal particles exposed to X-rays influence the diffraction effects. Thus, if the crystal particles have a distinct shape e.g., plate-like, rod-like or tubular, certain reflections may be broader than others. However, the diffraction characteristics of many of the clay minerals have considerable similarity so that identification based solely on diffraction data cannot always be made unequivocally. The diffraction and hence clay-mineral characteristics mainly depend on:

- layering of the tetrahedral and octahedral units
- types of interlayer cation (if any)
- substitution within the crystal lattice.

The size and shape of crystal particles, consistency limits and to a lesser degree the compaction, strength and other bulk material properties will depend on the expandability of the crystal lattice. This expandability which depends on the degree of crystallinity also determines the swelling behaviour of the clay mineral. For example, the amount of water adsorbed by clays decreases in the order Na-montmorillonite, Ca-montmorillonite, poorly ordered illite, poorly ordered kaolinite, well ordered kaolinite and well ordered illite (Grim, 1960).

2.4 SWELLING PROPERTIES OF CLAY MINERALS

2.4.1 INTRODUCTION

The expanding lattice is an attribute generally considered to be a characteristic of the montmorillonite group of clays. Some forms of micas (illites) also have considerable expansion while kaolinite shows relatively insignificant lattice expansion. Poorly crystalline minerals if present in the kaolinite may occasionally harbour interlayer water between the well-crystallised kaolinite units. This water may be indicated by changing d-spacings and may be confirmed by dehydration data.

Swelling potential refers to both the percent swell and the swelling pressure (Sridharan et al, 1986). Jenning, in 1963 (as reported Agarwal and Sharma, 1973), identified swelling pressure in various categories depending on the loading conditions, viz:-

(i) that pressure which must be applied to the soil, such that neither swell nor compression takes place when the *loaded* soil is inundated,

(ii) that pressure necessary to hold the soil at its original volume when the soil is inundated in its original *unloaded* condition, or in the case of actual field condition, a loading equal to the total overburden pressure would seem reasonable.

(iii) that pressure necessary to recompress the soil back to its original *unloaded* volume when the soil has been inundated and allowed to swell freely.

In (i) above, initial loading affects the swelling pressure generated upon soaking. According to Grim (1968), Mielenz and King (1955) found out that changing the initial loading of a clay from 5,000 psi to 3,000psi reduced the swelling pressure. This suggested that high loading would lead to higher swelling pressures. It would therefore seem reasonable to adopt a loading equal to the existing overburden pressure, if known. In view of this, method (ii) would be reasonable for those soils whose overburden is inappropriate such as laboratory model soils or surface soils while method (iii) would be applicable in all cases where swelling has already taken place. Research has shown that the swelling pressure is greatly reduced if clays are permitted to swell a little, which indicates that the initial adsorption of water produces the very high swelling pressure (Agarwal et al, 1973; Grim, 1960).

Many researchers have also attempted to define swell potential of a given expansive clay using variables such as initial moisture content and dry density (and/or void ratio), suction and external load (Mitchell, 1973; Brackley, 1973). In recent years, research has progressed in swelling pressure measurement methods adopting Jenning's definition (Agarwal and Sharma, 1973) and incorporating these variables. The current research is one example of such progress.

2.4.2 SWELLING TYPES

Swelling of clays may be classified in two major categories (Mitchell, 1973; Barshad, 1955).

- First, there is **intramicellar** swelling. This is also referred to as **intracrystalline, interlayer**, or **interlameller** swelling and involves the expansion of the crystal lattice itself. This is perhaps due to weak interlayer bonding and is characteristic of montmorillonitic clays, vermicilites, smectites, some chlorites, halloysite and hydrous micas (Mitchell, 1973). The presence and type of cations in the layers does, however, affect the degree of crystal swelling as discussed under swell mechanism below.
- Secondly, when strong interlayer bonding exists, expansion of the crystal lattice does not easily take place and **intermicellar** or **intercrystalline** swelling takes place. This type of swelling involves increase in bulk volume due to adsorption of water molecules between individual clay particles. This type of swelling can be measured by the measurement of total increase in volume. In contrast, intramicellar type of swelling can only be measured using diffraction methods (e.g. X-ray diffraction) (Barshard, 1955). Most probably, these two modes of swelling occur together, the degree of each mode being determined by the clay structure, moisture content, cation charge, pore solution chemistry and soil pore suction.

2.4.3 SWELL MECHANISM

In the study of expansive soils, much emphasis has been on identification of such soils, prediction of their swell and swell pressure magnitudes, and how in practice to make use of these soils. The causes and mechanisms of swelling mentioned above, which involve a deeper understanding of clay mineralogy, soil science and colloid chemistry have tended to take a secondary role (Mitchell, 1973). In the late 1950's and early 1960's, numerous researchers made attempts to gain insights in the swelling mechanism and causes especially through the electrical double layer theory, clay mineral type, particle size and pore solution chemistry (Lambe et al., 1960; Warketin and Schofield, 1962; Mitchell, 1973 and others). Since that time, attention in this area has steadily increased. During this period, other influential factors in the swelling of clays have slowly emerged such as the b-dimension and the hydroxyl interlayers (Mitchell, 1973; Barbour and Fredlund, 1989). The b-dimension has emerged to be of special significance, especially in montmorillonite as it correlates well with free swell magnitudes, the free swell decreasing with increasing b-dimension (Barshard, 1955). This is not, perhaps, suprising as the b-dimension is a characteristic of the clay mineral structure which plays a major role in swelling as already mentioned.

Mechanical effects such as particle arrangement have also been found to be important in soil swelling behaviour. According to Mitchell (1973), the importance of these effects was highlighted by Terzaghi (1931) when he presented convincing evidence that mechanical factors must be considered if swelling of soils is to be properly understood. Terzaghi had observed that two samples of the same clay could be at the same pore fluid concentration, yet one exerting a large swelling pressure and the other almost none. Swelling can therefore be seen as a phenomenon, involving both the solid and liquid phases. It is induced by negative pore pressures created by the strong surface tension forces on the pore water meniscus and/or by osmotic effects. In both cases, it results in water being pulled into the air voids.

Water adsorption in clays starts with the hydration of the external clay particle surface by a unimolecular layer of water (Barshad, 1955). This layer builds up with time to multimolecular water layers at a rate dependent on the type of clay. In some way, these multilayers of water eventually find their way into the interior surfaces of the clay particles. Possible modes of transfer of these unimolecular water layers include diffusion of water vapour through the clay particle and/or seepage at the clay particle edges (Barshard, 1955). At this stage the interlayer cations though hydrated, are still in position on the interior clay particle surfaces, attached to the oxygen sheets. As more molecular water layers find their way into the interlayer spaces, and with subsequent expansion of the interlayer distance, the cations get detached creating an external surface. If the water is in vapour form, as during curing, the expansion is minimal, depending on the vapour pressure or humidity. If in liquid form further expansion occurs. The ultimate expansion is dependent on the amount of water and the type of interlayer cation. The increase in swelling has been established to be in the interlayer cation sequence Hydrogen-Magnesium-Calcium-Potassium-Lithium-Sodium, with intramicellar swelling for several montmorillonites being limited to about 10Å (Barshard, 1955) i.e. from a basal spacing of about 10Å when dry to about 20Å when saturated, after which the layers tend to separate. Swelling results from an increase in the basal spacing (c-spacing) as water is adsorbed between the layers. The propensity to swell is indicated by the b-dimension which itself increases from about 8.94Å when dry to slightly above 9Å maximum. The greater the b-dimension the smaller the swelling potential. This was confirmed by Blackmore and Miller who also established that in the presence of calcium, montmorillonite does not swell by interplate distances greater than about 9Å (close to that suggested by Barshad 1955; Mitchell, 1973 and Brown, 1984). At this interplate distance, the particles stabilise into what they referred to as "tactoids" or "domains". This suggests a swelling level at which there is no further structural adjustment possible, making the b-dimension a very good indicator of swelling potential, not withstanding other influences such as the cation type and amount. The formation of stable “tactoids” for example is only likely to occur with calcium and magnesium cations while in the case of sodium, there is complete separation of platelets (Brown, 1984). The higher positive charges in divalent cations and their effects on the electrical double layer is likely to be the cause of this difference in swell behaviour. In order to understand the swelling mechanism further, it is important to have a brief look at the major factors. These include the clay type and particle size, the clay’s moisture content, pore solution chemistry, cation charge and the soil suction conditions.

2.4.3.1 Clay type and particle size

The decrease in swelling has been established to be in the sequence sodium-lithium-potassium-calcium-magnesium-hydrogen for the inter-layer cations (Bell, 1987). The extent of the clay water adsorbing surface is very much a function of the particle size, particle pore size and the void ratio (and hence density). These factors subsequently affect swelling and swelling pressure generation. For example, montmorillonitic clays have external adsorption surfaces, of the order of 22 - 90 m^2/g depending on the method of measurement. This is higher than for kaolinitic clays, 18 - 44 m^2/g (Barshard, 1955). This, partly explains montmorillonite’s relatively massive swelling per unit mass as shown in Table 2.4-1 below.

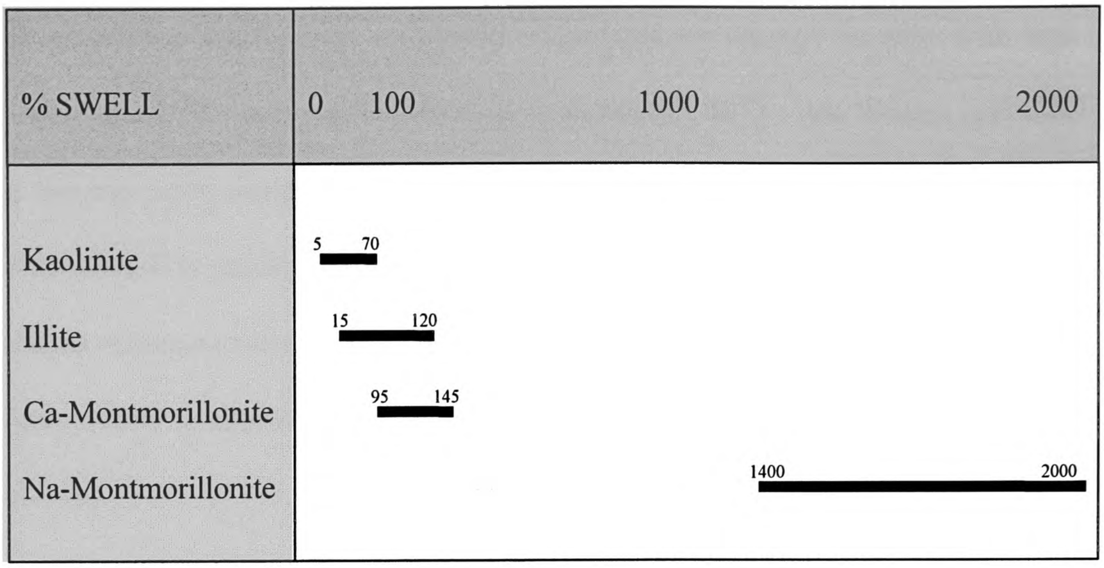


Table 2.4-1 - Typical free swell figures of common clays. (J. Krahn & D.G Fredlund, 1972)

The type of ions on the layer surface is another factor. In montmorillonites, the surface ions are predominantly oxygens while in kaolinites hydroxyl ions are more prevalent. The presence of even small amounts of hydroxyl interlayers in expansive clay minerals is known to reduce swelling significantly by their effects of reducing cation exchange capacity sometimes to as low as zero (Mitchell, 1973). The hydroxyl interlayers strongly bind adjacent clay layers together. This, further explains kaolinite's overall lower swelling as compared to montmorillonites. However, compared to montmorillonites, kaolinite has a larger cation charge per unit area leading to larger water adsorpability per unit surface area (Barshard, 1955). The coarse fraction of clays (0.2µm - 2.0µm) has been found to give swelling pressures less than predicted by the double layer theory as compared to the fine fraction (< 0.2µm), which gives values close to the theoretical one at the same charge densities. Hence, swell is easier to predict for the smaller fraction (Mitchell, 1973).

2.4.3.2 Moisture Content

It has been established that for clays compacted to the same dry density, the clays with high moisture contents exhibit lower swelling pressure (Ben Shalom, 1973). Ben Shalom attributes this to the fact that a clay sample having a higher moisture content would have a greater clay particle separation. It is possible to demonstrate (Wild et al, 1993) that expansion is directly proportional to moisture content of a clay soil. If d is the thickness of the water layer on the clay particle surface as shown in Figure 2.4-1 (a), the inter particle spacing will be 2d as in Figure 2.4-1 (b).

Volume of water on particle = Particle Surface Area × d

= (Specific Surface of clay (m^2/kg) × Wt. of clay particle (kg)) × d

Therefore, the distance d is equal to :–

$$\frac{\text{Volume of water}\left(m^3\right)}{\text{Specific surface of clay}\left(m^2/kg\right)\times \text{Wt. of clay solids}\left(kg\right)}$$

$$\text{i.e}\quad d=\frac{V_w}{m_sS}\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Where V_m = Volume of water (in m^3)

m_s = Mass of clay (in kg)

S = Specific surface of clay $(in\, m^2 / kg)$

If m_w = Mass of water and (in kg)

ρ_w = Density of water (in kg / m^3)

$$\text{Then} \quad V_w = \frac{m_w}{\rho_w}$$

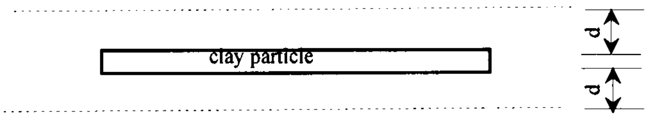
$$\text{and} \quad d = \frac{\mathbf{m_w}}{\rho_w \mathbf{m_s S}} \quad \text{..} \mathbf{(2)}$$

By definition, moisture content (M_c) *of a soil* $= \dfrac{m_w}{m_s} \times 100$

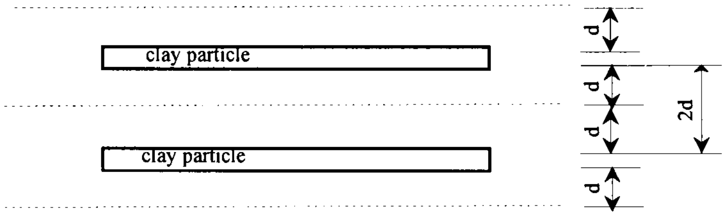
Therefore, the thickness of the water layer d around each particle is given by:

$$\mathbf{d} = \frac{\mathbf{M_c}}{\mathbf{100}\rho_w\mathbf{S}} \quad \text{...} \mathbf{(3)}$$

Since the density of water ρ_w and the specific surface of a given soil S are constants, it follows that d, the thickness of the water layer around each particle increases directly with increase in moisture content. In other words linear expansion should be directly proportional to moisture content.



(a)



(b)

Figure 2.4-1 (a) Clay particle and moisture content
(b) Clay particle and inter-particle spacing

2.4.3.3 Pore Solution Chemistry

It has been established that swelling may be caused by three water related factors viz: surface hydration or wetting, cation hydration and/or by osmotic pressure effects (Mitchell, 1973). The first two require very little water, far below typical optimum and/or natural water contents. Therefore, osmotic pressure effects are the main causes of swelling (Barbour and Fredlund, 1989; Wild *et al*, 1993).

Van't Hoff suggested an equation for osmotic swelling pressure viz:-

$$\mathbf{P_s = RTC} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 4$$

Where:

P_s is the swelling pressure

R is the gas constant

T is the absolute temperature (°K)

C is the molar concentration of the pore solution (mol/l)

The osmotic pressure changes induce volume changes depending on the pore fluid chemistry. This is as a result of water flowing in or out of the clay due to the osmotic gradients induced. Also, the pore solution cations reduce the electrostatic repulsive forces between clay particles, leading to suppression of the electric double layer. This suppression favours formation of floccs with subsequent changes in void ratio. Therefore, volume changes may be as a result of either :-

(i) change in the electrostatic repulsive forces between clay particles

or (ii) water flow in/out of the clay (Barbour, 1989).

2.4.3.4 Cation Charge

It has been established that the expansive properties of clay of high cation exchange capacity can be radically changed by the chemical nature of seepage water (Grim, 1960). The introduction of positive cations, by iso-structural substitution, reduces the effective negative charges on the clay particle surfaces, reducing as well the inter-particle repulsive forces. Increased substitution is associated with reduced charge deficiency and decrease in swell due to reduced repulsion. However, swelling is not directly proportional to resultant lattice charge deficiency although the influence of the type and amount of cations present in the system cannot altogether be neglected. For example, it has been established that expansion is particularly high for charge deficiencies of about one per unit cell (Mitchell, 1973; Barshard, 1955). According to Mitchell, Foster (1953 and 1955), showed that swelling does not relate in a consistent manner to cation exchange capacity of a clay soil but depended on the mode of substitution. Mitchell (1973) further reports that later, Low (1968 - 70), in his study of swelling and mineralogical details of various montmorillonites, found that there was more swell associated with octahedral substitution than with tetrahedral substitution (Mitchell, 1973). A thinner double layer was formed as a result of tetrahedral substitution, implying less swelling.

Theories used to predict swell in the past have been derived using homoionic cationic systems. Homoionic cationic systems contain mainly one type of cation such as a homoionic sodium clay or homoionic calcium clay. Most expansive soils however usually contain mixtures of calcium, magnesium, sodium and to a lesser extent potassium. Therefore homoionic theories may not necessarily be suitable for the case of mixed ionic systems.

2.4.3.5 Soil Suction

Suction may be defined as the negative pore pressure that draws water into the soil voids. Total suction is made up of the matric and the osmotic suction. In normal swelling of clay soils in general, the main cause of changes in total suction is matric suction (Krahn & Fredlund, 1972). Both total and matric suctions are dependent mainly on the moisture content, and to a lesser degree on the dry density. The situation is however different in the presence of salts such as sulphates, when osmotic suction can no longer be ignored and becomes a major influence in total suction.

Matric suction is caused by hydrostatic tension of the pore fluid which in turn depends on the fluid's surface tension. This tension is the main cause of capillary water rise. This mode of suction depends on dry density and water content. Thus, keeping the dry density and moisture content constant would minimise the variation in matric suction although the changes in dry density are of secondary effects on suction (Krahn & Fredlund, 1972). According to Krahn & Fredlund, there are conflicting observations on the effect of dry density on matric suction, the majority of researchers being of the opinion that density does affect matric suction. They also reported that Croney et al (1958) observed that suction is affected by dry density for incompressible material such as sand and chalk while on the other hand, Box and Taylor (1961) (also reported by Krahn & Fredlund) observed only a small matric suction decrease with increase in density at constant moisture content and at low suction ranges. Similarly, study on the effects of changing dry density and methods of compaction of various soil types observed little variation in matric suction on change in dry density (Krahn & Fredlund, 1972). Matric suction may be determined by measurement of the vapour pressure in equilibrium with soil water. This vapour pressure depends on dissolved salts in the pore fluid. Osmotic suction on the other hand is caused by salt concentration gradients which induce negative osmotic pressure. It may be determined and/or predicted by electrical conductivity measurements of the pore fluid. Most researchers agree that the soil suction due to osmotic pressure is mainly dependent on pore fluid concentration.

This chapter has reviewed the mineralogy, structure, characteristics and properties of clay minerals. The next chapter will look at changes in these properties and the nature of the reactions involved when clay soils are stabilised, particularly with lime. The chapter further reviews the occurrence of sulphates, their effects, particularly on consistency, strength and swelling of lime-stabilised clay soils, and on the ensuing hydration products.

CHAPTER 3 - SOIL STABILISATION

3.1 INTRODUCTION

Many of the important engineering properties of clay soils including plasticity, strength and volume stability are enhanced by the addition of lime (Grim, 1968; Ingles and Metcalf, 1972; Bell, 1988(A and B); Arabi and Wild, 1989 and others). The properties of such lime-soil mixtures vary and depend on the character of the clay soil, the mode and length of curing and the method and quality of construction. The latter determine the amount of lime used in the stabilisation process. When added to a clay soil, lime chemically attacks the clay mineral fraction. All clay minerals are attacked, although those possessing the highest silica normally react more strongly. In addition to the amount and type of the clay mineral present, other factors influence the effectiveness of stabilisation of clay by the addition of lime. These include the organic matter type and content, sulphate levels, moisture content at compaction and density of the soil. Organic matter can retard or inhibit hydration because it preferentially adsorbs calcium ions. The sulphate content affects the volume stability while the moisture content and density determine the long term strength development (Sherwood, 1962; Bell, 1988 (A and B) among others).

Typical total lime contents required for combined modification and stabilisation of soil are in the range 1 - 8 wt.% $Ca(OH)_2$ (Bell, 1988). The optimum lime content for kaolinite according to Sivapullaiah (1987) was found to be 6 wt.%. This was confirmed in the current work.

3.1.1 LIME

Lime as used for stabilisation may be in many forms such as quicklime (CaO), slaked or hydrated lime ($Ca(OH)_2$) and dolomitic lime. Quicklime seems to be a more effective stabiliser of soil than hydrated lime. When quicklime in a slurry form (which then becomes hydrated lime) is added to the soil, higher strength is developed than when it is added in powder form. The solubility of lime in water decreases with increase in temperature. A change in temperature from 20°C to 80°C decreases the solubility by a factor of two. Generally, between 1 - 3% of hydrated lime is required to modify soil while 2 - 8% is required for cementation to take place (Bell, 1988A). As a rule of thumb, Bell suggested that approximately 1% of lime is required for stabilisation for each 10% clay (< 2μm). The exact amount required would be determined by tests done on each side of this value of required lime content. In the current work the term lime will be used to signify hydrated lime ($Ca(OH)_2$).

When exposed to carbon dioxide, lime undergoes carbonation. Carbonation leads to a decrease in the availability of Ca^{2+} ions due to the formation, at early stages, of an amorphous phase with the formula $Ca_{1+x}C_3.O(OH)_{2x}.yH_2O$ ($x>0.005$, $y=0.6-0.8$) (Matsushita *et al.*, 1993). The amorphous phase is followed by crystallisation into calcite. Matsushita observed the changes of surface decomposition of carbonation intermediates by means of photoelectron spectroscopy (XPS) measurements, a method which has rarely been applied to the study of carbonation so far. This method involves determination of $Ca:CO_3$ ratios and any other structural changes such as state of the chemical bonding of

Ca. Molar ratios of CO_3^{2-} to Ca^{2+} of intermediates in a $Ca(OH)_2$ slurry indicated that the rate of carbonation in the vicinity of the surface was comparable to that in the bulk.

3.1.2 STABILISATION AND MATERIAL SUITABILITY

Lime is suitable for stabilisation for clays with at least 15% fines content (Rogers, 1988) and of plasticity index (PI) in the range 10 -15%. Soils with plasticity limits below 10% require a pozzolan for necessary reactions to take place while those with higher plasticities are hard to mix. Fly-Ash is commonly used as a pozzolan. Other pozzolans include blast-furnace slag and expanded shale. Clays with highest available silica, especially 3-layered ones which expose silica layers on both sides, are more reactive than 2-layered ones. Most clay soils in which kaolinite is absent or is a minor clay mineral respond more rapidly to lime treatment than do those in which kaolinite is the dominant clay mineral.

Soil containing significant levels of organic matter fails to respond to treatment with either lime or cement (Sherwood, 1962; Rogers, 1988). Organic matter interferes with the normal reactions between lime and the soil by decreasing the soils pH value. According to Sherwood (1962), retardation in cement stabilisation may be caused by organic compounds that combine with the lime liberated as the cement hydrates and which causes the pH to fall below the value required for hydration. This mechanism would suggest that in lime stabilisation, the retardation is caused by the bulk of the lime being consumed by the deleterious organic matter. Sherwood further suggests that it is the type, rather than the total amount of organic matter which is the critical factor. A simple determination of the total organic content is therefore a poor guide to the presence of deleterious compounds.

3.1.2.1 Mechanism

According to Croft (1964), when kaolinite is treated with 2 percent lime it undergoes an increase of some 28% in liquid limit. Further additions of lime give rise to little change in the liquid limit. Taken together with the changes of plastic limit, the resultant plasticity index of kaolinite shows an overall reduction. In contrast, the value of liquid limit for most montmorillonites gradually decreases with increasing lime content. In both clay types the increase in strength on lime stabilisation is attributed to the formation of poorly ordered (non-crystalline) reaction products which surround the clay soil particles.

Croft (1964) suggested that the effects on Atterberg limits are due to the action of hydroxyl ions which modify the affinity of the surfaces of the clay particles for water. Arabi and Wild (1989) suggested that the calcium ions are responsible for the reduction in the water affinity of lime stabilised material and that the development of long term strength appears to be due to the gradual formation of amorphous or semi-amorphous hydration products. Many more researchers concur on the formation of various types of hydrated calcium silicate calcium aluminate and calcium alumino-silicate cementitious products which increase the strength and durability of soil-lime mixtures (Bell, 1988; Cobbe, 1988; Sherwood, 1992 and others).

There are certain differences between lime-stabilisation and cement-stabilisation. The addition of cement leads to higher maximum dry density (MDD) and lower optimum moisture content (OMC). The clay particles are generally unchanged, but adhesion takes place, binding the individual particles together. This cementation, particularly in the early stages, is as a result of hydration of calcium silicates and aluminates from the cement, although the lime produced by cement hydration may react with the clay at a later stage and contribute in a small part to the cementation. On the other hand, addition of lime leads to lower MDD and higher OMC. The clay particles are "attacked" by the lime, and the resulting cementation, referred to as pozzolanic activity, is as a result of gradual formation of new products (i.e. calcium aluminate and/or silicate hydrates).

3.2 CLAY-LIME REACTIONS

3.2.1 INTRODUCTION

This section discusses the reactions involved for clay-lime mixtures in the absence of other reactants while section 3.4 will discuss those that are involved in the presence of various metal sulphates. There are basically four types of reactions (both physical and chemical) of soil with lime (Hunter, 1988, Jacques *et al.,* 1990); cation exchange, flocculation and particle aggregation (agglomeration), carbonation and pozzolanic reactions. When quicklime (CaO) is used in lime stabilisation, its first reaction is an exothermic hydration to form slaked lime ($Ca(OH)_2$) as shown in equation I (Bell, 1988; Rogers, 1988; Caijun Shi, 1993).

$$\mathbf{CaO + H_2O \longrightarrow Ca(OH)_2 + Heat} \quad \text{..I}$$

The heat generated is advantageous to cementation, making quicklime preferable for lime stabilisation. Firstly, the heat raises the temperature, which is desirable for more effective cementation. Secondly, the heat dries out water, a process very much beneficial in water-logged drainage problems. Quicklime's high reactivity and powdery nature, however, is injurious to health, and safety precautions are mandatory.

The reactions which follow the slaking of quicklime are similar to those that would take place if hydrated lime was used in the first place (Equation II).

$$\mathbf{Ca(OH)_2 \longrightarrow Ca^{2+} + 2OH^- + \uparrow pH} \quad \ldots\ldots\ldots\ldots\ldots\ldots \mathbf{II}$$

The hydrated lime, in the presence of more water, raises the mix pH to approximately 12.4, the pH of lime in solution ((Snedker and Temporal, 1988). In this high pH state, alumina and silica, which dissolve at a pH of at least 10.5, go into solution. At the same time dissolution of any existing sulphate minerals takes place. The reactions that then follow are complex and will depend among other variables on the mineralogical composition of the clay, prevailing temperature and the presence of other minerals such as sulphates.

3.2.2 FLOCCULATION-DEFLOCCULATION-AGGLOMERATION

Immediately upon addition of lime to clay soil and after dissolution of alumina and silica, cation exchange takes place. Cation exchange may be triggered by any of the following:-

(i) broken Si-Al bonds, especially at clay particle edges (Sloane, 1965) and cleavages, such as those created during compaction and/or grinding.

(ii) cation substitution within the lattice structure. This depends on the unit structure. In the tetrahedral structure, Si^{4+} may be replaced by Al^{3+} while in the octahedral one Al^{3+} may be replaced by Mg^{2+}.

In both mechanisms, there is an imbalance in the electron charges of the negative ions of O^{2-} and OH^- in the layered clay resulting in negative charges being induced on the clay particle surfaces. These negative charges form the basis of migration of cations to the clay particle surfaces. The number of broken bonds mentioned in (i) above increases with decreasing particle size while the degree of replaceability varies in the order below, where the cation to the left is more likely to be replaced by the one to the right.

$\mathbf{Li^+ < Na^+ < K^+ < Mg^{2+} < Ca^{2+} < Ba^{2+} < Al^{3+} < H^+}$ (Cobbe, 1988; Arabi, 1989)

| | | | | | |

0.6 0.95 1.33 0.65 0.95 1.35 0.5 (Ionic Radii (Å))

Cation exchange leads to modifications in the thickness of the hydrous electrical double layer. Reduction of this layer leads to flocculation while its enlargement will lead to deflocculation and subsequent dispersion. Flocculation is due to the increase in the Van der Waals attractive forces as a result of the reduction in the repulsive charges upon cation adsorption due to depression of the diffuse electrical double layer as a result of an increase in electrolyte concentration. Whether cation exchange leads to flocculation or whether both cation exchange and flocculation take place simultaneously has really never been established. Small numbers of the cations with larger positive charges such as Ca^{2+} and Mg^{2+} would be required to neutralise the negative charges on the clay particle surfaces, resulting in the compression of the electric double layer and hence more flocculation. On the other hand, large numbers of cations with smaller charges such as Li^+, Na^+ or K^+ would be required to neutralise similar negative charges on the clay particle surfaces, resulting in the enlargement of the electric double layer with subsequent deflocculation and even dispersion (See Figure 3.2-1).

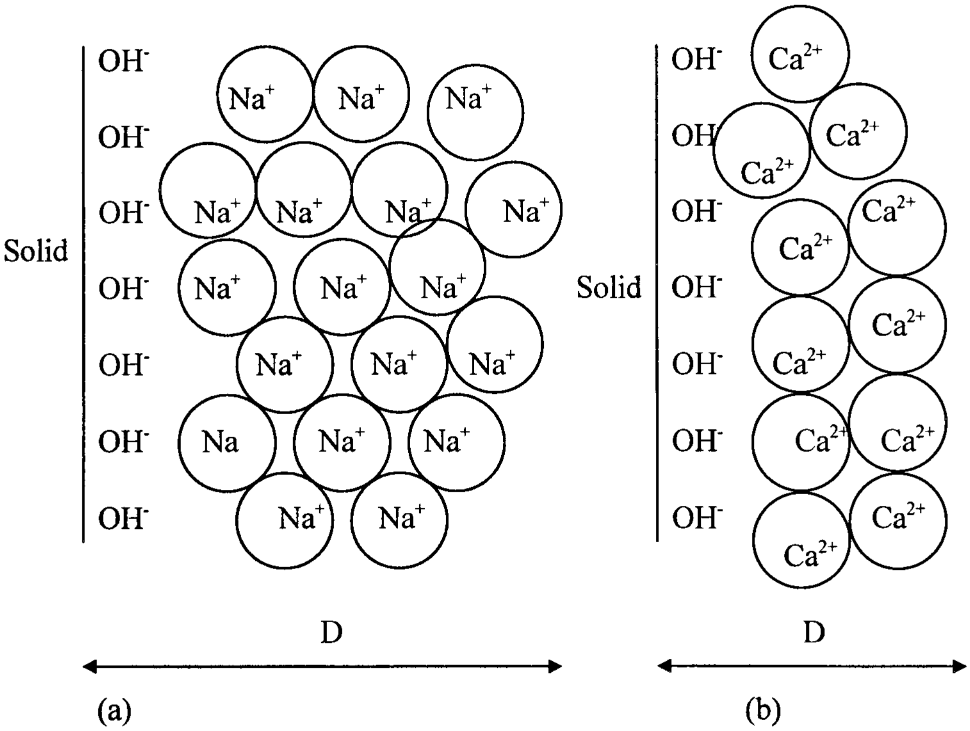


Figure 3.2-1 The diffuse double layer (D) when (a) sodium* and (b) calcium* ions are the counter-balancing cations. *(* it should be noted that the cations will be surrounded by a 'hydrosphere' of polar water molecules).*

Flocculation coarsens suspended particles and decreases the number of particles at a rate depending on solution and particle surface chemistry. This leads to closer clay layer packing within floccs. Deflocculation on the other hand keeps each individual clay particles apart from the rest, increasing the fineness of particle agglomerates and the number of individual particles. They may be balanced by adsorption of cations on the clay particle surfaces in a cation exchange process. Deflocculation may also be caused by high concentrations of cations on the clay particle surfaces by the increased repulsive positive charges they create (Arabi and Wild, 1989).

With the addition of lime, Ca^{2+} cations are introduced in the soil mix and they initiate the cation exchange. This causes modification of the electrical double layer and the characteristic flocculation process of fine clay particles. These effects, which occur quite rapidly, cause changes in consistency limits, explaining the soil's improved workability as a result of low plasticity and friable character developed in the soil (Sherwood, 1962; Ingles and Metcalf, 1972; Bell, 1988; Cobbe, 1988; Arabi and Wild, 1989). Also, with the addition of lime, more OH^- ions are introduced in the clay layers. The OH^- ions which result in a surplus negative charge attract H^+ ions and the polar water molecules will therefore be squeezed into the clay layers. The total effect of these processes is the general raising of liquid and plastic limits.

Changes in maximum dry density and optimum moisture content are determined by the nature of grouping and orientation of the individual clay particles. These particles may be in a dispersed state where the maximum dry density will be high and the liquid limit low relative to the undispersed state, or they may be in a state of flocculation and/or agglomeration where the maximum dry density will be low and the optimum moisture content high relative to the dispersed state. These states of the clay particles are very much determined by the magnitude of charges on the clay particles. Therefore any situation in which the clay particles' negative charges are reduced, as in the cases of lime and/or sulphate addition, will lead to a reduction in the maximum dry density and an increase in the optimum moisture content.

Cation exchange capacity decreases in the order kaolinite-montmorillonite-illite (Bell, 1988; Arabi and Wild, 1989). Expandable clays tend to react more readily with lime, losing plasticity immediately (Bell, 1988). Most researchers agree on the fact that flocculation and agglomeration explains the initial material property changes and bonding mechanisms in lime stabilised clay mixtures. The long term changes are caused by the slower silicate bonding (Ingles and Metcalf, 1972; Wild *et al.,* 1988 among others).

3.2.3 POZZOLANIC ACTIVITY

The cementing agent in both cement- and lime- stabilisation is the tough, water-insoluble gel of calcium silicate (Ingles and Metcalf, 1972; McCallister *et al.,* 1992). McCallister *et al.,* observed that the C-S-H gel is rather permanent in nature, impervious and hence lime-stabilised soils are not susceptible to leaching. There is however a difference in the way this gel is formed in both cases. In the case of cement, the gel is principally formed from the hydration of anhydrous calcium silicate (cement). In the case of lime, the gel is formed only after attack on and removal of silica and alumina from the clay minerals of the soil.

Thus, cement stabilisation is less dependent on the soil type while lime-stabilisation is different for each soil type.

Base (cation) exchange and chemical combination (silicate bonding or pozzolanic reaction) commence at the same time, the former being an immediate effect while the latter takes a considerable time to complete (Croft, 1964; Bell, 1988). Base exchange alone has been rejected as the explanation for the cementitious properties (Croft) and strength increases with age have been attributed to the progressive dissolution of SiO_2 and Al_2O_3. In clay soils, the main phases formed are amorphous or poorly crystalline and have been identified as calcium-silicate hydrates (C-S-H), calcium aluminate hydrates (C-A-H) and calcium alumino-silicate hydrates (C-A-S-H) (Croft, 1964, Sloane, 1965, Arabi and Wild, 1989; McCallister *et al.,* 1992). Of these hydrates, C-S-H gel is the principal cementitious product although in the case of high alumina clays such as kaolinite, small amounts of crystalline calcium-aluminate hydrate phases (such as C_3AH_6 and C_4AH_{13}) and of calcium-alumino-silicate hydrates (such as C_2ASH_8) are formed (Croft, 1964; Sloane, 1965; Arabi and Wild, 1989, Abdi, 1992).

In hydrated clay lime systems, the primary reactants will be determined by the type of clay as the lime always mainly provides $Ca(OH)_2$. In this regard, clays high in alumina will provide high amounts of Al_2O_3 in addition to silica while those high in silica will provide essentially SiO_2 to the system. Other clay properties - cation exchange capacity, type of exchange cation etc. will influence the reaction kinetics. The primary reaction products of hydration will be determined by the relative amounts of lime and clay, the prevailing temperature and reaction time (curing period). Generally, the reactants will be CaO from the added lime, Al_2O_3 and SiO_2 from the clay and H_2O from the added water. In other words, the reactants form a CaO-Al_2O_3-SiO_2 -H_2O system.

Most of the published work in systems involving CaO, Al_2O_3, SiO_2 and H_2O has been conducted under concrete research using various forms of PC (and PC blends with other materials) as sources of CaO, Al_2O_3 and SiO_2. The work includes that of Collepardi *et al.*, (1978), Bailey and Chescoe (1980) and Mehta (1983) who have worked on C_3A hydration, and De Silver and Glasser (1992), Caldarone *et al.,* (1994) and Wild and Khatib (1997) who have worked on PC - metakaolin blends. Work with lime includes that by Croft (1964) on lime - PFA and lime - PFA - clay mixes, and also Wild *et al.,* (1990) who worked on lime - PFA mixes. The work with lime-stabilised fly-ashes (Croft, 1964) show that the earliest indication of the production of new phases are the appearance of low angle humps on X-ray diffraction patterns with the first lines, indicative of new crystalline minerals, observed only after four weeks of curing. These broad diffuse reflections were considered to be due to the formation of gel-like varieties of hydrated monocalcium silicate (C-S-H).

Croft also observed that the removal of carbonaceous matter was of little importance in determining the final composition. When Croft included kaolinite into the fly ash-lime pastes, the aluminates of the hydrogarnet series C_3AH_6-$C_3AS_nH_{6-2n}$ were observed. With montmorillonite, no changes were observed although the crystallinity was slightly enhanced. Tests by Croft would seem to suggest active participation by clay minerals in the clay-fly ash-lime reactions. Croft also established that fly ashes highest in alumina were marginally more reactive and reactivity was more determined by lime content and curing temperature. He concluded that CSH, C_2ASH_8 and C_4AH_{13} tend to form at ordinary temperatures (≈25°C) while C_3AH_6 at elevated temperatures (> 55°C) or at prolonged curing. Also, high CaO/Al_2O_3 ratios favour precipitation of C_4AH_{13} while, based on work on fly ash-lime and fly ash - lime - montmorillonitic clay, he concluded that high CaO/SiO_2 favours that of CSH. In general, C-S-H appears to form readily in all systems containing SiO_2 in significant amounts. Similar observations were made by Collepardi *et al.*, (1978) and by De Silva and Glasser, (1992). Collepardi worked on C_3A - lime hydration and De Silva and Glasser with metakaolin - lime. In both cases, C_4AH_{13} is formed in mixes with high lime content.

De Silva and Glasser (1992) considered the $CaO-Al_2O_3-SiO_2-H_2O$ system by observing the reactions of metakaolin ($Al_2O_3-2SiO_2$) with lime ($Ca(OH)_2$). They report that the main hydrates considered to be important in the $CaO-Al_2O_3-H_2O$ system below 100°C are $Ca(OH)_2$, C_4AH_{13}, C_2ASH_8 and hydrogarnet (C_3AH_6). Additionally, the system contains metastable but persistent phases of C-S-H gel. Other reported hydrates at 20°C were the carbonated version of C_4AH_{13}, i.e. $C_3C\overline{C}.11H$ (especially at prolonged curing), and C_2ASH_8. C_4AH_{13} tended to disappear within 180 days (≈ 25 weeks) leaving gehlenite hydrate (C_2ASH_8) and C-S-H gel. Hydrogarnet tended to form at higher temperatures and none was formed at 20°C, confirming earlier observations by Croft. De Silva concluded that at high lime contents, C_2ASH_8 and C_4AH_{13} tended to form while at low lime contents, and above 85°C these compounds were more unstable and C-S-H increased its crystallinity. In clay - lime systems, lime-clay reactions are very slow and reaction products are of very low crystallinity. Thus although the principal phases which form in these systems have been characterised, if the clay comprises a naturally occurring clay soil it is often not possible to fully identify all the reaction products.

3.3 PROPERTY CHANGES IN LIME STABILISED CLAYS

3.3.1 INTRODUCTION

Lime-sand and cement-sand mixtures are unaffected by immersion in sulphate solutions, even for a long duration, if the cement has a low C_3A content. However, clay - lime and clay - cement mixtures disintegrate within a few days. This clearly shows that it is the clay fraction of the soil that the construction engineer should pay attention to. In most cases therefore, any discussion on material changes specifically refers to the clay portion. These material property changes include changes in the liquid limit (LL), plastic limit (PL), plasticity index (PI), optimum moisture content (OMC) and in the maximum dry density (MDD). Other changes include volume stability, the California bearing ratio (CBR), the unconfined compression strength (UCS) and where applicable changes in freeze thaw properties.

3.3.2 LIME STABILISATION AND CONSISTENCY LIMITS

The liquid limit of clay soils is generally lowered by the addition of lime. Nevertheless, the liquid limit of kaolinitic clays may remain unchanged after lime treatment or even increase (Bell, 1988; Rogers, 1988; Arabi and Wild, 1989). The fall in liquid limit is very rapid in montmorillonite while the plastic limit rapidly rises. This results in a rapid fall in the plasticity index. Illites show a similar trend but less dramatic. The rate of increase in plastic limit with lime addition increases in the order kaolinitic clays - illitic clays - montmorillonitic clays. Kaolinitic clays are rather variable, with most researchers reporting an increase in liquid limit on addition of lime (Abdi, 1992). In these clays, lime treatment sometimes increases the plasticity index. In addition, some researchers have observed a decrease in liquid limit with lime addition. Abdi, (1992) observed a decrease in both the liquid limit and plasticity index beyond 6wt.% lime ($Ca(OH)_2$) addition. Abdi reasoned that the use of clay with a very high kaolinite content (84% by weight) could be the cause of the erratic behaviour.

The changes in consistency limits are attributable to flocculation and agglomeration as a result of the cation exchange upon lime addition. According to Croft (1964), the increase in liquid limit depends on the OH^- ion concentration in the pore fluid which modifies the affinity of clay particles to water. The addition of lime results in the introduction of more OH^- ions. Water molecules, which are polarised, are therefore attracted and bound to the clay layer surfaces by the formation of hydrogen bonding (Arabi and Wild, 1989) as discussed in Chapter 2. The shrinkage characteristics of clayey soils are also improved significantly by the addition of lime, increasing the shrinkage limit and lowering the linear shrinkage (Wild *et al.*, 1986).

3.3.3 LIME STABILISATION AND COMPACTION

3.3.3.1 Dry Density and Moisture Content

The period during which the mixed components can be left prior to compaction is less sensitive for lime stabilised soils than for cement stabilised soils. Not only is any delay in compaction less critical, but also compaction moisture content is not as critical (Ingles and Metcalf, 1972; Bell, 1988; Rogers, 1988). This is because lime flattens the compaction curve such that a specified density can be achieved over a much wider range of moisture contents. Relaxed moisture control specifications are therefore possible. Indeed quality is better ensured by moisture content control than by density specification. Also, the optimum moisture content is moved towards higher values by the addition of lime, enabling soils in a wetter condition to be compacted satisfactorily.

The reduction in maximum dry density and the increase in optimum moisture content are, as outlined previously, principally attributed to flocculation and agglomeration (Rogers, 1988; Cobbe, 1988) Also, the replacement of clay with lime contributes to the reduction in maximum dry density because clay has a higher density than lime (Abdi, 1992). A similar clay replacement mechanism affecting the maximum dry density can be observed by the addition of metal sulphates. This is because these additives are either of lower density (see Table 3.3-1 below), or are more soluble in water than clay particles. The results on the reductions in MDD and any other changes due to sulphate additives are discussed in more detail in Chapter 7.

MATERIAL	RELATIVE DENSITY
Kaolinite	2.57
Kimmeridge Clay	2.75
Lime	2.30
$Na_2SO_4.10H_2O$	2.68
K_2SO_4	2.66
$CaSO_4.2H_2O$	2.32
$MgSO_4$	2.66
GGBS	2.90

Table 3.3-1 - Densities of clay, lime, GGBS and some common sulphates.

3.3.4 LIME STABILISATION AND STRENGTH

Clays generally show a significant increase in strength when stabilised with lime. Strength gain in the soil normally will more than compensate for the apparent adverse changes in compaction optima. The strength gain is influenced by several factors such as clay type, type and amount of lime added, curing time and curing method, moisture content, unit weight, and time elapsed between mixing and compaction (Ingles and Metcalf, 1972; Bell and Coulthard, 1990).

(i) Type of Clay:- Expansive clays develop strength more rapidly in response to lime addition than do other clay types although the final strength achieved is greater in kaolinitic clays. In many cases, only a small amount of clay is needed in a soil for reaction with lime to be effective as the amount of silica or alumina required to sustain pozzolanic reaction in soils is relatively small (Bell and Coulthard, 1990).

(ii) Type of Lime:- Montmorillonitic clays are reported to give lower strengths with dolomitic limes than with high calcium or semi-hydraulic limes. Kaolinitic clays on the other hand have been shown to yield the highest strengths when mixed with semi-hydraulic limes and the lowest strengths are obtained with high calcium limes (Ingles and Metcalf, 1972; Bell and Coulthard, 1990).

(iii) Amount of Lime:- Strength does not increase linearly with lime content, and in fact excessive addition of lime reduces strength (Bell, 1988; Abdi, 1990). The optimum lime content tends to range from 4.5 per cent to 8 per cent, higher values being required in soils with higher clay fractions. The control lime content used in this research is in the middle of this range at 6wt.% lime content.

(iv) Curing Method:- Higher temperatures accelerate curing, resulting in higher strengths (Bell, 1988; Bell and Coulthard, 1990). Bell reports that specimens cured at 35°C developed twice or more the strength of those cured at 25°C. Further, at temperatures below 4°C the soil - lime pozzolanic reaction is severely retarded and may even cease.

Saturation of soil specimens by soaking in water before testing for unconfined compressive strength simulates some of the worst conditions to which a stabilised soil may be subjected as it results in a marked reduction in strength. Increased curing temperatures result in a significant reduction in this loss in strength due to soaking. Laguros *et al.*, (Bell, 1988) found that high levels of relative humidity (of 90% and above) gave the greatest ultimate strength gain when comparing different curing conditions. Also, the pH value of a clay - lime mixture is an important factor controlling the rate of gain of strength. The ultimate strength is related to the overall reduction in pH value during curing.

(v) Curing Time :- The strength increases rapidly at first, notably during the first seven days of curing (Rogers, 1988), then increases more slowly at a more or less constant rate for about 15 weeks. This supports the view that the primary cementitious products due to lime-clay reaction begin to form at an early stage even though reaction continues for a very long period. These products start forming during and after the flocculation process. In his work on lime-stabilisation of various types of clays Brandl (1981) (as reported by Bell, 1988 and by Bell and Coulthard, 1990), observed that the rate of increase in strength was very small between one or two years and that no further changes in strength took place, even in active clays, after seven years.

(vi) Unit Weight and Compaction Moisture Content:- Lime-soil mixtures compacted at moisture contents slightly above optimum attain, after brief periods of curing, higher strengths than those compacted with moisture contents slightly less than optimum. This is probably because the lime is more uniformly dispersed in a more homogeneous environment when excess water is present. Also, sufficient water is available for cation exchange to take place as well as maintain low air voids (Cobbe, 1988). The strength of soils compacted below optimum moisture content can be enhanced by further addition of water after compaction. Interestingly, the strengths of lime stabilised clay soils decrease with increasing natural moisture content (Bell, 1988). One would expect the strength to increase with increasing natural moisture content, unless the natural moisture content is far higher than the optimum compaction moisture content. Holm observed that even three months after lime treatment the strength of clays with high natural moisture contents remain low.

The compactive effort influences the strength significantly. Mateous (1964), as reported by Bell (1987), showed that when the compactive effort was increased from standard to modified AASHO, the compressive strength of lime-soil mixtures increased by 50 - 250 per cent for both 7 and 28 day curing periods. Mitchell and Hooper (1961), as reported by Bell and Coulthard (1990), reported that samples of lime-clay soil compacted within one hour of mixing attained a higher strength than those which were compacted after 24 hours had elapsed. In contrast, Arabi and Wild (1989) found that the effect of delaying compaction of a Devonian red marl treated with 6 wt.% lime and cured at 25°C for 12 weeks in a moist environment led to no strength change. However at higher curing temperatures (50 and 75°C), the strength decreased significantly with delay in compaction, the higher the curing temperatures the greater the reduction in strength.

3.3.5 SWELLING OF LIME STABILISED SOILS

In normal swelling of clay soils (see section 2.3), the main cause of change in the total suction is matric suction. However in the presence of lime and/or salts such as sulphates, osmotic suction must also be taken into account. The various types of swelling to occur in unstabilised clays and the mechanisms involved have been discussed in Chapter 2. The addition of lime to the clays result in formation of cementitious products which cement the clay plates together. This cementation, coupled with cation exchange involving Ca^{2+} ions from the lime, reduce the water absorption properties of the clay particle surfaces (Bell, 1988; Rogers, 1988; Arabi and Wild, 1989). As a result, the swell potential of the clays is generally reduced. However, Sivapullaiah *et al.*, (1987) reports increase in free swell of lime treated kaolinitic red earth soils with increase in lime content which reaches a maximum, and then gradually decreases to a final equilibrium level (although this increase in free swell may of course be due to the presence of expansion producing minerals in the soil such as sulphates as discussed later).

The Department of Transportation (DTp) allows an average swell for lime stabilised material of less than 5mm measured on the standard 127 mm high CBR mould (approximately 4% linear expansion) after not more than 72 hours of mellowing followed by 3 days of curing and 4 days of soaking. No individual test specimen is allowed to have a swell of more than 10 mm (approximately 8% linear expansion). Under normal circumstances, these limits are rarely exceeded unless the presence of sulphates is confirmed. Mineral admixtures which react with lime sometimes reduce expansion and/or increase the mortar strength. Silica fume for example (in concentrations of 8 - 10 wt.% SiO_2), reduces free expansion 1.5 - 2.5 times.

3.3.6 OTHER PROPERTIES OF LIME-STABILISED SOILS

The **CBR** of clayey soils is increased by the addition of lime (Bell, 1987). The CBR increases immediately after the addition of lime and continues to increase with time if there is lime in excess of the lime fixation point.

Lime stabilisation has been found to increase the value of **Young's modulus** by some 15 times after three weeks of treatment and around 35 times after 16 months. The modulus has been found to increase with increase in curing temperature (Bell, 1987).

The **permeability** of a clay soil increases when treated with lime (Bell, 1987; Wild *et al.*, 1987). This is directly proportional to the amount of the clay fraction. Those clay soils compacted on the dry side of the optimum moisture content develop a higher permeability than those compacted wet of the optimum.

Flocculation as a result of lime-stabilisation increases the mix void ratio which in turn, reduces the thermal conductivity. This reduced thermal conductivity prevents the frost encroachment from the stabilised layer top surface. With increased curing, interparticle bonding increases and the rate and depth of frost penetration is reduced and thus the overall **resistance to frost** action increases rapidly as does the volume stability. The reduced suction forces in clay mixed with lime (Arabi *et al.*, 1989) reduces the supply of water and enhances further the frost resistance as less water is available for freezing.

3.4 EFFECTS OF SULPHATES ON LIME STABILISATION

3.4.1 OCCURRENCE OF SULPHATES

The earth's crust contains various elements mainly in combination with oxygen in the form of oxides such as silica (SiO_2) and alumina (Al_2O_3) and natural salts of varying types and concentrations. Their type and distribution depends primarily upon the climate and geology. Among the most commonly encountered, calcium sulphate occurs as gypsum or selenite ($CaSO_4.2H_2O$), sodium sulphate as thenardite ($Na_2SO_4.10H_2O$), potassium sulphate as arcanite (K_2SO_4) while magnesium sulphate occurs as epsomite ($MgSO_4.7H_2O$). All tend to occur naturally in regions of limited rainfall (Grim, 1968; Sherwood, 1962; Obika and Freer-Hewish, 1990) such as parts of Australia, Africa and the Gulf region although significant amounts may also be encountered in other wetter regions. The salts occur either contained in ground water or in the surface or subsurface soil. Certain salts such as $MgSO_4$ and Na_2SO_4 can also be contained in Industrial waste (Obika and Freer-Hewish, 1990; Li *et al.,* 1996) which may then be used in pavement and/or other construction. In the humid temperate regions, where soils are largely acid in character, little or no calcium is found as sulphate, or as carbonate (calcite) or phosphate, except when rock phosphate is added to the soil at high rates as a fertiliser (Grim, 1968). In the U.K., gypsum or selenite is abundant in some soils such as Oxford clay and Kimmeridge clay. Other sulphates in these clays include those of sodium and magnesium.

Sulphates result from the oxidation of sulphide minerals, principally pyrite (Sherwood, 1962; Perry *et al.,* 1995). They are usually positively identified as the salty efflorescence commonly seen at the soil surface in arid areas. Soils of the humid temperate regions contain 50-500ppm soluble sulphates (0.0005 - 0.005%), while high sulphate concentrations of 10,000ppm (1%) are common in arid and semi arid areas (Grim, 1968; Gjorv, 1989). Irrigation water is also known to raise the sulphate content of soils appreciably. Sulphates may be present within the soil already, or be produced by oxidation of sulphides especially those of iron e.g. pyrite. Such oxidation is done by ground water. Such water may also transfer sulphates from other sites. Sulphate well bonded to the clay and therefore insoluble may weaken with time and go into solution as soluble sulphate. This change depends on the moisture content (Littleton, 1991). In their natural state, sulphates occur as SO_4. However, in soil testing and analysis, sulphates are normally expressed as SO_3. This is the situation in BS 1377. The test for total sulphate content (BS 1047) provides a measure of the sulphates (SO_3) already in the soil plus those sulphates converted from the oxidation of sulphides. Total sulphate content is determined as the acid soluble sulphate. In addition, water soluble sulphate is determined and this helps in ascertaining the potential for migration of sulphates (BS 1377 Part 3) and also the level of sulphate present in ground water.

Solubility influences behaviour between the less damaging (in terms of strength development) gypsum (calcium sulphate ($CaSO_4.2H_2O$)) and the more damaging sulphates of sodium and magnesium. The solubilities of some of the common sulphates are shown in Table 3.4-1. From the current available literature on the effects of sulphates on lime stabilised clays, it is erroneous to quote an acceptable level of sulphate in terms of expected swell. The current and other works have established that the effects of sodium, magnesium and potassium sulphates are more deleterious than those of gypsum despite the former being in less abundance. Therefore, the decision on suitability of a clay soil for stabilisation can only be made when the total amount and type of sulphate present in the soil are known, and the effects each sulphate is likely to have on the stabilised soil have been established.

Sulphate	Solubility (g SO_4/l)
$CaSO_4.2H_2O$	1.44*
K_2SO_4	130
$MgSO_4$	225
$Na_2SO_4.10H_2O$	> 225

* or 1.22 g (SO_3)/l

Table 3.4-1 - Solubilities of commonly occurring sulphates.

3.4.2 LIME-CLAY-SULPHATE REACTIONS

3.4.2.1 Introduction

At high pH values of at least 12.4 such as that provided by lime in solution, the clay fraction of soil reacts with sulphates (Snedker and Temporal, 1990). The presence of sulphates in the clay-lime mix introduces additional cations such as Mg^{2+}, Na^+ or K^+ into the mix. Extra cations further reduce the negative charges created by excess OH^- ions introduced by the addition of lime further increasing the Van der Waals attractive forces (Sivapallaiah *et al.,* 1987). With multi-valent cations, which have high polarizability due to their charge size, special bonds can be formed between interlamellar cations and the clay particle surfaces. In such cases, swelling of the soil can be restricted, suggesting a reduction in water intake and hence a comparatively lower reduction in liquid limit as compared to monovalent cations. These special bonds, together with higher attractive forces, trigger increased flocculation which allow the soil to have more voids and to take in more moisture. The monovalent cations, not being as effective in this neutralisation process, leave the clay mix with mild negative charges which do not allow the same degree of flocculation. In fact there is a dispersive tendency of the individual clay particles leading to a greater reduction in voids than would be the case when more floccs and voids are developed in the presence of divalent cations. It has been suggested (Sherwood, 1962) that small proportions of metal sulphates as secondary additives may be beneficial to soil-lime mixtures by increasing the strengths without significant increase in moisture adsorption and swelling. At high concentrations however, sulphates like sodium sulphate increase the pH of the pore solution to such high levels that lime ($Ca(OH)_2$) becomes almost insoluble (Li *et al.*, 1996). The effects of sulphates on lime treated soils are different from the effects of sulphates on untreated clays (Bell, 1988). In lime-treated soil, the unconfined compressive strength (UCS) increases at low sulphate contents (of the order of 1%). This strength increase is greater when the water content in the soil exceeds the optimum moisture content or compaction moisture content (Bell, 1988). In contrast, the UCS of untreated clay is reduced by the presence of sulphates regardless of moisture conditions (Strevens and Littleton, 1989). Strevens and Littleton observed that the reduction in UCS was exacerbated if sulphate solutions were used in contrast to when the sulphates were incorporated in the dry state, implying that soluble sulphates such as those of sodium, magnesium and potassium are likely to have more deleterious effects than those of calcium.

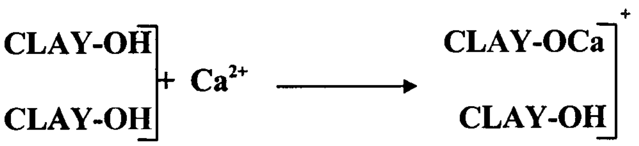
The influence of sulphates on swelling will depend on the amount and type of sulphate, the amount of alumina (and hence the type, the amount and the particle size of the clay), the temperature and the humidity (Mitchell, 1986). All these effects of sulphates on lime stabilised soil are due to the formation of $CAS\bar{S}H$ and $CA\bar{S}H$ hydrates. It would therefore be most appropriate to discuss the formation and properties of these hydrates before discussion of their effects on stabilised material.

3.4.2.2 Ettringite Formation

Clay-lime reactions have already been discussed in section 3.2. In the presence of sulphates further complex reactions, and modifications of the lime-clay reactions, take place. After the dissolution, at high pH, of alumina and silica from the clay and of the sulphate minerals if present, a colloidal product forms (Mitchell, 1986; Wild *et al.*, 1989), consisting of a complex calcium-sulphate-aluminate-silicate hydrate ($CAS\bar{S}H$). This compound's $\underline{S}$/S ratio increases progressively with curing /soaking time due to its property of attracting sulphate ions and rejecting the silicate ones. This is perhaps due to differences in solubilities of sulphates and silicates. Eventually, within this colloidal product, a compound with little or no silica in it, commonly known as ettringite is precipitated. Ettringite may be represented either in the cement chemistry notation as $C_3A3C\bar{S}H_{32}$ or $C_6A\overline{S_3}H_{32}$ (i.e. $3CaO.Al_2O_3.3CaSO_4.32H_2O$) or in the structural chemistry notation as $Ca_6[Al(OH)_6]_2(SO_4)_326H_2O$. The rate at which ettringite precipitation takes place will depend on several factors as discussed later. It is just one of several fairly stable phases that form from the colloidal product. As the sulphate concentration decreases structural adjustments of this colloidal hydrate take place with time, and other unstable phases also form. One example of such a phase is monosulphate ($C_3AC\bar{S}H_{12}$)

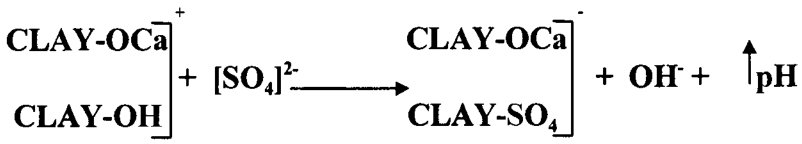
which has been widely reported in PC-sulphate systems (Kuzel, 1996; Odler and Yaoxin Chen, 1996).

The formation of ettringite may be explained by observations on $[SO_4]^{2-}$ adsorption on clay particles in solution (Bolan *et al.,* 1993). Electrostatic attraction of Ca^{2+} ions onto the hydroxyl groups on the clay particle surfaces, say during lime stabilisation, induces positive charges on the clay particle surfaces.



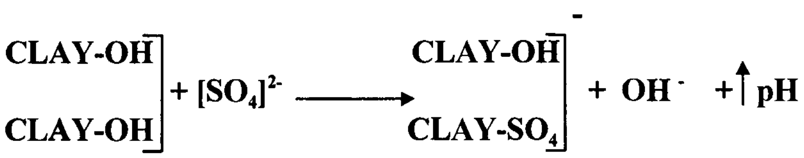
$$\left.\begin{array}{l}\textbf{CLAY-OH}\\ \textbf{CLAY-OH}\end{array}\right] + \mathbf{Ca^{2+}} \longrightarrow \left.\begin{array}{l}\textbf{CLAY-OCa}\\ \textbf{CLAY-OH}\end{array}\right]^{+} + \mathbf{H^{+}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \textbf{I}$$

The adsorption of $[SO_4]^{2-}$ due to the created positive charge on the clay then follows.



$$\left.\begin{array}{l}\textbf{CLAY-OCa}\\ \textbf{CLAY-OH}\end{array}\right]^{+} + \mathbf{[SO_4]^{2-}} \longrightarrow \left.\begin{array}{l}\textbf{CLAY-OCa}\\ \textbf{CLAY-SO_4}\end{array}\right]^{-} + \mathbf{OH^{-}} + \uparrow\mathbf{pH} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \textbf{II}$$

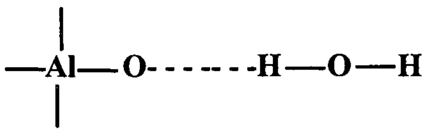
The $[SO_4]^{2-}$ ions on their own are also capable of displacing hydrogen even on sites without a positive charge, further increasing the OH^- ion concentration.



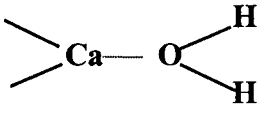
$$\left.\begin{array}{l}\textbf{CLAY-OH}\\ \textbf{CLAY-OH}\end{array}\right] + \mathbf{[SO_4]^{2-}} \longrightarrow \left.\begin{array}{l}\textbf{CLAY-OH}\\ \textbf{CLAY-SO_4}\end{array}\right]^{-} + \mathbf{OH^{-}} + \uparrow\mathbf{pH} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \textbf{III}$$

The source of $[SO_4]^{2-}$ may be a divalent cation sulphate, such as $CaSO_4$ or $MgSO_4$, or a monovalent one such as Na_2SO_4 or K_2SO_4. The H^+ ions released during the cation adsorption partly balance the OH^- ions released during the $[SO_4]^{2-}$ adsorption in equations

II and III. There is therefore some noticeable increase in pH due to $[SO_4]^{2-}$ adsorption as the H^+ ion concentration reduces. Meanwhile, the polar H_2O molecules and/or OH^- ions interact with aluminate and lime particles, forming intermediate components (i) and (ii) below.



and



(i) (ii)

……………..IV

This reaction strains the original Al----O and Ca----O bonds, weakening and eventually breaking some of them, increasing Ca^{2+} and $Al(OH)_4^-$ ions in the pore solution (Deng Min *et al.,* 1994). This facilitates the formation of new phases including ettringite by the mobilisation of H^+; OH^- from equations I and II and $Al(OH)_4^-$, Ca^{2+} and $[SO_4]^{2-}$ as well as water molecules from the pore solution.

Precipitation of ettringite is as a result of $[SO_4]^{2-}$ ion supersaturation. The minimum pore fluid sulphate concentration necessary to stabilise ettringite in various calcium sulpho-aluminate systems has been found to depend on pH, temperature and $[SO_4]^{2-}$ ion concentration among other factors. Above 50°C, ettringite is not generally formed at sulphate concentrations below 5 x 10^{-4} mol/litre sulphate while at 5°C only 2 x 10^{-7} mol/litre would be required (Glasser, 1996).

$$\mathbf{Ca^{2+}+2Al(OH)^{4-} + 3[SO_4]^{2-}+ 4OH^- + 26H_2O \leftrightarrow \{Ca_6[Al(OH)_6]_2.24H_2O\}(SO_4)_3 2H_2O (V)}$$

The formation of ettringite, sometimes coupled with later formation of gypsum, lowers the concentration of Ca^{2+} and $[SO_4]^{2-}$ in the pore solution.

$$\mathbf{Ca^{2+} + [SO_4]^{2-} + 2H_2O \longleftrightarrow CaSO_4.2H_2O} \text{ .... } \mathbf{VI}$$

If the observations reported by Mehta (1983) in systems involving cement hydration were to happen in clay lime stabilisation (which is highly likely as the reactants in the systems - lime, alumina, sulphate etc. and the environmental conditions are very similar), pore solution of high alkalinity (high pH) would lead to formation of fine ettringite crystals which would form in situ i.e. on or close to the clay particle surfaces. If water is available, this ettringite formation would be accompanied by large expansions. Alternatively, and especially at low pH, $Al(OH)_4^-$ ions would move into the bulk pore solution and ettringite may precipitate partially or completely in voids, giving rise to little or no expansion (Deng Min *et al.,* 1994; Yan Fu *et al.,* 1996; Glasser, 1996). Recent research in cement related cases has shown that ettringite withdraws water from the pore solution, increasing the concentration of OH^- ions (and hence the alkalinity of the pore solution) (Shayan and Ivanusec, 1996). This helps in maintaining the pH for further ettringite formation until all the reactants are depleted.

Research has also shown that primary phases such as monosulphate may react with carbon dioxide to form ettringite at the onset of carbonation (Kuzel, 1996). A review of past literature does not have any detailed coverage of this mode of ettringite formation.

3.4.2.3 The rate of ettringite formation

As mentioned above, much of the reported work regarding ettringite formation relates to hydration of cement rather than lime-soil reaction. However because the basic chemistry is the same in both systems, these observations are relevant to the current work. Thus, from observations on C_3A hydration by numerous researchers, formation of a cementitious gel coating around clay particles during lime-clay-sulphate hydration is also likely to occur. Mehta (1972) while working on the influence of lime and gypsum on the hydration of C_3A observed that the hydration of C_3A was retarded in the presence of lime and or gypsum. In the absence of gypsum, hydration was retarded by C_4AH_x formation coating C_3A grains. Later, Collepardi *et al.,* (1978) worked further with gypsum and sodium sulphate on C_3A hydration and observed that hydration in the presence of gypsum was retarded by the formation of ettringite crystals coating the grains. The formation of this coating restricts sulphate ion bearing pore water access to the particles and hydration slows down. Such views were also shared by Pachenko (1990), arguing further that the coating reduced the rate of further ettringite formation. Mehta had earlier argued that the deposits of ettringite around C_3A grains were not dense enough to account for the retardation of the hydration, explaining the retardation in terms of reduced C_3A solubility in solution saturated with sulphate ions. Arguments that a colloidal gel rather than ettringite crystals coating would be the first to cover the grains would appear to be most appropriate because a gel (especially as it is known to be rather impervious) would be most effective in reducing grain access. It is reasoned that it is from this gel that fibrous material and ettringite crystals precipitate. Pachenko suggested that the increasing volume of ettringite crystals within this initial coating creates tensile stresses resulting in the development of microfissures on the shell and renewed access to the grains. The rate of ettringite formation is subsequently observed to increase again. Wild *et al.*, (1993) attributes the reduced ettringite formation within the colloidal gel to increased fluid pressure due to osmotic imbibition of water and not to ettringite growth. This membrane formation and rupture process continues until all reactants are depleted or until further reaction is terminated by development of stable crystalline phases.

The rate of ettringite formation is also affected by the addition of other various chemicals. De Silva and Glasser (1992) found that the low solubility of $CaSO_4$ delayed the formation of ettringite. This delay was accelerated by the presence of NaOH which further lowered the solubility of $CaSO_4$. Sodium hydroxide and alkalis in general inhibit the formation of ettringite by shifting the equilibrium of the reaction represented by equation V to the left (De Silva, 1992, Diamond, 1996). On the other hand, in the presence of extra gypsum, the rapid dissolution of Na_2SO_4 in water furnishes the necessary sulphate ions to promote rapid ettringite formation.

There is little in the literature to confirm whether ettringite is formed in the presence of sodium sulphate and gypsum, as in most reported cases there is no recorded expansion (Sivapullaiah *et al.*, 1987). Some researchers have however indicated that ettringite formation indeed does take place (Li *et al.*, 1996). In his work on the effects of NaCl and NaOH on laboratory soils prepared from commercial quality siliceous sand and clay, Lees *et al.*, (1982 and 1983) observed that sodium ions may "disturb" the aluminium bonding, creating a situation where calcium ions may more easily unite with alumina and silica to form new materials. The weakening of silica and aluminium bonding is facilitated by the formation of intermediate sodium silicate and sodium aluminate hydrates (Equation VIII) (Lees *et al.*, 1982 and 1983).

$$\mathbf{Ca(OH)_2 + Na_2X \longrightarrow CaX + 2NaOH \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots VII}$$

Where X is sulphate, silicate, aluminate or hydroxide

This step is a cation exchange where Na^+ replaces Ca^{2+} to form a Na-clay from a Ca-clay.

This leads to smaller particles (Deflocculation).

$$\left.\begin{array}{l}\mathbf{NaOH + SiO_2\ (soil\ silica) \longrightarrow NSH}\\ \mathbf{NaOH + Al_2O_3\ (soil\ alumina) \longrightarrow NAH}\end{array}\right] \begin{array}{l}\textbf{Hydrated Na-}\\ \textbf{Silicates and}\\ \textbf{Aluminates}\end{array} \ldots\ldots\ldots\ldots\ldots\ldots \mathbf{VIII}$$

These hydrates later react with Ca^{2+} ions to end with calcium-silicate and calcium-aluminate hydrates, CSH and CAH respectively (Equation V).

$$\left.\begin{array}{l}\mathbf{NSH + Ca \longrightarrow CSH + Na}\\ \qquad\qquad\quad \textbf{or}\ \mathbf{CNSH + Na}\\ \\ \mathbf{NAH + Ca \longrightarrow CAH + Na}\end{array}\right] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \mathbf{IX}$$

3.4.2.4 Nature of Ettringite

There are conflicting observations, theories and explanations of the nature and form of ettringite which is produced in different chemical environments. This makes the understanding of the undoubted influences of ettringite on the expansive behaviour of ettringite containing systems very complex. In their study of the microstructure of C_3A in the presence of gypsum, numerous researchers (Mehta, 1972-83; Hampson and Bailey, 1983) observed that calcium-sulpho-aluminate hydrate ($CA\bar{S}H$) phases appear to have a structure that is strongly dependent upon chemical environment, particularly pH, temperature and sulphate activity. This has been confirmed by recent research which has shown that ettringite can form in two ways: long fine and needle-like crystals and/or short, stubby ones (Shayan and Ivanusec, 1996), the character of crystallisation being influenced by the environment i.e. the presence of lime or other alkalis, and reactive aggregates.

From observations on formation and expansion of ettringite in several reports, calcium aluminate and calcium sulpho-aluminate hydrates precipitate from solution from a pH≈10.0 onwards (Mehta, 1972 and 83; Hampson and Bailey, 1983; Gabrisova *et al.*, 1991; Deng Min *et al.*, 1994; Shayan and Ivanusec, 1996). Below this pH level, only gypsum and aluminium sulphate are the stable phases. The first hydrate to appear (at pH≈10.0) is hydrogarnet ($3CaO.Al_2O_3.6H_2O$ or C_3AH_6). Calcium sulpho-aluminate precipitate (ettringite $C_3A3C\bar{S}H_{32}$)) appears at a pH ≈10.5-10.7 and on further increase in pH, monosulphate ($C_3AC\bar{S}H_{12}$) appears at pH≈11.6. The precipitate fibres get smaller and more rounded with rising pH and beyond a pH of 12.5, the fibres start to disappear. At higher pH≈13.2, no fibres are generally observed.

From the various reports on ettringite formation and growth mentioned, the characteristics of freshly precipitated ettringite at low pH≈11.5 are different from those at high pH≈12.5 (say that found in a saturated lime solution). At the higher pH, the ettringite crystals are fine needle-like and prismatic crystals (Deng Min *et al.*, 1994), and tend to form on the aluminium bearing particle surfaces. In the absence of lime, (low pH), they tend to form as large widely scattered crystals distributed through an extensive region in the bulk solution.

Mehta (1983), in agreement observed that ettringite formed in the presence of lime consists of small sized crystals and that ettringite formed in the absence of lime is in larger crystals (six times as big), but further observes that the former is almost colloidal in texture and not formed of prismatic crystals. Collepardi *et al.*, (1978) while working on the influence of lime, gypsum and sodium sulphate on the hydration of C_3A observed that that the size and thickness of ettringite obtained by C_3A hydration rapidly decreased in the presence of lime from 0.3μm to 0.1μm.

In the presence of alkalies such as KOH and NaOH, it is possible to increase the pH further to 13.2 or even 14 when Na_2SO_4 is present (Li *et al.*, 1996; Shayan and Ivanusec, 1996). Li *et al.*, and Shayan and Ivanusec observed that this increase in pH further reduces the size of ettringite and even dissolves it.

3.4.2.5 Properties of ettringite

General:- Ettringite is responsible for both beneficial and deleterious phenomena. In Portland cement especially, beneficial factors include compression stresses in shrinkage-compensation and self stressing concretes. Deleterious ones include heave, loss of strength and cracking. There are conflicting theories as to whether ettringite is a primary, secondary or even an unessential contributor to the process for retarding C_3A hydration.

Since sodium sulphate does not retard C_3A hydration as calcium sulphate does and neither ettringite nor monosulphate ($C_3AC\bar{S}H_{12}$) are observed by DTG, DTA, or XRD, it then follows that it is the formation of ettringite rather than simply the presence of sulphate in solution which is involved in the retardation process. These observations should provide important indicators of the types of mechanisms operating in the current work on clay-lime-sulphate systems. Several factors are however important in determining the properties of ettringite.

Temperature:-At low temperatures (below 15°C), and in the presence of carbon dioxide, ettringite undergoes carbonation to form thaumasite (Mitchel, 1986; Edge and Taylor, 1971). Here, carbon dioxide reacts with water and forms carbonic acid which dissolves calcite, if present in the clay, enabling carbonation of ettringite to thaumasite. This is an iso-structural substitution of Al^{3+} by Si^{4+} on the one hand and of SO_4^{2-} by CO_3^{2-} on the other, forming a complex calcium-silicate-hydroxide-sulphate-carbonate hydrate of the formula $C_3S\overline{SC}H_{15}$ or $2CaO[Si(OH)_6]_2 2(SO_4)_2 CO_3 24H_2O$. At higher temperatures, ettringite remains stable until a temperature of 50°C when its solubility rapidly increases and at 100°C it becomes quite unstable and disappears (Grounds *et al.,* 1996; Glasser, 1996; Odler and Yaoxin, 1996).

Sulphate ion concentration:- From observations of properties of ettringite in cement, almost all the ettringite is eventually transformed to lower sulphate content monosulphate at low sulphate concentrations. Little or none of the ettringite is present after 24 hours of hydration in low sulphate containing systems (Mehta, 1983). The monosulphate also disappears after some time. The sulphate is probably taken in by the C-S-H gel and also retained in solid solution in C_4AH_{13} (Odler and Yaoxin, 1996; Glasser, 1996). Kuzel, (1996) observed that the conversion of ettringite to monosulphate takes place when the sulphate concentration falls below 2.35 mg/l. Also, the conversion must be under CO_2 free conditions, less than 0.5%.

Alkalinity:- The solubility of ettringite has been observed to increase with the alkali content of the pore fluid (Glasser, 1996, Diamond, 1996; Shayan and Ivanusec, 1996).

3.4.2.6 Ettringite and Swelling

It is generally agreed among scientists that expansion of lime-stabilised clays in the presence of sulphates is the result of ettringite formation, though its role in expansion is different as viewed by various scholars (Pachenko, 1990). In badly damaged lime-stabilised pavement layers, 20-40% by volume of the total material has been observed to consist of thaumasite (Mitchell, 1986).

Ettringite formation and the expansion mechanism has been explained by two theories; crystal growth theory and swelling theory. In lime stabilised clay in the presence of sulphates, expansion is believed to be partly caused by the growth of ettringite crystals formed on the clay particle surfaces (Mitchell, 1986). Secondly, there is the osmotic pressure that induces water intake, identified with pressures arising from concentration differences of dissolved ions between the solid particles and the surrounding liquid phase (Krahn and Fredlund, 1972). This forms a colloidal gel from which ettringite crystallises. The gel has the ability of attracting large numbers of water molecules, causing inter-particle repulsion, thus causing an overall expansion of the system. Although expansion takes place during the ettringite formation stage, ettringite formation, or even its amount, should not be considered to be a measure of the expansion magnitude. Heller and Ben-Yair (1964) observed no direct correlation between the degree of expansion of cement upon sulphate attack and the amount of ettringite present. They also observed that although theoretically, there should be 7-8% reduction in volume on completion of ettringite formation, ettringite formation is often associated with expansion.

It is not certain whether ettringite formed in the voids causes expansion. Yan Fu *et al.*, (1996) working on the hydration of different calcium aluminate hydrates reports that the magnitude of expansion is relatively small when the ettringite crystals grow too quickly in the early stages because the structure is not well cemented. The ettringite then just fills in voids during these stages of low strength. Numerous other authors share this view (Glasser, 1996). Others are of the opinion that all ettringite forms produce expansion and the difference between ettringite forms determine the magnitude of expansion (Mehta, 1983). Mehta and his co-workers found that ettringite formed in the presence of lime was gel like, with a large surface area and unsatisfied negative charges. They confirmed that the colloidal (or gel like) "ettringite" would imbibe large numbers of water molecules and generate swelling pressure, leading to an overall expansion of the system. Other researchers (Wild *et al.*, 1993B) hold similar views on water absorption by a colloidal layer. However, it may not be appropriate to classify this as ettringite because by definition ettringite is a crystalline mineral of fixed composition. In view of recent observations on research on delayed ettringite formation, some researchers are of the view that the earlier theories put forward by Mehta about existence of amorphous ettringite seem to have been overlooked, especially for ettringite formed in brief high temperatures (Glasser, 1996). A range of other views also exist. Wang *et al.*, (1996) suggested that swelling forces upon ettringite formation are weak and do not contribute to much expansion. Rossato *et al.*, (1992) demonstrated that the effects of swelling pressure were apparently small, being exhausted by a small restraint of the order of 0 - 0.1 MPa. The current work which will be discussed in Chapter 8 does not however seem to indicate this. Glasser (1996), reports in his study on the role of sulphate, mineralogy and curing temperature in delayed ettringite formation that there is no doubt that under some circumstances, yet to be fully defined, ettringite formation can be expansive. He points out that early work on restrained pressure generated from ettringite forming reactants showed that the mechanical pressures exceeded 350 Mpa, much greater than the strengths of well-made, well-cured concrete.

The detailed process of ettringite induced expansion is complex and although the formation of ettringite is undoubtedly of importance in swell formation, other properties of ettringite are also important. These include its stability under prevalent conditions and the influence of other ions, such as chloride ions if present and other admixtures.

3.4.3 PROPERTY CHANGES IN LIME-STABILISED CLAYS IN THE PRESENCE OF SULPHATES

3.4.3.1 Introduction

Expansive effects of sulphates in lime stabilised clay soils has been reported by Sherwood, (1962); Mitchell, (1986); Sivapullaiah *et al.,* (1987); Hunter, (1988); Strevens and Littleton, (1989); Snedker and Temporal, (1990); Abdi (1992) and Wild *et al.,* (1993, 1996). Similar effects of sulphates on industrial by-products such as pulverised fuel ash (Pfa) when combined with lime have also been observed and have also been reported by Wild *et al.,* (1990). There is little else reported on the influence of sulphates on other property changes such as compaction behaviour, and strength development. Abdi (1992) reported on the strength development of lime-stabilised industrial kaolinite in the presence of gypsum while Waswa *et al.*, (1993) reported similar developments on a lime-stabilised Kenyan lateritic soil (commonly known as *Murram*).

The engineering properties of lime stabilised materials are affected very significantly by the presence of sulphates, which may be present either in the parent stabilisation material, in the water used for mixing and/or in the ground water. In many cases these effects from sulphates are due to the modified cation exchange and pozzolanic reactions as a result of modified water solution chemistry. The effects will depend on the sulphate cation type as well as the amount present.

3.4.3.1 Pore solution chemistry

The effects of the addition of a sulphate to the pore solution chemistry of clay-lime systems will depend on the type and amount of sulphate. The addition of gypsum for example would result in the addition of Ca^{2+} cations as well as the introduction of SO_4^{2-} anions. With the addition of other sulphate types, the Ca^{2+} cations will remain those provided by the added lime while new cations as well as SO_4^{2-} anions will be introduced. The amount and solubility of the added sulphate will determine the number of the added anions and cations. It is this new list of ions that will participate in the cation exchange that ensues.

3.4.3.2 Cation exchange

The addition of extra Ca^{2+} cation by the addition of gypsum will lead to an increase in the overall number of cations attracted to the clay particle surfaces. As for the addition of other sulphate types, the cation exchange will depend on the position of the added cation in the lyotropic series $\mathbf{Li^+ < Na^+ < K^+ < Mg^{2+} < Ca^{2+} < Ba^{2+} < Al^{3+} < H^+}$ (Cobbe, 1988; Arabi and Wild, 1989), relative to the cations already present in the clay-lime system. The latter will predominantly be Ca^{2+} from the lime and any other inter-layer cations such as Na^+ and/or K^+. The ensuing cation exchange will determine whether flocculation-agglomeration or deflocculation-dispersion predominates. The divalent cations which result in enhanced neutralisation of the repulsive negative charges on the clay particle surfaces and a reduced electric double layer will lead to greater particle-particle attraction and hence flocculation-agglomeration while the monovalent cations will lead to lesser particle-particle attraction and an enlarged electric double layer and hence an inclination towards deflocculation-dispersion.

3.4.3.2 Sulphates and consistency limits

The water retention properties of a clay soil-lime mixture after the cation exchange process has occurred will determine the modified properties of liquid limit, plastic limit and hence the plasticity index. A flocculated structure will accommodate more water in the voids, raising both the liquid limit and the plastic limit as compared with a dispersed structure. Numerous researchers have reported the effects of calcium ions in lime-stabilised clays on the consistency limits (Sivapullaiah *et al.,* 1987; Bell, 1988; Arabi and Wild, 1989). The overall effects of the presence of other cations in the pore fluid will depend on whether the effects due to these cations support or counter those due to calcium ions. Monovalent cations (because of their lower charge and larger hydro-sphere than monovalent cations) would tend to counter the effects of calcium and cause deflocculation while divalent cations (with similar properties to Ca cations) would tend to increase the flocculation potential. However, the exact relationship between pore solution cations and subsequent consistency limits (LL, PL and PI) depend on other factors as well such as the clay mineral type. These limits cannot be merely quantified on the basis of presently available research on cation exchange. For example, while calcium ions tend to lower the liquid limit of montmorillonitic clays, the liquid limit of kaolinitic clays is increased. The cation exchange capacity is therefore only a very rough guide to the likely effects on the complicated and sometimes unpredictable water retention properties of clay minerals.

3.4.3.3 Sulphates and compaction

Compaction is basically a physical-mechanical process, determined by the ease of particle packing. On a micro level, cation exchange will influence the particle-particle separation, with divalent cations leading to closer particle-particle spacing and the monovalent ones leading to dispersion. On the macro scale, the bigger the floccs the more air is trapped between the particles and there is reduced efficiency of packing leading to reduced maximum dry density (MDD). On the other hand, in the dispersed condition, fewer floccs will result in more particles in a given volume due to less entrained air voids and reduced flocc-flocc friction. This leads to increased MDD. This closer particle to particle packing also leads to less water spaces and to a lower optimum moisture content (OMC). In the case of divalent cations, more water would be accommodated in the voids of a flocculated structure, raising the OMC.

3.4.3.4 Sulphates and strength

Alkali metal compounds at low concentrations produce substantial improvement in the soaked compressive strength of cured soil-cement (Grim, 1968). Those alkali metal compounds forming insoluble salts with calcium have been found to be the most beneficial. Several researchers have worked on the effects of some of the commonly encountered sulphates on both unstabilised and lime-stabilised clays viz.:-

Calcium Sulphate (Gypsum):- Several researchers have confirmed that gypsum addition provides a considerable contribution to the strength of lime stabilised clay soils (Grim, 1960; Abdi, 1992; Waswa *et al.,* 1993) This contribution is further enhanced by the presence of NaOH. Lambe *et al.,* (year of publication unknown) observed that alkaline activators (such as NaOH) increase the amount of $Ca(OH)_2$ reacted in a particular time. The effect of NaOH on the strength is significant in the early stages, but is less so or insignificant in the later stages.

The beneficial effects on strength development due to the presence of gypsum are however marred by sulphate attack (ettringite formation) reported by Sherwood, (1962); Mitchell, (1986); Sivapullaiah *et al.,* (1987); Hunter, (1988); Strevens and Littleton, (1989); Snedker and Temporal, (1990); Abdi (1992) and Wild *et al.,* (1993 and 1996). This form of attack will be discussed in greater detail in the next sub-section on sulphates and swelling.

Magnesium Sulphate:- According to Bonen (1993), magnesium sulphate is among the most damaging sulphates in soils. Sherwood (1962) reported dramatic reduction in strength of more than 50% in the presence of $MgSO_4$, even at concentrations as low as 0.2wt.% SO_3. These strength reductions were accompanied by big swells. Ettringite formation is thought to be the cause of early strength development in sulphate containing lime-stabilised systems. However ettringite is slow to form and even unstable in the presence of magnesium sulphate. The sulphate ultimately causes the ettringite to decompose to gypsum and hydrated alumina. The presence of magnesium sulphate leads to severe decalcification of the C-S-H gel leading to surface deterioration with further sulphate ingress and subsequently to the surface deposition of gypsum (Heller and Ben-Yair, 1964) i.e.

$3CaO.2SiO_2aq + 3MgSO_4.7H_2O \rightarrow 3CaSO_4.2H_2O + 3Mg(OH)_2 + SiO_2gel$ (Heller and Ben Yair, 1964).X

The sulphate attack is similar to that normally occurring in Ordinary Portland cement when magnesium sulphate is present whereby gypsum, brucite ($Mg(OH)_2$) and a poorly crystalline M-S-H gel, mainly serpentine ($M_3S_2H_2$), are formed in addition to ettringite. Decalcification (which is indicated by darkening of backscattered electron (BSE) images of polished sections of pastes (Gollop and Taylor, 1996)) releases calcium ions, facilitating easier deposition of gypsum. The gypsum formed may then react with more aluminate in the soil to form ettringite, (especially when most of the $MgSO_4$ which attacks ettringite has reacted), while the magnesium hydroxide (brucite) formed may react further with silica to yield more magnesium silicate gel. This latter reaction is however slow as the brucite is of low solubility and tends to form a hard surface coating on the C-S-H gel, preventing it from further attack from $MgSO_4$.

In high concentrations of magnesium sulphate, two competing factors operate in the sulphate attack process, viz. 1) the more efficient coating of the C-S-H surfaces by precipitated magnesium hydroxide on the one hand and 2) the increased attack due to the higher concentration of sulphate ions on the other. The microstructure of the material will determine which is the dominant factor. The greater the porosity of the mix, the more magnesium hydroxide is required for blocking all the channels. Therefore in well compacted clay, it is expected that the magnesium hydroxide coating is rather effective, due to reduced surface area of reacting surfaces. In this case, high magnesium sulphate which facilitates the formation of the brucite coating more effectively is less deleterious than at low concentrations. In porous materials, the brucite coating is ineffective and high concentrations will be very deleterious.

Sodium Sulphate:- Sodium compounds, which form insoluble compounds with calcium, have proved to be beneficial to strength development (Grim, 1960). The most beneficial additives have been found to be sodium sulphate in addition to caustic soda, soda ash, sodium sulphite, sodium metasilicate and sodium aluminate. Sherwood (1962) worked on various lime-stabilised soils containing sodium sulphate. He observed that considerable strength enhancement (more than 50%) occurred in some soils, while there was reduction in others. Heller and Ben-Yair (1964) reported that hydrated calcium silicates are not attacked by Na_2SO_4 as is the case for magnesium sulphate. Early research work on the $CaO-Al_2O_3-SO_3-Na_2O-H_2O$ system by Dosch and Zur Strassen (1967) (as reported by Li *et al.*, 1996) indicated that the deleterious effect on strength by Na_2SO_4 is probably due to the formation of expansive products (AFm/AFt) similar to those formed in the presence of gypsum. More recently Li *et al.*, (1996), reports the formation of hexagonal or pseudohexagonal layered structures similar to the AFm/AFt phases common in CaO-Al_2O_3-$CaSO_4$-H_2O systems but different from the latter in the fact that the structures contain sodium between the layers instead of calcium. Also, high concentrations of Na_2SO_4 raise the alkalinity to very high pH levels. At such pH levels ($pH > 14$), no Ca^{2+} ions were detected in the interstitial solution by Li *et al.,* (1996) as $Ca(OH)_2$ was almost insoluble. Overall, research indicates that high concentrations of Na_2SO_4 would lead to detrimental effects (Li *et al.,* 1996; Shayan and Ivanusec, 1996), attributed to the incorporation of Na in the C-S-H and development of a more dispersed system.

In Portland Cement attack by sodium sulphate, deposits of calcite are commonly identifiable by XRD with little or no gypsum formed. In other words, the formation of $CaCO_3$ is preferred to that of $CaSO_4$ (gypsum) or Na_2CO_3. This suggests that the mode of attack due to sodium sulphate is rather different form that due to the presence of magnesium sulphate although in both cases, significant decalcification of the C-S-H gel must take in order to release Ca^{2+} ions. In both cases, the attack leads to subsequent weak cementation leading to increased porosity and/or permeability and in turn, easy ingress of CO_2 and other deleterious agents.

Potassium Sulphate:- The detrimental effects in strength due to the presence of potassium compounds together with those of lithium have been found to be similar to those of sodium compounds not only in cement (C_3A) hydration (Shayan and Ivanusec, 1996) but also in soils (Heller and Ben Yair, 1964). The potassium compounds have however been found to be marginally less detrimental.

3.4.3.5 Sulphate and swelling

The presence of sulphates in lime-stabilised clay causes swelling both during the curing stages and during any subsequent inundation (Mitchell, 1986; Hunter, 1988; ; Barbour *et al.,* 1989; Snedker and Temporal, 1990; Abdi, 1992). Mitchell and Hunter report very large amounts of heave in excess of 100% leading to pavement failure in the Stewart Avenue lime treated sub-base in Las Vegas, Nevada, USA. Snedker and Temporal also report heave of at least 60% on the Banbury IV contract, part of the M40 Oxford to Birmingham motorway. In the Las Vegas case, Mitchell and Hunter attributed the heave to the expansive reaction between sulphates and the lime-stabilised sub-base material. Snedker and Temporal attributed the heave on the M40 motorway to similar reactions. In a closely related situation, Sherwood (1962), mentions a case in which the presence of calcium sulphate in the soil resulted in the disintegration of a soil cement road base in South Australia. No further reports or details on this road failure were available to the author.

In all cases, reports in the literature suggest that the swelling may be caused by two mechanisms.

- Firstly, there is swelling caused by changes in both suction and/or interparticle electrostatic repulsive forces as a result of changes in pore solution chemistry. Salt concentration gradients induce increases in osmotic suction causing imbibition of water by the stabilised material thus resulting in swelling.
- Secondly, there is swelling caused by the formation and subsequent growth of ettringite. This growth is increased on soaking when more water is available. Sources of water that generally cause heave include permeable backfill, areas of poor surface

drainage such as parking yards and construction joints (for example those occurring between a concrete medium and an asphaltic pavement).

These two mechanisms may be part of the same overall process. From the current available literature on the effects of sulphates on lime stabilised clays, it is not possible to quote an acceptable level of sulphate in a bid to assess the expected swell, because each system of reactants will have its own critical level.

3.4.3.6 Summary

It is apparent that short-term property changes of lime-stabilised clay soil (i.e. consistency limits and compaction) are as a result of changes in pore solution chemistry and hence the cation exchange process. These changes may be more significant on mellowing (a period ranging from 24 - 72 hours (1 - 3 days) during which the wet material is left to mix with water much more effectively), particularly if the material also contains sulphates. The long-term changes (i.e. strength and volume stability) are determined by the much slower pozzolanic activity. The presence of sulphates will affect the nature and rate of the activity, thus having significant effect on strength and swelling behaviour, depending on the sulphate type and concentration. The next chapter will look at the possibility of stabilising clay soils using ground granulated blastfurnace slag (GGBS), with a view to reducing or even eliminating the sulphate related swelling when clay soils are stabilised, particularly with lime or lime bearing material. Inclusion of GGBS has been triggered by the fact that it has been used in Portland Cement (PC) and PC-blends to combat sulphate attack in concrete. It was therefore felt important to establish whether these beneficial effects may be simulated in soil lime-stabilisation. Thus, the next chapter will review the chemical composition and properties of GGBS and its hydration in order to assess the likely nature of clay-lime-GGBS and clay-lime-GGBS-sulphate reactions, and the possible potential of GGBS in soil stabilisation.

CHAPTER 4 - SLAG STABILISATION

4.1 INTRODUCTION

Ground granulated blastfurnace slag (GGBS) comes from iron blast furnaces as a by-product of the iron making industry. It is a glassy calcium-magnesium alumino-silicate with potential cementitious reactivity. The latent hydraulic properties of blastfurnace slag were discovered in Germany in 1862 (Bijen, 1996) and commercial use of slag-lime cements then followed in the same country in 1865. Latent hydraulicity means that once activated a material reacts with water to give a cementitious material. In the United Kingdom, this potential, in blastfurnace slag, was first realised in Scotland in 1914 when granulated blastfurnace slag was ground with Portland cement.

It has been proved that the carrier of the latent hydraulic properties in slag is the glass component (Smolczyk, 1980; Xuequan Wu *et al.,* 1990; Shao-Dong Wang *et al.,* 1995;). The glass content is governed by the subsequent cooling process. The glass content of most modern slags amounts to about 90wt.% with a moisture content after the granulation process in the range 8 - 12wt.%. In the slag manufacture, the granules or pellets are ground into a fine powder similar in fineness to Portland cement (specific surface 320 - 380 m^2/kg) with a specific gravity in the range 2.85 - 2.94 (s.g of Portland cement is ≈ 3.15).

The use of GGBS is well established in many cement applications where it provides enhanced durability, high resistance to chloride penetration, resistance to sulphate attack and protection against alkali silica reaction (ASR). Its use in soil stabilisation is however still a novel process in the U.K although it has been used in South Africa. The well established sulphate resisting properties imparted to cements by blending them with GGBS suggests that by blending lime with GGBS, the latter may impart similar sulphate resisting properties to lime-stabilised clays (Wild *et al.,* 1996). In both hydrated lime-sulphate containing clay mixes and Portland cements, the phases present are similar - ettringite, C-S-H, C-A-H and C-A-S-H gels. Since Portland cement hydration products are practically the same as those of slag-Portland cement blends (Smolczyk, 1980; Regourd, 1980), then it is likely that those of lime-slag-clay are similar or at least comparable with those of cement/slag blends. A review of literature on the latter will therefore form a strong basis for extrapolating the findings to establish the behaviour of the former.

4.2 CHEMICAL COMPOSITION AND PROPERTIES OF GGBS

Table 5.3-1 in Chapter 5 shows the chemical composition and physical properties of GGBS and Portland cement from Civil and Marine Slag Cement Ltd., UK. From the table, it can be seen that the chemical and physical properties of GGBS and Portland cement are similar. Slag, used together with Portland cement, has been found to impart distinct properties not normally found in Portland cement. Shao Dong Wang *et al.,*

(1995) has summarised the advantageous and disadvantageous properties of alkali-activated slag cement and concrete. For example there are numerous reports on the heat dissipation of GGBS-Portland cement blends (Smolczyk, 1980; Xuequan Wu *et al.*, 1990; Caijun Shi *et al.*, 1993; Shao Dong Wang *et al.*, 1995). Smolczyk observed that slag hydrates much more slowly than PC and this gradual hydration makes GGBS-Portland cement blends not only evolve less total heat but also reduce the rate at which the heat is evolved.

The alumina content in slag increases the reactions with any available sulphate in the system to form early ettringite using any available Ca^{2+} ions in the system. This reduces the system's sulphate content, thus minimising delayed sulphate attack. Also, the reduced amount of free lime in hydrated GGBS-PC blends (Daimon, 1980) ensures less ettringite formation. In addition, the reduced porosity and permeability of hydrated GGBS-PC blends inhibits (see next paragraph) diffusion of aggressive agents into GGBS concrete. Hence other forms of resistance such as resistance to chloride attack and to alkali aggregate reaction (ASR) are also enhanced, making slag preferable for marine applications such as injection grouts in marine environments and construction of marine structures such as power stations and bridge piers (Regourd, 1980).

Due to the relatively high silica content in GGBS, there is proven enhanced C-S-H formation relative to PC alone. This additional C-S-H occupies pore spaces, normally occupied by calcium hydroxide and thus leads to reduced porosity and permeability of slag hydrates (Bijen, 1996). The reduced porosity and permeability limits the volume of liquid in voids and this, together with the resultant stronger structure, provides resistance to frost damage.

The use of slag introduces sulphides mainly of iron and manganese into GGBS-Portland cement blends causing an early blue-green hue to appear on the surface (Kukko and Mannonen, 1982; ACI Committee Report ACI 226.1R-87, 1995; Bijen, 1996). The colour is a surface effect only and has no adverse effects, and it disappears as the sulphides oxidise to sulphates upon exposure to the atmosphere. The interior of the mix may however retain the colour for a considerable time, as observed in normal compressive test specimens when broken.

4.3 SLAG HYDRATION

The effectiveness of slag hydration depends on chemical composition of the GGBS; alkali concentration of the reacting system; glass content of the GGBS; fineness of the GGBS and temperature during the early phases of the hydration process. The initial reaction during slag hydration gives products which coat the slag grains, inhibiting further hydration reactions (Daimon, 1980). Therefore, slag used on its own hardly shows any hydration. Daimon studied the hydration of calcium alumino-silicate glass powders (C_2AS) and found that during their hydration, a low permeability coating low in calcium and of approximate composition ASH_6 and 0.2μm in thickness was formed on their surfaces. This coating liberated Al_2O_3 and SiO_2 on reaction with lime $Ca(OH)_2$. Similar observations were made by Caijun Shi *et al.*, (1993) on a Canadian slag of typical slag composition. He hypothesised that when GGBS contacts water, the Si-O, Al-O, Ca-O and Mg-O bonds on the surface of the glassy slag break under the polarisation effect of OH^- ions from water. Because the Ca-O and Mg-O bonds are much weaker than Si-O and Al-O bonds, more Ca and Mg enter into water than Si and Al, and a Si-Al-rich layer forms quickly on the surface of the slag. This layer may absorb some H^+ in the water, resulting in an increase of OH^- or pH of the solution. However, this concentration of OH^- still cannot break enough Si-O and Al-O bonds for the formation of significant amount of C-S-H, C-A-H or C-A-S-H and M-A-H. This is confirmed by Caijun Shi *et al.,* who found that even at 150 days only a small amount of C-S-H forms. For this reason therefore, utilisation of GGBS is based on its activation.

4.3.1 SLAG ACTIVATION

The rate of slag hydration can be influenced either chemically, mechanically or thermally (Regourd, 1980). In the current work, activation is chemical activation by the added lime and also sulphate. In chemical activation, an activator is required and/or an alkaline medium. In the case of blended Portland cements, although minor amounts of alkalis are released, the hydration of slag is mainly activated by the hydration product $Ca(OH)_2$ (Gjorv, 1989; Hakkinen, 1993; Bijen, 1996). Thus lime ($Ca(OH)_2$), may be added either as an additive or released from Portland cement hydration. Daimon (1980) reports very low optimum lime content requirement, of the order of 0.3wt.%, for activation of a slag containing 10wt.% gypsum. He observed that higher amounts retarded the activation. A similar retarding effect was applied by Douglas *et al.,* (1991) when he used a small quantity of hydrated lime (approximately 3wt.%) to retard the setting time of alkali activated slag concretes. Another group of activators include sodium sulphate (Na_2SO_4), potassium aluminium sulphate (alum ($KAlSO_4.H_2O$)), gypsum ($CaSO_4.2H_2O$), hemihydrate ($CaSO_4.5H_2O$), anhydrite ($CaSO_4$) and phosphogypsum.

According to Xuequan Wu *et al.,* (1990), Na_2SO_4 shows some of the best effects at early age, while alum is the best at later age. Xuequan Wu *et al.,* concluded that the relatively high activation by these activators is when they involve both alkali and sulphate activation. Numerous researchers agree on the fact that calcium sulphate, despite being used in accelerating the reaction of slag hydration, is not an activator but plays a special role as a powerful reactant (Taylor, 1990; Daimon, 1980). A reactant participates significantly in the reaction process while an activator creates a conducive environment for the reaction process without necessarily playing a significant role in the reactions. Sulphate activation using gypsum alone is extremely slow. Therefore, gypsum is normally used in conjunction with another activator, usually NaOH (Xuequan Wu *et al.,* 1990). The acceleration of hydration reactions by gypsum is probably because the ettringite formed in its presence provides a sink for the Ca^{2+} and $Al(OH)_4^-$ ions released from the slag.

4.3.1.1 Mechanism of activation

The activation of slag is a complex process involving structural disruption of slag with the formation of hydration products. The slag hydration will therefore depend on the ease of breakdown and dissolution of the glassy structure under the effect of OH^- and H_2O. During the activation process, the anions and cations play different independent roles. However, researchers like Shao-Dong Wang *et al.,* (1995) and Taylor (1990) are of the opinion that the anions play a somewhat more dominant role. For example, a solution of Na_2SO_4 may cause both sulphate attack and alkali-silica reaction (ASR). Daimon (1980) and Talling (1989) working on mechanism and kinetics of slag cement hydration and on alkali activation of slag respectively observed that the alkali metal ions serve as catalysts of slag hydrolization by the formation of a dispersed coagulation structure, and also as structure forming agents in the subsequent stages of development and strengthening of hydrate formations. Thus, as argued by Shao-Dong Wang *et al.,* (1995), the catalytic role is a process involving cationic exchange with Ca^{2+} cations. i.e.

$$\textbf{-A-O}^- + \textbf{X}^+ \longrightarrow \textbf{A-O-X} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \textbf{I}$$

where X is a displaceable cation such as Na^+ or K^+ from the activator present and A is Ca, Si or Al from the slag.

The alkaline activators thus accelerate the dissolution of Si and Al by breaking the Si-O, Al-O as well as the Ca-O bonds in the slag glass through the formation of the intermediate products (A-O-X) represented by equation I. Similar reactions involving breaking of Si-O, Al-O and Ca-O bonds occur in lime stabilised clay as discussed in Chapter 3. The dissolution leads to increased ionic concentration consisting among others of $[SiO_4]^{4-}$; $[AlO_4]^{5-}$; Ca^{2+} as well as the formation of intermediate X-S-H. The presence of OH^- ions further facilitate the adsorption of Ca^{2+} ions both from slag and/or any from lime and Portland cement, displacing the displaceable cation (X^+). i.e.

$$\text{-A-O-X} + OH^- \longrightarrow \text{A-O-X-}OH^- \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{II}$$

$$\text{-A-O-X-}OH^- + Ca^{2+} \longrightarrow \text{A-O-Ca-OH} + X^+ \quad \ldots\ldots\ldots\ldots\text{III}$$

The cations released again in equation III restore the basicity of the liquid phase. The products in this equation are precipitates of low-solubility hydrated silicates, aluminates and alumino-silicates of calcium and sometimes of magnesium as well (i.e. C-S-H, C-A-H, C-A-S-H and M-S-H). At the same time, in the alkaline environment provided by the slag activator, the precipitation of a (secondary) calcium compound takes place. i.e.

$$Ca(OH)_2 + XR + H_2O \longrightarrow XOH + CaR + \uparrow pH \quad \ldots\ldots\ldots\ldots\text{IV}$$

where X is a cation such as Na^+ or K^+ as previously defined and R is an anion such as OH^-, SO^{2-}_4, CO^{2-}_3 or SiO^{4-}_4.

The XOH in the above equation helps in maintaining the pH, enabling further reaction to take place. If SO_4^{2-} ions are also present, and if the pH is adequate (at least 11.7), the concentrations of Ca^{2+} and Al^{3+} ions are however reduced by the precipitation of ettringite. When the pH reaches approximately 12, the stability of ettringite is greatly enhanced and the hydration of slag is greatly accelerated (Xuequan Wu *et al.,* 1990). Xuequan Wu observed that in order to maintain active hydration of slag, it is necessary to supply sufficient OH^- ions, to create a high pH environment for breaking the slag glass network and for stabilising ettringite, and also sufficient SO_3 as well as alumina to continue the formation of ettringite. This may be achieved by adding certain kinds of activators containing these species.

From the above equations, cations play the role of intermediate structure forming components which maintain and balance OH^- anions before the formation of long term hydrates. The presence of excess of a calcium salt such as gypsum would be disadvantageous because it would decrease the alkalinity by the reversal of the vital equation I which uses alkali cations to break the A - O bonds (Shao-Dong, 1995). Lime, like gypsum, is not a simple activator but a main reactant as well. It activates slag by raising the pH, facilitating the dissolution of Al_2O_3 and SiO_2 from slag as well as providing extra Ca^{2+} ions. The reactions that follow are similar to those represented by equations I - III with the exception that there are no intermediate products (in the absence of other anions besides OH^-). Depending on the concentrations of both Ca^{2+} and SO_4^- ions (if present), the activation of slag may occur via the formation of ettringite.

4.3.2 HYDRATION PRODUCTS: THEIR STRUCTURE AND PROPERTIES

4.3.2.1 Hydration Products

When Portland cement hydrates, the principal hydration products are calcium hydroxide (CH) and calcium silicate gel (C-S-H). Those of the slag hydration are essentially similar but the quantities of CH are in varying degrees lower than those which would be given by the Portland cement (Regourd, 1980; Xuequan Wu *et al.*, 1990; Gollop and Taylor, 1996). Talling (1989), in his study of the effects of curing conditions on alkali activated slag, also observed X-ray diffraction spacings (d-spacings) similar to those belonging to C_4AH_{13}, suggesting the formation of C-A-H as well.

In addition to CH, C-S-H and C-A-H, ettringite is also a principal hydration product in Portland cement and also in slag-Portland cement blends, especially when high slag contents (80 - 85%) are used as in super-sulphated cement which includes 10 - 15% anhydrite and Ordinary Portland cement as an activator. The presence of $Ca(OH)_2$ even in small quantities creates a highly alkaline environment, suitable for Al_2O_3 and SiO_2 dissolution. These are liberated from the slag and/or any other source in the reacting system such as clay or Portland cement. In the presence of $Ca(OH)_2$, $CaSO_4$ reacts with Al_2O_3 to form ettringite.

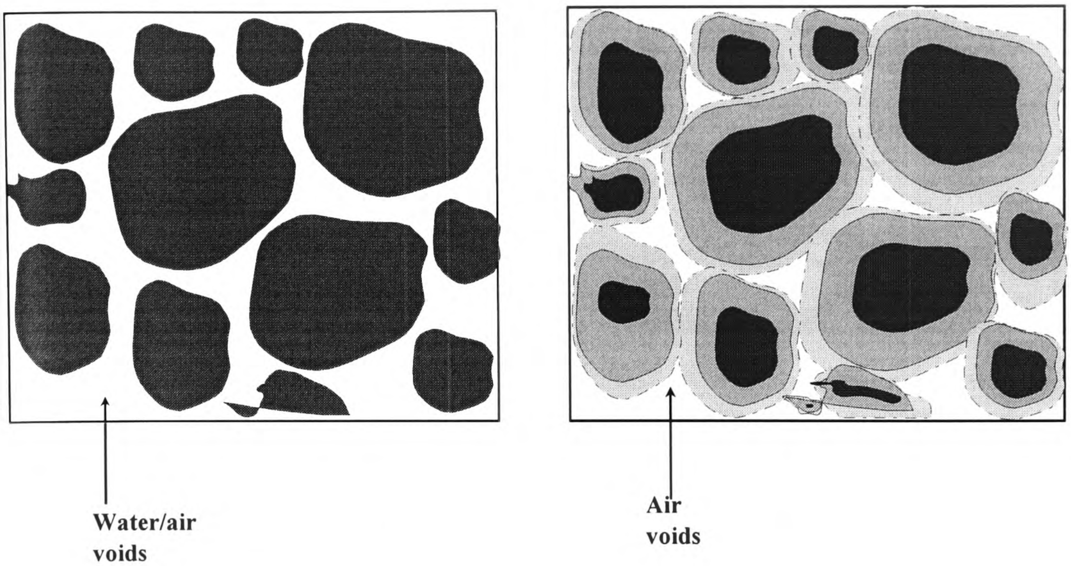
GGBS, due to its high alumina and silica content, produces somewhat more complex hydrates than OPC. By blending slag with GGBS-Portland cement, on hydration the formation of $Ca(OH)_2$ is reduced and a higher proportion of the main insoluble cementitious calcium silicate hydrates and calcium aluminate hydrates result (Xuequan Wu *et al.,* 1990).

When slag is activated by soda (NaOH), it gives C-S-H, C_4AH_{13} and C_2ASH_8, the same phases which are formed when lime reacts with metakaolin. When $Ca(OH)_2$ is the activating agent, as is commonly the case, C_2ASH_8 does not form as it is unstable in the presence of calcium hydroxide (Regourd, 1980). The C_4AH_{13} and C_2ASH_8 form hexagonal plates which play the role of crystalline bridges between slag grains. Some sodium may be bound by the hydration product, forming Na-substituted C-S-H or C-'N'-S-H (Shao Dong Wang *et al.,* 1995). In the presence of gypsum, and without alkali, the reactions lead to formation of C-S-H, ettringite ($C_3A.3CaSO_4.32H_2O$) and aluminium hydroxide ($Al(OH)_3$) (Regourd, 1980). Under these conditions, Regourd detected ettringite only after 15 days and lines of gypsum were still present at 28 days. Used with alkalis, Regourd (1980) observed early products, C-S-H fibres and ettringite, from the second day, at which time the gypsum was already consumed.

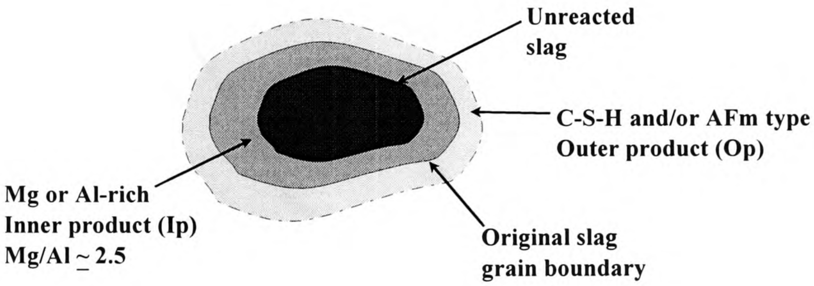
4.3.2.2 Structure and properties of hydration products

X-ray diffraction of hydrated alkali-activated slag (AAS) paste shows C-S-H of low crystallinity (Talling, 1989). The microstructural features in the slag/activator paste consist of a poorly crystallised hydrated layer, topo-chemically formed (i.e. on the grain surface) (Daimon, 1980; Regourd, 1980; Richardson *et al.,* 1994). This layer was referred to by Regourd as a "pseudomorphic" layer. Richardson *et al.,* (1994) adopted a combination of TEM and Si and Al NMR spectroscopy to study the hydration of a commercial blastfurnace slag and a synthetic slag glass paste. He found that the outer "pseudomorphic" layer of hydrates could be classified into an outer product (Op), formed in the pore water or solution-filled spaces, and an inner product (Ip) formed within the boundaries of the original anhydrous grains (See Figure 4.3-1 (b) and (c)). The outer product Op depends on the type and content of slag. It may contain C-S-H and/or AFm type phase and may be Mg or Al rich as Mg or Al-hydroxide phases.

GGBS hydrates are generally found to be more gel-like, than the products of hydration of Portland cement, and so add density to the cement paste (Smolczyk, 1980; Taylor, 1990; ACI Committee Report ACI 226.1R-87, 1995). Therefore, the hydration products of GGBS-Portland cement blends have a "pore-blocking" effect resulting in increased long term hardening of the cement paste (See Figure 4.3-2). The blocking of pores leads to higher strength and lower permeability (Macphee *et al.,* 1989, Bijen, 1996) which besides other improved binding and adsorptive effects, enhances resistance of GGBS concrete to attack from sulphates.

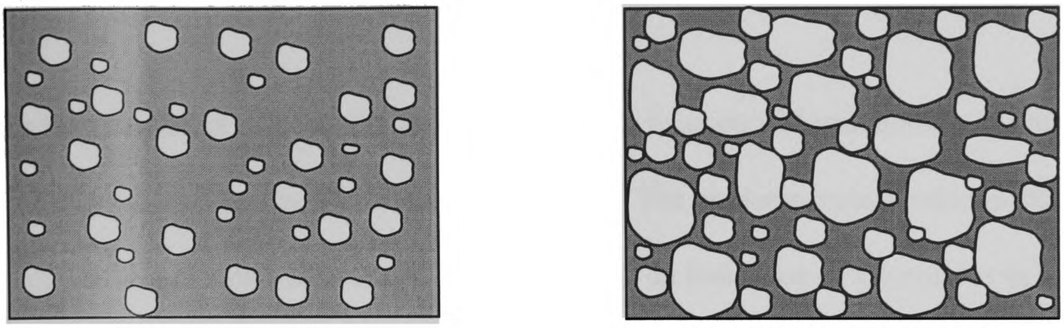


(a) UNHYDRATED SLAG (b) HYDRATED SLAG



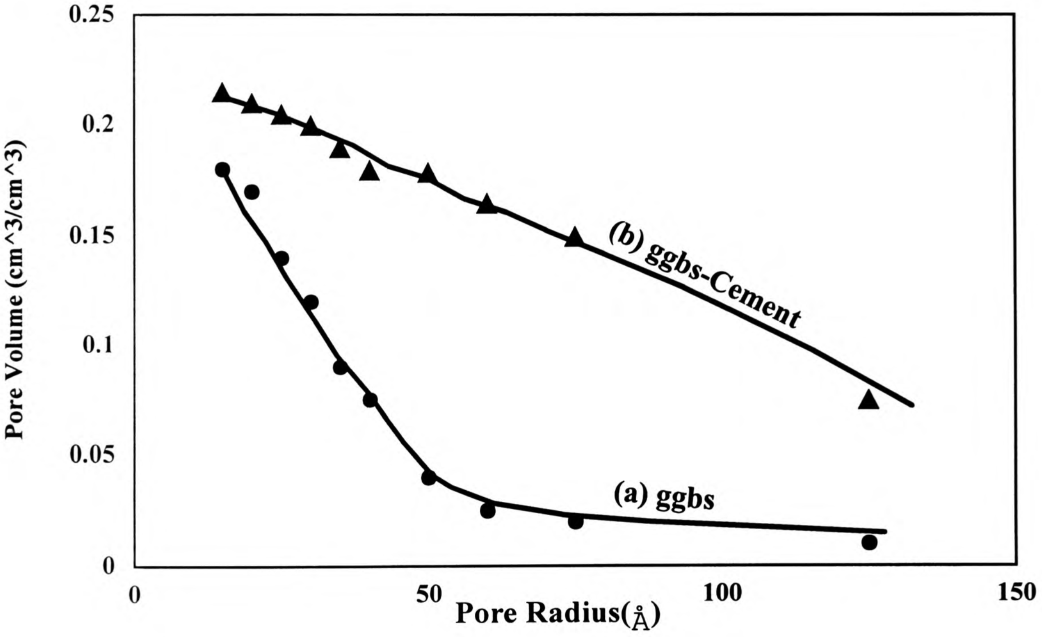
(c) SLAG HYDRATION PRODUCTS

Figure 4.3-1 - Schematic hydration of slag



(a) PORES IN SLAG HYDRATION

(b) PORES IN SLAG-CEMENT HYDRATION



(c) (adopted from Roy and Parker 1983)

Figure 4.3-2 - Pore size distribution of hydrated slag and 40% slag-60% Portland cement blend

4.4 CLAY-LIME-SLAG REACTIONS

The introduction of slag into the lime-clay hydration reaction will undoubtedly modify the lime-clay reaction products discussed in Chapter 3. The products include calcium silicate, aluminate and alumino-silicate hydrates. Currently, an indication of the manner in which these products may be modified by the introduction of slag can only be obtained from the previous findings on activated slag systems as virtually no previous work has been carried out on clay-lime-slag systems. The slag clearly provides additional alumina, calcia, silica and magnesia to the system, depending on the type and amount of slag.

The strength of slag-lime-clay mixtures is likely to be governed by the same factors observed in the slag-Portland cement blend hydration. These factors include properties of the C-S-H gel such as its amount, porosity and permeability; fineness of all reactants involved; temperature and curing time. The lime in the lime-clay mix will provide the required alkaline environment for slag activation and hydration. The observed increases in strength in GGBS-Portland cement blends are also likely to take place in slag-lime-clay mixes since the slag will introduce extra and more freely available alumina and silica, compared to the lime-clay system alone, enhancing the formation of the strength contributing silicates and aluminates.

4.4.1 PRESENCE OF SULPHATES

In the presence of sulphates in the soil, expansive reactions are likely to occur. Researchers have observed that the presence of $[SO_4]^{2-}$ ions in either Portland cement, GGBS or GGBS-Portland cement blends result in the formation of a potentially expansive system mainly through the formation and subsequent growth of ettringite (Mehta, 1972; Regourd, 1980; and others). According to Regourd (1980), in the presence of sulphate ions, the first hydrates formed around the slag grains dissolve and a second layer of hydrates of a rougher structure is formed which does not oppose the penetration of water. This encourages further reactions including sulphate attack similar to that of PC.

Although high alumina content, is associated with early strength, attack is exacerbated if the GGBS is high in Al_2O_3 (> 18wt.%) (Xuequan Wu *et al.,* 1990; Shao-Dong Wang *et al.,* 1995). In high alumina slag, more Al_2O_3 is liberated during hydration than in low alumina slag resulting in the potential for a greater amount of the expansive product ettringite to be formed. However, according to Gollop and Taylor (1996), materials made with slag cements tend to soften and disintegrate as a result of sulphate attack rather than expand, suggesting that decalcification tends to take place as opposed to expansive ettringite formation.

Wild *et al.,* (1993 and 1996) have worked on clay-lime systems with and without the presence of slag and/or gypsum. In lime-treated kaolinite clay in the presence of gypsum, they proposed a swelling mechanism which involves an osmotic process associated with initial nucleation and growth of ettringite crystals on the surface of clay particles. They also observed that clay-lime-slag-gypsum systems are likely also to be expansive as the principal reactants - $Ca(OH)_2$, SiO_2, Al_2O_3, SO_4^{2-} and H_2O are the same. However, Wild *et al.* observed that the presence of slag in clay-lime-gypsum systems lowered the expansion normally associated with ettringite formation in the system as reported in various case studies (Mitchell, 1986; Hunter, 1988; Snedker and Temporal, 1990; Abdi, 1992).

4.4.1.1 Sulphate Resistance

One method widely employed to prevent sulphate expansion in Portland cement based mortar and concrete and to prevent subsequent weakening due to decalcification of the C-S-H gel, has been to replace the cement by ground granulated blastfurnace slag. A similar method has been reported by Wild *et al.,* (1996) (as mentioned earlier) for the prevention of sulphate expansion in the case of clay-lime-gypsum systems by incorporating ground granulated blastfurnace slag (GGBS). When slag blended Portland cement paste is attacked by sulphates such as those of sodium and/or magnesium, the changes have been found to be similar to those found in normal Portland cement but in this case less gypsum is formed. The same kind of decalcification of the C-S-H gel by sulphates is shown to take place but to a lesser degree (Gollop and Taylor, 1996). The use of slag increases the consumption of lime, thus reducing the Ca^{2+} ions available to form gypsum and the expansive ettringite from the sulphate thereby increasing resistance to sulphate attack. Resistance to attack is favoured by use of high proportions of slags low in Al_2O_3. Surprisingly, Gollop and Taylor also suggest that the gypsum content in Portland cement blends may also be supplemented by additional calcium sulphate to enhance durability. The thinking behind this suggestion is that increased content of calcium sulphate in the blend will cause some of the aluminate to remain bound in ettringite from the very early stages of hydration and will therefore not be available to be "attacked" by sulphates from external sources at a later stage. This effect has been demonstrated by Gollop and Taylor (1996) for OPC-GGBS paste to which 5% gypsum was added. At relatively low pH (which can occur in a system in the presence of slag), ettringite is likely to form in relatively large crystals which are deposited in the material voids where they cause little or no expansive effect (Mehta, 1973; Gollop and Taylor, 1996). The hydration of the slag consumes more lime than it is producing (Lange and Mortel, 1995). At high slag contents, little or no ettringite is formed (due to consumption of lime), further increasing sulphate resistance. Therefore if lime in lime stabilised clay is progressively replaced by slag (as was done in the reported case by Wild *et al.,* (1996)), not only is the free lime content decreasing due to the replacement but also due to the lime-slag reactions. Thus as slag replacement levels increase there will be a systematic reduction in pH and ettringite will become less stable relative to gypsum and swelling will reduce.

The formation of ettringite as in Portland cement hydration or as in lime-stabilised clays in the presence of sulphates need not necessarily result in expansion and swelling. For example, although the hydration of slag in the presence of calcium sulphate is known, from work on super-sulphated cements (in which 80-85% of GGBS is blended with 10-15% of anhydrite and Portland cement is included as an activator (Taylor, 1990)), to produce C-S-H gel and ettringite, expansion is not a problem. In this case, the calcium sulphate is rapidly consumed (within a few days) and the slag particles provide nucleation sites on which well developed ettringite crystals form. The manner in which the ettringite forms is such that little expansion occurs.

4.5 FUTURE OF GGBS

There are currently, several attempts to find new ways to utilise blastfurnace slag (Wild *et al.*, 1996; Higgins *et al.*, 1997). With more research on its activation, the activated slag composites will give the construction industry new applications and formulations for better performance and more economic construction.

Because the basic understanding of the properties of GGBS have already been established, its future will more depend on how its economic activation and hydration patterns are developed. Thus,

- firstly, there is the problem of understanding the slag activity in detail. Similar slag glass contents and chemical compositions have been found to possess different reactivities. This is one of the most important problems in this field which must be resolved. Therefore, detailed work should be performed on the structure of glass. Activation of GGBS using natural minerals such as alum and other salts, mine wastes and/or activation based on chemical industrial waste by-products such as sodium sulphate may be an added economic advantage.
- secondly there are other major concerns which include lower early strengths, longer setting times and delayed swelling. The key to solving these problems lies in the activation of the hydration of slag at the early stages.
- thirdly, due to its slow hydration, a revised curing regime would have to be adopted, especially for use in situations where good control of moisture is difficult such as in highway construction. Otherwise, its use could lead to increased susceptibility to reduced formation of hydrates especially at early stages. Also, due to the slow

hydration, there would be the risk of carbonation and prolonged and/or delayed water consumption leading to loss in moisture.

Notwithstanding all the shortcomings, use of slag is greatly favoured by environmental considerations. Its use is therefore more likely to increase than decrease. Firstly, it is a by-product, thereby conserving the use of primary mineral resources, and secondly there are little or no energy considerations other than grinding and transportation as energy has already been expended in the blast furnace. As slag incorporation in PC has been in existence now for several decades, it would appear that there is a higher potential in its future applications in clay - lime systems for use in highway pavement construction than in any other foreseeable sector.

After reviewing clay soils in general and their possible stabilisation using lime and/or GGBS, the remaining chapters will now focus on the achievement of the main objectives outlined in Chapter 1. This focus will start in the next chapter with a detailed review of the materials used in the investigations.

CHAPTER 5 - MATERIALS

5.1 SOIL

5.1.1 KAOLINITE

Artificial soil mixtures have certain advantages over "real soil" in fundamental studies of soil behaviour (Sloane, 1965; Rossato *et al.,* 1992, Smith *et al.,* 1993). These include avoidance of problems posed by sampling, disturbance, material availability and inherent geological variability. Artificial batches prepared in the laboratory can be made homogeneous and can give properties that do not vary with time or from one batch to another. The use of artificial soil, however, has its disadvantages such as behaviour not typical of natural clays, especially in the mechanical properties which result from the artificial particle size distribution, mineral composition and soil geological history. For this reason therefore, it is desirable also to perform parallel studies on real soils.

Standardised (artificial or model) kaolin-based soils have been widely used in studies of soil behaviour and in physical model tests (Sloane, 1965; Rossato *et al.,* 1992, Abdi, 1992; Smith *et al.,* 1993). Sloane 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 used sand blended with pure kaolin commercially processed and distributed by Whitfield and Son Ltd. Stoke on Trent, England, U.K. The kaolin was distributed as "Speswhite" high plasticity fine china clay. Abdi used fine-grained kaolinite processed and distributed by English China Clay (ECC International Ltd. U.K) under the trade name "Standard Porcelain" while Smith used high grade commercially obtained kaolinite from Lewiston, Montana, U.S.A.

The principal advantages of kaolin for such studies include (1) its commercial availability, (2) the material's consistent microstructure for microfabric studies due to the relatively large clay particle size (Rossato *et al.,* 1992) and (3) the extensive data available from tests on kaolin soils. In the current study, industrial kaolinite, was used as a source of kaolinite. It was supplied by ECC International Ltd. St. Austell, Corwall, U.K., under the commercial trade name "Standard Porcelain", either as a white (china) clay with friable lumps (or agglomerates), or as a white powder, both consisting of 84% kaolinite, 13% mica, 1% feldspar and 2% other minerals. The lumpy clay was ground in the laboratory and used for the initial Proctor tests (these involve large volumes of material) to establish, approximately, the density and moisture content to be adopted for the preparation of specimens for other tests. The powdery version of the Standard Porcelain was on the other hand used for the more long-term and/or sensitive tests such as UCS, linear expansion and swelling pressure, that did not require large quantities of material. Unless otherwise stated, 'kaolinite' in the text refers to the powdery version of Standard Porcelain. Table 5.1-1 shows the particle size distribution of "Standard Porcelain" while Table 5.1-2 shows the chemical and mineralogical composition of the "as supplied" material from ECC International Ltd. Table 5.1-3 on the other hand shows the engineering properties of both the lumpy and the powdery Standard Porcelain, while Table A8-6 in Appendix 8 gives X-ray diffraction data of a typical kaolinite - Kaolinite-1A (Aluminium Silicate Hydroxide ($Al_2Si_2O_5(OH)_4$).

Table 5.1 -1 Particle size distribution of "Standard Porcelain" (ECC International Ltd., U.K., 1987)

Particle Size Distribution (%)		
Sieve Size	**Powdery Standard Porcelain**	**Lumpy Standard Porcelain**
> 53 μm	0.03	0.05 - 1.0
> 10 μm	4	10 - 20
< 2 μm	70	28 - 57

Table 5.1-2 Chemical analysis and mineralogical composition of "Standard Porcelain" (ECC International Ltd., U.K., 1987)

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 (L.O.I)	12.5
Mineralogical Composition	
Kaolinite	84
Micaceous material	13
Feldspar	1
Other minerals	2

Table 5.1-3 Engineering Properties of Standard Porcelain

Consistency Limits	
Liquid limit (%)	61
Plastic Limit (%)	32
Plasticity Index	29
Others	
Specific Gravity	2.57
Maximum Dry Density (MDD)(Mg/m^3) (Standard BS Compaction)	1.53
Optimum Moisture Content (%)	25
pH	4.6
Natural Moisture Content (%)	2.5

5.1.2 KIMMERIDGE CLAY

Some of the sulphate containing soils in the U.K include London Clay, Oxford Clay, Kimmeridge Clay and Lower Lias Clay. Kimmeridge Clay was chosen for this study for its proximity and recent use in the construction of the M40 Oxford - Birmingham Motorway. It was obtained with the assistance and permission of Oxford City Council from a site near Oxford. It occurred in two forms, one as a firm to stiff dark (or blue) grey clay and/or as a yellow grey (or brown) silty clay. The material was sampled 1 - 3 metres below the ground level. Borehole logs from this site report Kimmeridge Clay as occurring at depths between 0.5 - 9 metres below ground. The two types of clay mentioned above have been identified to be the same material, the change in colour being thought to result from localised weathering and oxidation (Littleton and Willavise, 1992). The clay also contains pyrite (Iron sulphide (FeS_2)) and fine crystals of selenite (gypsum). The results of chemical and mineral analyses of the Kimmeridge Clay were carried out by Frodingham Cement Company Ltd. and are shown in Table 5.1-4 below.

Table 5.1-4 Mineral phases in Kimmeridge Clay

Mineral	Chemical Formula
Quartz	SiO_2
Calcite	$CaCO_3$
Ankerite	$Ca,(Fe,Mg)(CO_3)_2$
Dolomite	$CaMg(CO_3)_2$
Gypsum (Selenite Crystals)	$CaSO_4.2H_2O$
Muscovite (Mica)	$(K,Na)(Al,Mg,Fe)_2(Si_{3.1}Al_{0.9})O_{10}(OH)_2$
Illite (Mica)	$(K,H_3O)Al_2Si_3AlO_{10}(OH)_2$
Dickite (Kaolin)	$Al_2Si_2O_5(OH)_4$
Anatase	+ Probable trace amount TiO_2

The presence of dickite, a type of kaolinite, is significant as it makes the comparison of test results with those of the model industrial kaolinite (which also contains mica as a minor phase) relevant, perhaps reducing the need for elaborate X-ray and/or electron microscopy comparisons between the two clays and/or their reaction products. Thus, a study using kaolinite for example might be expected to reflect the likely reactions in the Kimmeridge Clay and vice versa. The sulphate content of the Kimmeridge Clay (also determined by Frodingham Cement Company Ltd) is shown in Table 5.1-5 below.

Table 5.1-5 Sulphate content (wt.%) of Kimmeridge Clay

Total Sulphur	0.71 %
Sulphide (S^2)	0.02 %
Water Soluble Sulphate (SO_3)	1.41 %
Total Sulphate (SO_3)	1.73 %*

* *The total sulphate of 1.73 % SO_3 translates to 3.72 wt.% gypsum ($CaSO_4.2H_2O$). This sulphate level is within the range of those used in the kaolinite study (2, 4, 6, and 8wt.% gypsum equivalent to 0.93, 1.86, 2.79 and 3.72 wt.% SO_3 respectively).*

5.2 LIME

Hydrated lime under the trade name "Limbux" was supplied by Buxton Lime Industries Ltd. Buxton, Derbyshire, UK. Tables 5.2-1 and 5.2-2 show its physical properties and chemical composition respectively, while Table 5.2-3 shows its grading. The X-ray diffraction data for hydrated lime (Calcium hydroxide ($Ca(OH)_2$) and quick lime (Calcium Oxide (CaO)) are shown in Tables A8-7 in Appendix 8.

Table 5.2-1 Physical properties of lime (Buxton Lime Industries Ltd.).

Trade (or Product) Name	"Limbux" 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 5.2-2 Chemical composition of lime (Buxton Lime Industries Ltd.).

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

Table 5.2-3 Particle size distribution of lime (Buxton Lime Industries).

Size μm	% Passing
500	100.00
355	99.99
250	99.98
180	99.93
125	99.74
90	99.59
63	94.71

5.3 SLAG

Ground granulated blastfurnace slag (GGBS) was supplied by Civil and Marine Slag Cement Ltd. at Llanwern, Newport U.K. Table 5.3-1 shows its chemical composition and physical properties together with a typical composition for Ordinary Portland Cement for comparison.

Table 5.3-1 Chemical composition and physical properties of GGBS and a typical Portland cement (Civil and Marine Slag Cement Ltd., UK).

	Composition (%)	
Oxide	**GGBS**	**Portland**
CaO	42.0	63.0
SiO_2	35.5	20.0
Al_2O_3	12.0	6.0
MgO	8.0	4.0
Fe_2O_3	0.4	3.0
MnO	0.4	0.03-1.11
S_2	1.2	-
SO_3	0.2	2.3
Insoluble Residue	0.3	0.5
Specific gravity	2.9	3.15

5.4 CHEMICALS

The major chemicals used in the study were of reagent grade with a purity of at least 97%. They were calcium sulphate dihydrate ($CaSO_4.2H_2O$), magnesium sulphate ($MgSO_4$), sodium sulphate (Na_2SO_4) and potassium sulphate (K_2SO_4), all from either Aldrich Chemical Company, Gillingham, Dorset, England, U.K., or from Phillip Harris and Sons Ltd., Scientific Centre, Pentwyn, Cardiff, South Wales, U.K,. Other chemicals included silica gel, 'carbosob' and buffer solutions for pH meter calibration, all obtained from either of the above companies.

This chapter has identified and characterised the materials used in this work. The next chapter will look at the manner in which the various compositions of the two clay soils, the lime, the GGBS and the chemicals reviewed in this chapter were utilised. This will be achieved by focusing on the instrumentation and experimental procedures adopted.

CHAPTER 6 INSTRUMENTATION AND EXPERIMENTAL PROCEDURE

6.1 INSTRUMENTATION

6.1.1 LINEAR EXPANSION

Figure 6.1-1 shows the apparatus used in the measurement of linear expansion. It consisted of a 14-litre capacity glass tank of dimensions 360 mm length x 230 mm depth. The tank was supplied by Fisons Scientific Equipment Ltd. Loughborough, Leicestershire, U.K.

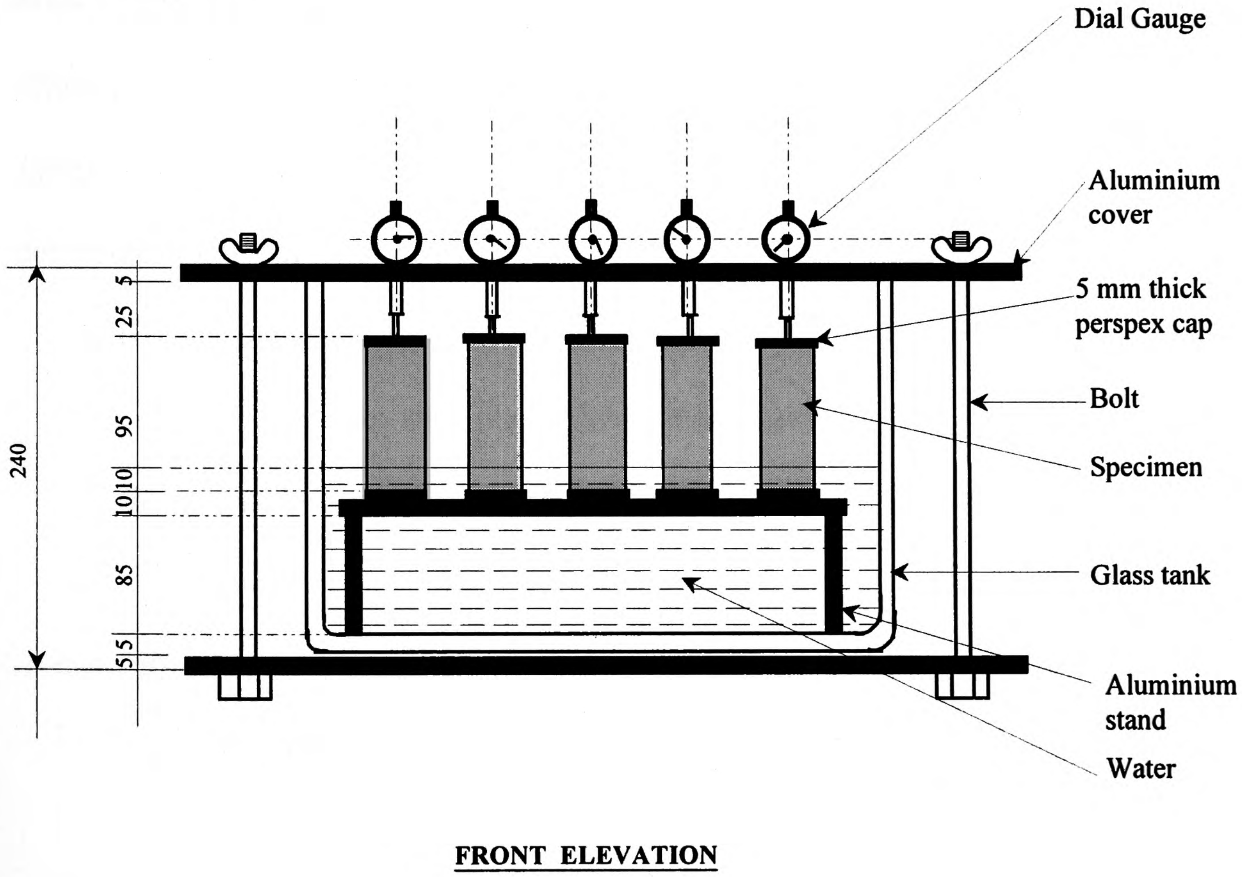


Figure 6.1-1 Chamber employed to monitor the linear expansion during moist curing and subsequent soaking at 30°C and 100% relative humidity.
(Not to scale; dimensions in mm.)

The glass tank was seated on an aluminium base plate and covered by a similar top plate fastened to the bottom plate by 6 No. steel bolts fitted with washers and nuts. On the top plate, twelve Batty CL1 dial gauges capable of measuring displacements of up to a maximum of 25 mm to the nearest 0.01 mm were fitted so as to enable a maximum of twelve soil samples to be monitored simultaneously. The samples were supported by an aluminium stand placed inside the glass tank.

6.1.2 SWELLING PRESSURE

6.1.2.1 Introduction

There is no standard method for arriving at the swelling pressure of soils (Sridharan *et al.*, 1986). From its definition (Chapter 2), it follows that swelling pressure may be determined by any of three methods :-

(i) Applying pressure to a soil sample such that neither swell nor compression takes place when it is inundated.

(ii) Holding a soil sample at its original volume by physical constraint and measuring the force required to continue doing so when it is inundated.

(iii) Allowing an inundated sample to swell and then recompress it back to its original inundated volume.

The first two methods have been widely used by various researchers (Agarwal and Sharma, 1973; Abdi, 1992 and others). In these methods, the consolidation test apparatus (oedometer) may be used conventionally, and also in other ways, to determine the swelling pressure. In the conventional manner, a specimen of known initial thickness and dry unit weight is allowed (on addition of water and under a seating pressure), to swell to an equilibrium position. Subsequently, loads are added in convenient increments to reverse the swell and the specimen is allowed to consolidate at each load. A plot is made of the volume change (δV) at the end of each consolidation stage (from the original volume at the equilibrium position) against the logarithm of the applied pressure (log P) (i.e. δV-log P curve). The swelling pressure is taken to be the applied pressure at zero volume change (i.e. the intersection of the extrapolated δV-log P curve and log P axis).

Another method of using the consolidation test apparatus involves continually controlling the volume of an inundated specimen by the continual addition of loads such that there is neither swell nor compression, and the specimen maintains its original volume. Eventually, the swelling pressure shows no further increase and is thus given by the ultimate applied load.

In yet another method, three or more identical specimens are placed in separate oedometers at identical initial load settings. The loads on the dry specimens are then increased to different loading levels and the systems allowed to reach equilibrium. Water is then added to the cells and the specimens allowed to swell and/or compress under the different loads, to produce different equilibrium void ratios. Interestingly, these equilibrium void ratios vary linearly with load and all plot in a straight line (Sridharan *et al.*, 1986). The intersection of this line with the line of zero volume increase represents the load under which the sample would not undergo volume change on saturation. The pressure equivalent of this load represents the swelling pressure.

A number of researchers in the past have measured swelling pressure of soil samples using essentially similar methods, which involve the use of an oedometer which confines the soil and restrains its movement. This has been done using a proving ring for load measurement, with or without fitting other attachments and without taking into account the deformation of the proving ring (Agarwal and Sharma, 1973; Abdi, 1992). The minute volume changes which take place during swell pressure measurements have in the past caused some concern since swelling pressures are very sensitive to the deformation of the soil sample (Escario, 1973). For this reason some researchers have taken special precautions to compensate for the proving ring deformation (Agarwal and Sharma, 1973). In all cases, the observed swelling pressure will depend on density, moisture condition, confining pressure, soil type and the pore solution chemistry as already discussed in Chapter 2.

One problem with all these tests is that they allow either small temporary or permanent volume changes and these can, depending on their reversibility and the elastic properties of the soil, provide stress relief and hence lead to reductions in the pressures finally observed. In the current work therefore it was decided to develop a system in which these effects would be either eliminated or greatly minimised. In this system the specimen was totally confined, and the pressure measured using a none displacement transducer (see Figure 6.1-2). Thus the only movement possible was the elastic distortion of the container and this was considered to be extremely small as discussed later in the next section. The use of membranes and diaphragms was avoided in order to avoid deformations that are hard to assess. The transducer system was equipped with a transducer excitation and conditioning (power supply)/visual display unit together with a multi-channel switch mechanism (8 channels) connected to the power supply/visual display unit to enable monitoring of eight samples simultaneously (Figure 6.1-3). In summary, the system generally consisted of three major units/parts:-

1) Restraining mould and housing frame.

2) Transducer.

3) Transducer conditioning/indicator unit

6.1.2.2 Housing Frame and Moulding

Cylindrical specimens were contained in thick walled cylinders of either perspex or brass which provided restraint to any lateral expansion (Figures 6.1-2 and 6.1-3). Various methods of restraining the sample were investigated in order to establish the system that would result in maximum pressure, while at the same time provide adequate restraining conditions (i.e. without lateral expansion). In all these cases, use of membranes as already stated was avoided to avoid hard to account for deformations. The variations tested are shown in Figure 6.1-4. They included :-

1) open ended 50 mm internal diameter, 100mm long perspex tube (5 mm thick walls),

2) perspex tube as in case 1) but closed at one end,

3) large diameter perspex tube (5 mm thick, 75 mm diameter, 100 mm long) open at one end.

4) open ended brass tube (10 mm thick walls and 50 mm internal diameter).

In cases 1) and 2), three Jubilee clips were fastened around the perspex tubes with the object of increasing the rigidity of the latter. The fastening was done with a Type 3 Black and Decker 9019 powered (3.6 V (DC), 180 RPM) screw driver. This ensured uniform fastening on all clips. The jubilee clips were positioned at regular intervals 20mm apart. The theory of thin walled cylinders was adopted to assess the degree of possible lateral deformations for restraining conditions using brass or perspex. Figure 6.1-5 shows a hollow cylinder with internal and external radii of a and b respectively. If we take a small element within the cylinder wall at radius r, and consider a case where pressures P_i and P_o are pressures applied at the inner and outer walls respectively (e.g. P_i applied by the soil sample and P_o applied by lateral restraining conditions on the outer wall of the cylinder such as jubilee clips), the theory of mechanics of thin walled cylinders gives the displacement of such an element. The displacement along the r-direction (u_r) and the radial and circumferential stresses (σ_r and σ_θ respectively) are given by equations I, II and III in Figure 6.1-5.

Figure 6.1-6 shows the variation of the radial displacement (u_r) under various lateral confining pressures (P_o), using the dimensions of the brass and perspex cylinders used in the current work, and at values of P_i within the anticipated soil swelling pressure range. The outer confining pressure (P_o) is obviously equal to zero except in cases where some restraint was provided by Jubilee clips. For analysis, Figure 6.1-6 uses five P_o levels (P_o = 0, 50, 100, 200 and 800 kN). In all cases, the displacements obtained were considered negligible (the deformation being within ± 0.04 mm). Since in practice the open ended perspex cylinders showed higher swelling pressures than the other systems investigated during trial pressure measurements (See Figure 6.1-4 (a)), and since these cylinders did not show any significant deformations (Figure 6.1-6), they were adopted in all swelling pressure measurements.

In order to hold the sample together with the sample restraining perspex, and also to restrain any vertical movement, a rigid steel and aluminium frame was used (see Figures 6.1-2 and 6.1-3). The frame consisted of two aluminium plates fastened with four steel bolts. Water was introduced to the sample via six 5 mm diameter holes arranged on a horizontal plane in a hexagonal pattern towards the lower end of the perspex cylinder, 10mm from the bottom plate. The resulting swelling pressure from the sample was transmitted to the transducer via 2 loading discs and a ball bearing.

6.1.2.3 Transducers: Selection and Specification

Transducer selection and specification was dictated by the swelling pressure initially anticipated. Agarwal and Sharma (1973), reported that when unstabilised clay soil is confined, particular soil types can exhibit considerable pressures of the order of 1000 kN/m^2. Abdi (1992), recorded a maximum swell pressure of 270 kN/m^2 on soil samples containing 6wt.% lime and 6wt.% gypsum. Considering that these samples were not fully restrained, it is not unreasonable, therefore, to anticipate higher swelling pressures similar to those recorded by Agarwal, when fully restrained stabilised soils are subjected to high levels of sulphate. Based on these facts, two Type 0234 trial soil stress compression pressure cells in the range 0 – 200 psi (0 – 1379 kN/m^2) were purchased from Kulite Sensors Ltd., Basingstoke, Hampshire, *UK.* Unfortunately, the transducer pressure sensitive area turned out to be only 25 mm in diameter (approximately half the sample diameter (51 mm), resulting in transducer pressure range reduction by a factor of 4.16. The transducers could only measure sample pressures of up to a maximum of 331 kN/m^2 (approximately 1/4 of the maximum range). The original transducers were therefore found unsuitable for the highly expansive systems, and transducers in the range 0 - 800 psi (capable of measuring maximum pressures from soil specimens of 1326 kN/m^2) were purchased. These transducers were, after laboratory re-calibration, found to be in the range 0 - 400 psi, capable of measuring up to maximum pressures of 663 kN/m^2 only. As these pressures were also soon exceeded, the transducers were returned to Kulite in exchange for others in the range 0 - 1000 psi (maximum specimen pressure of 1657 kN/m^2). Unfortunately these were also short-lived, (due to lack of robustness and rigidity), although they managed to give an indication of maximum swelling pressures encountered in the clay-lime-sulphate system under test as reported in Chapter 7.

The transducers required an activation direct current (DC) with a voltage in the range 7.5 - 10V in order to supply a maximum full scale output of 100 mV $\pm$ 1% at 20°C. They were suitable for use within the temperature range -15°C to 50°C. Being fluid filled, the diaphragm was supposed to exhibit virtually zero deflection under load. The basic sensing element was a silicon pressure transducer of, supposedly, high robustness and high output. The full properties of Type 0234 soil cells are given in Table 6.1-1.

6.1.2.4 Transducer Conditioning/Output Unit

In order to satisfy the power requirements of the soil cells, an EIRELEC 6000 Series strain gauge indicator/millivolt indicator unit was also purchased from Kulite Sensors Ltd. The unit was designed to operate on a 240 V power supply although this could be re-selected to 120 V if needed via a voltage selector located at the built-in transformer. The unit had a built-in 1.3 - 10 V DC excitation voltage supplied at 120 milliamps and was used to excite the transducers at a setting of 10 Volts (DC). Transducer connections were wired directly to 5-pin plugs via the 4-core shielded cables supplied with the transducers. The 5-pin plugs were compatible with any of the eight 5-pin sockets on an 8-switch box unit which was also fitted with a rotary channel selector. With this switch mechanism, the EIRELEC Series 6000 indicator/millivolt unit could power eight transducers. The extension cables in all cases were kept below a recommended 5 metre length in order to avoid gain errors. Figure 6.1-3 shows the arrangement for one soil sample (the entire arrangement can handle eight samples simultaneously), which includes the holder frame, transducer, indicator unit, and switch mechanism. Also indicated are possible future extensions including automatic data logging equipment and/or a PC for data access and/or manipulation.

Table 6.1-1 - Characteristics of Kulite Soil Pressure Cell Type 0234 *(Kulite Bulletin: KG-1000)*

Model	Type 0234 Soil Pressure Cell
Range (Psi)	
1st Batch	0 - 200
2nd Batch	0 - 800
3rd Batch	0 - 1000
Overpressure	2 Times Rated Pressure Range
Operational Mode	Compression
Pressure Media	Any Liquid, Solid (or some gases)
Rated Electrical Excitation	7.5V (DC) (Normal)
Maximum Electrical Excitation	12V (DC) (Maximum)
Input Impedance	750 Ohms (Normal)
Output Impedance	350 Ohms (Normal)
Full Scale Output	100 mV (Normal) ± 1% at 20°C
Resolution	Infinite
Operating Temperature	-15°C to 50°C
Compensated Temperature Range	0°C to 30°C
Humidity	100% Relative Humidity
Insulation Resistance	100 Megohms @ 50V (DC)
Case Material	Stainless Steel
Electrical Connection	4 conductor shielded polyurethane cable assembly in lengths up to 5 metres.
Weight	250g
Sensing Principle	4 Arm Strain Gauge Bridge

6.1.2.5 Transducer Calibration and Performance

In order to confirm the manufacturers transducer ratings, a local calibration was carried out. Here, known loads were applied to the soil pressure cells and transducer output (in millivolts) recorded from the EIRELEC Series 6000 power supply/output unit. A linear relationship exists between applied load (kN) and transducer output in mV as shown in Figure 6.1-7(a). From the applied load, the equivalent pressure on a 51 mm diameter sample could also be calculated (Figure 6.1-7 (b)). Using these calibrations, any subsequent transducer output (mV) was easily converted to the equivalent soil sample swell pressure.

6.1.2.6 System Operation

When exposed to water, the samples would tend *to* swell and the resulting pressure was transmitted to the transducer via a brass loading disc resting on the sample. Irrespective of the angle of contact between the contact loading disc and the sample, a uni-axial load would be transmitted to the transducer via the loading ball bearing separating the two brass discs. This uni-axial load would be distributed over the transducer sensitive area of 25 mm diameter and the pressure was read directly in millivolts from the visual display. The swelling pressure was determined from the transducer calibration (Figure 6.1-7). The calibration was obtained by carefully loading the transducers using an M30K JJ Instruments testing machine and recording the applied load (in kN) and the transducer output (in mV) from the indicator unit (Figure 6.1-7(a)). The extra loading due to discs 1 and 2 together with the ball bearing (see Figure 6.1-2), whose total weight of 193 g contributed to an excess pressure of 0.95 kN/m^2, was added to the applied load and by dividing the total applied load by the area of the sample, the pressure on the soil sample would be obtained, hence the callibration chart in Figure 6.1-7(b).

Eight separate specimens could be monitored simultaneously and the system is expandable to incorporate data logging and/or other computer peripherals. It was deliberately made simple to reduce functional errors but to be highly sensitive to pressure changes, depending on the individual transducer sensitivity. The sensitivity and accuracy of the transducers reduced with increasing transducer range. The system was specifically designed to measure swelling pressures for samples of dimensions 50 mm in diameter and 100 mm in length and would mainly be suitable for remoulded samples. For undisturbed samples taken from the field, the same frame may be used together with conventional 50 - 54 mm in-situ soil samplers. A modified frame may be adopted for other sizes of undisturbed samples. More threads may also be incorporated on all the four bolts. All tests were conducted at a constant temperature, in a temperature controlled West 2000 environmental chamber, to avoid variations in pressure due to temperature variations.

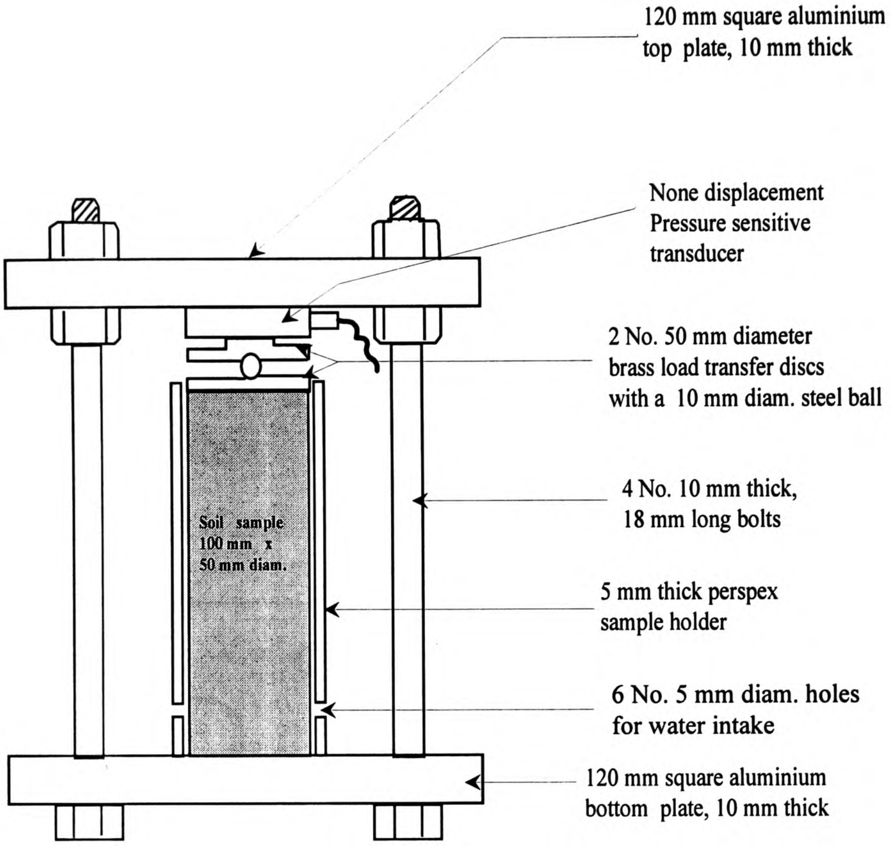


Figure 6.1-2 - Soil sample Retaining Frame and Mould, Transducer and Loading Plates.

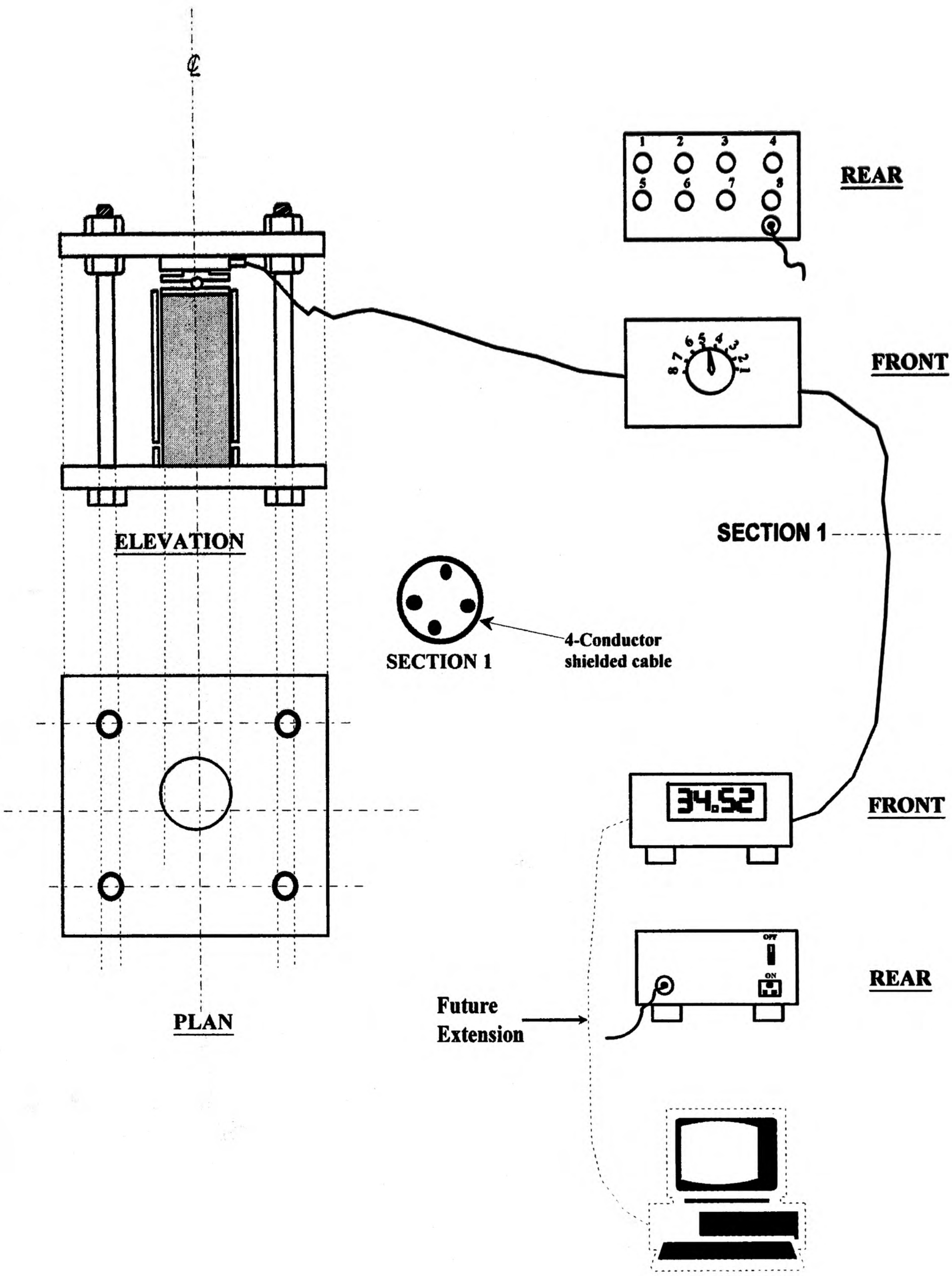


Figure 6.1-3-Arrangement of soil sample, holder frame, transducer, indicator unit and switch mechanism.

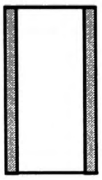
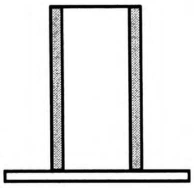
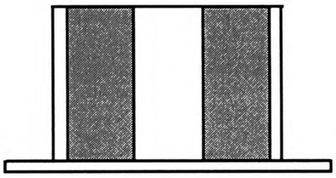
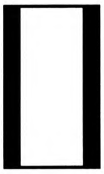
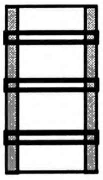
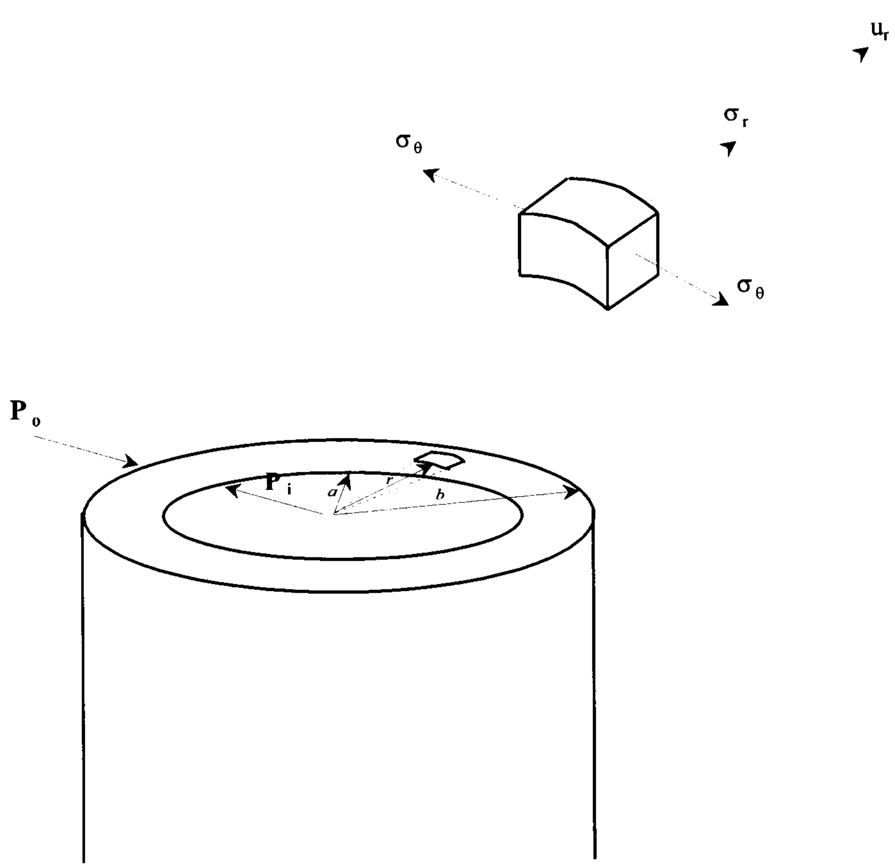
			TRIAL PRESSURE (kN/m^2) (at 2wt.% MgSO$_4$)
(a)		OPEN PERSPEX	342
(b)		CLOSED PERSPEX	334
(c)		SAND AND PERSPEX	187
(d)		OPEN BRASS	161
(e)		OPEN PERPEX WITH JUBILEE CLIPS	156

Figure 6.1-4 - Variations in restraining conditions



$$u_r = \frac{r}{E}\left(\frac{a^2}{b^2 - a^2}\right)\left[(1-\nu)+(1+\nu)\frac{b^2}{a^2}\right](P_o - P_i)\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{I}$$

$$\sigma_r = \frac{a^2}{\left(b^2 - a^2\right)}\left(1 - \frac{b^2}{r^2}\right)(P_o - P_i)\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{II}$$

$$\sigma_\theta = \frac{a^2}{\left(b^2 - a^2\right)}\left(1 + \frac{b^2}{r^2}\right)(P_o - P_i)\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{III}$$

Where:-

E = Young's modulus of restraining cylinder material (≈3.3 kN/mm^2 for perspex and ≈101 kN/m^2 for brass)

ν = Cylinder material Poisson's ratio (≈ 0.35 for both brass and perspex)

Figure 6.1-5 - Thin walled cylinder theory

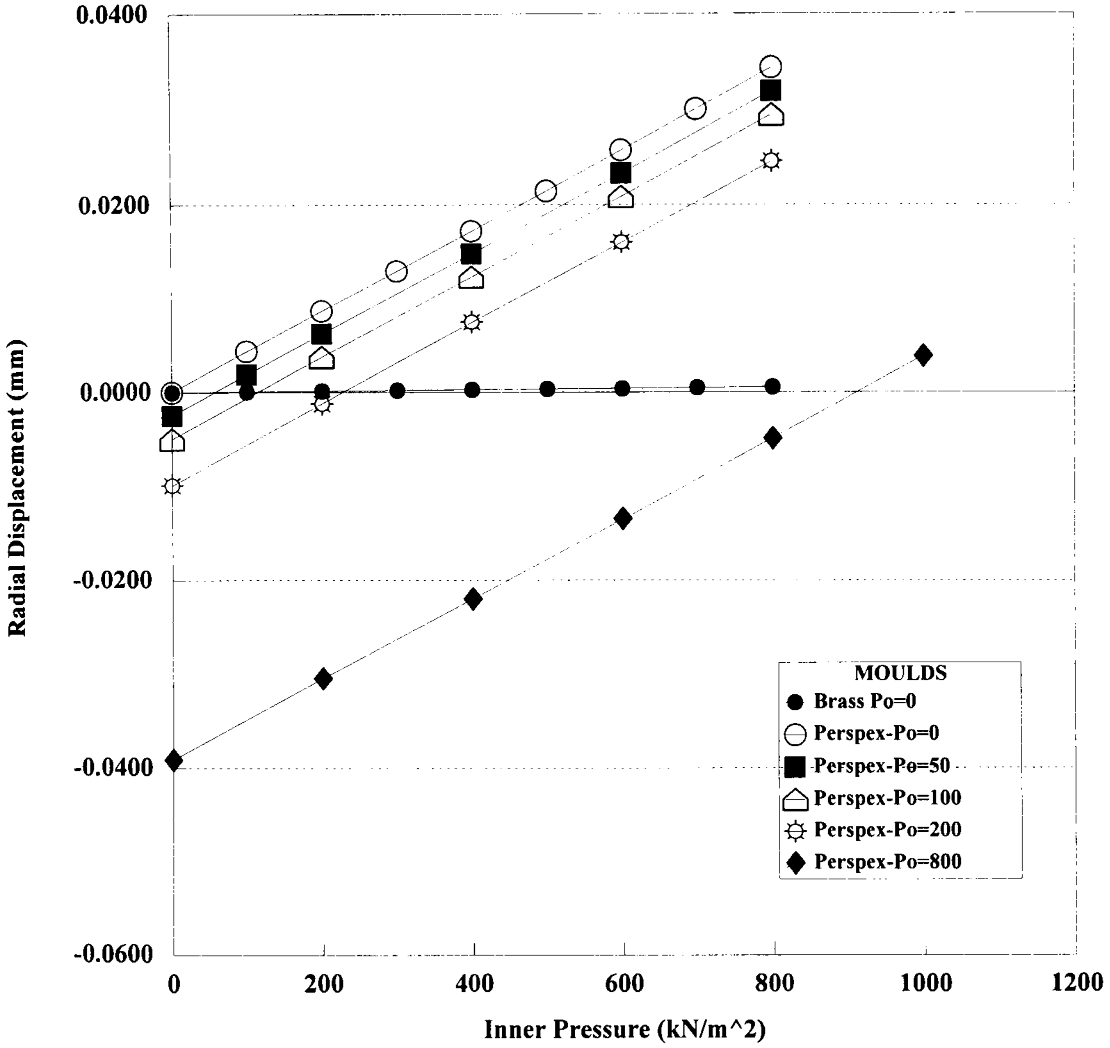


Figure 6.1-6-Radial displacement vs. Inner pressure of stressed perspex and brass moulds at various inner and outer pressures Pi and Po

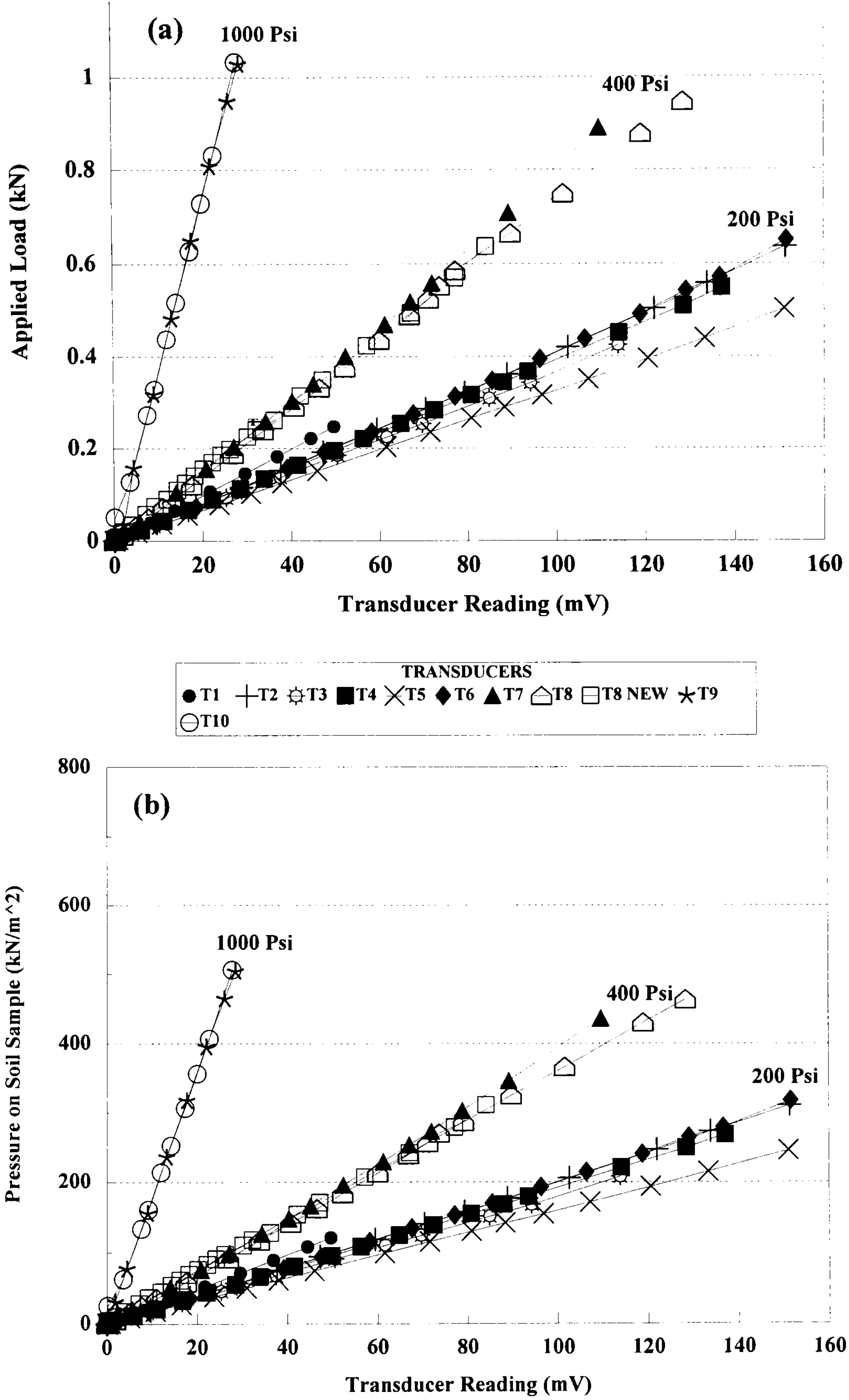


Figure 6.1-7 - (a) Applied Load (kN) vs. Transducer reading (mV)
(b) Pressure on 51 mm Diameter soil sample (kN/m^2) vs. Transducer reading (mV).

6.2 EXPERIMENTAL PROCEDURE.

6.2.1 CONSISTENCY LIMITS

6.2.1.1 Liquid Limit

The consistency limits tests were carried out in accordance with BS 1377 (1990) Part 2 - Classification tests (Tests 4(LL) and 5 (PL)). For materials that were either fine or water soluble (such as lime, kaolinite and the various sulphates), no sieving was done. In the case of Kimmeridge Clay, the material was first air dried for several days, ground, and then sieved through a 425 μm sieve as required by BS 1377 (1990). Normally, the consistency tests were performed in accordance with BS1377 (1990) (British Standard Methods of test for soils for civil engineering purposes) and without any mellowing period (a period ranging from 24 - 72 hrs (1 - 3 days) during which the wet material is left to mix with the water much more effectively) being allowed, the test being done within five hours of initial water addition. It should be noted that mellowing is not a universal procedure and is mainly practiced in the United Kingdom. However when it became apparent that field trials, which were to be conducted in accordance with the British practice of mellowing were likely using gypsum as the sulphate, it was found inevitable to study the effects of mellowing. Thus, mellowing tests were only conducted in the kaolinite - lime - GGBS and Kimmeridge Clay - lime - GGBS systems using gypsum and in accordance with BS 1924 (British Standard Methods of test for lime stabilised soils for civil engineering purposes). The mixed material was placed in sealed polythene bags and kept in an environmental chamber for 3 days (72 hours) at 30°C and 100% relative humidity.

During testing, a small amount of water was first added to the dry soil and the material thoroughly mixed into a fairly hard plastic mass. A small amount of this material, approximately 100 g was set aside for the determination of the plasticity index later. Some of the remaining material was then used to fill a brass cup (56 mm in diameter and 41 mm deep) in accordance with BS 1377 (1990). A metal cone (of angle $30 \pm 1^{\circ}$ and 35 mm in height) was allowed to penetrate into the material's surface for 5 seconds (automatically timed by an attached electrical timing device). After 5 seconds, the penetration of the cone was automatically stopped by a locking mechanism incorporated in the penetration apparatus and the penetration of the cone determined by a scale and dial pointer attached to the cone. The penetration was recorded and a small amount of material taken within the zone of penetration, for moisture content determination. The moisture content was determined in accordance with BS 1377 (1990) using the oven drying method. After removal of material for the determination of the moisture content, the residual material in the cup was mixed with the rest of the sample and more water added. Further penetration tests, together with their corresponding moisture contents, were performed so as to obtain at least five set of points in the penetration range 5 - 30 mm. The liquid limit was taken as the moisture content corresponding to a penetration of 20 mm, from a graph of penetration (in millimetres) against moisture content (%).

6.2.1.2 Plastic Limit

In order to determine the plastic limit, material set aside after initial mixing during liquid limit determination was gently rolled on a flat plastic plate into rods and rolling continued until the rods crumbled when they were of approximate diameter of 3 mm. Rods thinner than this would indicate a mix wetter than the plastic limit while crumbling at thicker diameters normally indicates drier conditions. When the desired crumbling occurred, a few crumbs were taken for moisture content determination. This moisture content (at which the clay crumbles into rods of 3 mm in diameter) is defined as the plastic limit of the material. From the liquid limit and the plastic limit, the plasticity index of the material was obtained as the difference between the two limits.

6.2.2 INITIAL CONSUMPTION OF LIME (ICL)

Clay portions weighing 20.0g were placed in six conical shaped flasks fitted with corks. To five of these flasks, 2, 3, 4, 5, and 6wt.% of calcium hydroxide (expressed as a percentage of the weight of the clay) was added. To the sixth flask, no lime was added and to a seventh flask only 20.0g of lime were added. 100 ml of de-ionised water was added to all the seven flasks and each shaken manually for 30 seconds every 10 minutes for one hour. The pH of each of the solutions was then determined using both an analogue 7020 Electronics Instruments Ltd. pH meter and also using a digital 3020 Jenway pH meter, fitted with a 4025 Jenway clock and printer device.

BS 1924 recommends a temperature of 25°C for pH determination and reporting, and suggests a pH temperature correction viz.:

$$pH_{25} = pH_T + 0.03(T - 25)$$

where pH_{25} = pH at 25°C

pH_T = pH at the prevailing temperature.

T = Prevailing temperature (°C).

The above temperature correction was applied to all pH readings taken at a prevailing temperature of 22°C. A further calibration was done based on the pH value of 12.4 (pH of pure lime solution).

6.2.3 COMPACTION

Compaction tests were used to determine the maximum dry density (MDD) and the optimum moisture content (OMC) of various systems containing combinations of clay, lime, sulphates and GGBS. The maximum dry density and optimum moisture content were later used for the preparation of samples for unconfined compressive strength (UCS) determination, linear expansion, weight gain upon soaking and swelling pressure measurements. Mixing of the dry materials and of the dry materials with water was done using a Model SE-401 Hobart 40 Qt mixer. British Standard (BS) 1377 (1990) compaction (Proctor) test procedure was used for compaction. In this test compaction was achieved by dynamic compaction using an automatic Proctor/CBR compaction machine. The material was compacted in three equal layers in a mould of dimensions 105 ± 0.5 mm in diameter and 115.5 ± 1 mm in height, each layer being subjected to 27 blows using a

2.5 kg rammer. After weighing the mould together with compacted materials a small amount of material was taken for moisture content determination. A five point dry density-moisture content curve was used to determine the maximum dry density and optimum moisture content.

The first series of compaction tests was to determine the compaction properties of the basic raw materials - both unstabilised kaolinite and Kimmeridge Clay. Secondly, tests were carried out to determine the proctor compaction properties of the two clays upon stabilisation with varying amounts of lime. From these compaction tests using the stabilised clay soils, the maximum dry density and optimum moisture contents obtained at the initial lime consumption level (ICL) were used as the control compaction values. Mixes containing these lime levels were also taken as control in subsequent works such as tests for unconfined compression strengths and for linear expansion. Thirdly, compaction tests were performed using the kaolinite-6wt.% lime (control mix) with varying amounts of the sulphates - calcium sulphate ($CaSO_4$), magnesium sulphate ($MgSO_4$), sodium sulphate (Na_2SO_4) and potassium sulphate (K_2SO_4) (i.e. 0.93, 1.86, 2.79 and 3.72% SO_3) in order to establish the effects of various amounts of sulphates on the proctor compaction parameters. The last series of compaction tests were performed with lime-stabilised control mixes for the kaolinite and Kimmeridge Clays containing varying amounts of GGBS. For the case of kaolinite, kaolinite - 6wt.% lime mixes were compacted in the absence of and containing 6wt.% gypsum (2.79% SO_3) and with the lime gradually substituted with GGBS. For the Kimmeridge Clay, 5wt.% lime was gradually substituted with GGBS. No gypsum was added as the clay naturally contained 1.73% SO_3 (in the form of approximately 4% selenite (gypsum) crystals).

6.2.4 SAMPLE PREPARATION

For the purpose of sample preparation, it was found necessary to establish a target dry density and moisture content values so that density would be maintained for all samples and for all sulphate types and contents used. In the kaolinite - lime - sulphate system, the lowest observed MDD was 1.378 Mg/m^3 using $MgSO_4$ and the highest was 1.490 Mg/m^3 for the control mix (using 6wt.% lime). With these two extremes, a mean MDD value of 1.41 Mg/m^3 was adopted for all mixes. Likewise for OMC, the lowest recorded was 24.8 % using the control mix while the highest was 30 % using 6% magnesium sulphate. A mean value of 27% was adopted for all mixes. Similarly for the kaolinite - lime - GGBS - gypsum and Kimmeridge Clay - lime - GGBS systems, a mean dry density value of 1.41 Mg/m^3 for both systems and mean moisture content values of 30 and 24% were adopted respectively.

Using these mean values, dry materials, enough to produce three compacted cylindrical test samples of dimensions 50mm diameter and 100mm length, were thoroughly mixed in a variable speed Kenwood Chef 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 prescribed dry density and moisture content. The pre-fabricated mould ensured that the material was not over compressed. Compaction was achieved using a hydraulic jack and a mould ensuring no further compaction was subjected to the soil once the desired volume had been attained. The densities would therefore be the same as would be obtained using the standard proctor test since the dry density and moisture content remain constant. The cylinders were extruded using a steel plunger, trimmed, cleaned of releasing oil, weighed, measured and wrapped in several runs of cling film. The cylinders were labelled and placed in polythene bags before being placed on a platform in sealed plastic containers. Water was always maintained below the platform to ensure that there was no evaporation from the samples. The plastic containers were then placed in an environmental chamber capable of maintaining temperatures to ± 1°C and humidity to ± 2% relative humidity. The samples were moist cured for various curing periods ranging from 1 to 20 weeks at 30°C and 100% relative humidity. Appendix 1 shows the material quantities using mean values of MDD, OMC and known mould (hence sample) volume. Samples were therefore expected, within experimental error, to be of the same density, volume and moisture content for all the material compositions in a given system.

6.2.5 UNCONFINED COMPRESSIVE STRENGTH (UCS)

At the end of the prescribed moist curing periods, samples were removed from the environmental chamber. Any surface moisture on the cylinders was removed with paper tissue, prior to their being weighed. In most cases, two cylinders per mix proportion were subjected to unconfined compressive strength (UCS) tests. A third test was sometimes necessary especially when the strength variation in the first two tests differed by more than 10% of the mean strength. Before testing, the end surfaces of samples to be tested were gently abraded to ensure a flat surface and 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 1mm/min. After testing, a small quantity of material was taken from the interior of the tested sample for moisture content determination to establish the moisture condition at the end of each curing period.

6.2.6 LINEAR EXPANSION

Samples to be tested for linear expansion were placed on a platform in a glass tank and covered with a lid fitted with dial gauges and containing some water below the platform. (see Figure 6.1-1). This process which was termed moist curing was done as soon as the samples were fabricated. After moist curing for 7 days, the cylindrical samples were partially immersed in water to a depth of 10 mm above their base by simply increasing the water level in the tank with a siphon to ensure that disturbing the specimens was kept to a minimum. This process was termed soaking. During both moist curing and soaking, the tank was contained in an environmental chamber where conditions were maintained at 30°C and 100 % relative humidity. Axial linear expansion during moist curing and during soaking was monitored on a daily basis until no further significant expansion occurred. The samples were unrestrained other than the thin layer of cling film around them. Both the moist curing and the soaking environments were sealed systems in order to reduce the availability of carbon dioxide that would otherwise cause carbonation of the lime. Clearly excessive carbonation of the lime would reduce the amount of lime available for pozzolanic reaction and is therefore undesirable.

6.2.7 SWELLING PRESSURE MEASUREMENTS

Samples used in the determination of swelling pressure were prepared in the same manner as those used for UCS, those for linear expansion and those for weight gain upon soaking. The samples were placed in open ended perspex tubes and both sample and perspex were placed at the bottom plate of the sample holding frame (Figures 6.1-2 and 6.1-3). The brass loading plates and the ball bearing were placed in position, the transducers were put in place and the top plate was fastened down using the four steel bolts. The entire arrangement was placed in two layers of polythene bags in the environmental chamber to avoid evaporation and a small amount of water placed at the bottom of the sample frame to maintain a relative humidity of close to 100%. The bags were then sealed and the transducer lead wires coming out from the bags were fed through a hole at the side of the environmental chamber and connected to the monitoring system. The samples were allowed to cure at 30°C for 7 days while monitoring the swelling pressure that developed under the restraint. Readings were taken on a daily basis and on the seventh day the samples were flooded to cover the holes on the perspex and readings were continuously taken until no further swelling occurred, taking care not to exceed the transducer loading limit. Once the maximum swelling was attained (or the transducer limit approached), the assembly was dismantled and the procedure repeated for other mixes.

6.2.8 ANALYTICAL TECHNIQUES.

6.2.8.1 Introduction

In the study of materials, it is frequently necessary to observe, analyse and explain phenomena occurring on a micrometre or sub-micrometre scale. Various analytical methods are now available for identification, qualitative, quantitative and micro-structural (morphological) studies of organic and inorganic materials. In the current work, X-ray powder diffraction and scanning electron microscopy were used to provide some indication of the principal reaction products. The following sections give a brief description of the underlying theory and outline the type of instrumentation used. The scope of the current work dictates that only an overview of the main practical aspects need be included.

6.2.8.2 X-ray diffraction

Analytical methods using X-rays belong to a wider range of analytical techniques referred to as spectroscopic analysis. Spectroscopy is the study of transitions of a system (usually an atom or a molecule) between its states of defined energy (Howath, 1973). Most microstructural analysis procedures involve the production of electrons (electron microanalysis), their acceleration to high speed so as to impinge on a small specimen on the electron beam's pathway and the study of the properties of the spectrum of electrons backscattered by, or transmitted through, the specimen. When a static or dynamic finely focused electron beam is aimed at the surface of a specimen, a wide range (or spectrum) of electrons and other emissions is released due to variations in energy states. There is a wide range of energy states and various types of spectroscopy exploit any one of these energy states. The properties of the spectrum released when electrons impinge on a specimen bear large amounts of qualitative and quantitative information on the specimen. This whole range of information possessed by this electron spectrum may be used in different methods to obtain composition, surface topography and crystallography details of the specimen. The spectrum may be made of characteristic X-rays, backscatterred electrons, auger electrons, secondary electrons and photons (See Figure 6.2-1).

When the electron beam is static, the area of beam focus is studied (or probed). Methods using this technique are referred to as electron probe micro-analysis (EPMA) and form a good quantitative technique (Bland *et al.,* 1991). When the beam is swept (or scanned) across the specimen, the properties of the electron spectrum bear the properties of the region of specimen scanned. These properties vary as a result of differences in surface topography as the electron beam is swept across the specimen. This method of probing is referred to as scanning electron microscopy (SEM). When thin sections of material are used, it is possible, using transmitted electron microscopy (TEM), to measure the energy loss when the electrons are transmitted through the section. These transmitted electrons bear characteristic specimen details.

In the current work, only X-ray and SEM methods were used for the observation and characterisation of clay and other minerals as well as for pozzolanic and other reaction products. X-ray Diffraction (XRD) methods were used in the kaolinite - lime - sulphate system (using the sulphates of calcium, magnesium, sodium and potassium) and also in the kaolinite - lime - GGBS - gypsum system. Scanning electron microscopy (SEM) methods were used in the latter system only. The results of these analyses are reported in Chapter 7.

The use of X-rays in the identification of clay minerals started in the early 1930's with work by Pauling, Ross, Kerr *et al.,* Their use is based on the fact that each crystalline substance has its own characteristic atomic structure which diffracts X-rays in a characteristic pattern (Barr *et al.,* 1995). Recognition of this pattern establishes the diffracting substance. Used in materials science, the method is useful for the confirmation and/or identification of crystalline products. Complete absence of diffraction lines indicate amorphous substances. The method may be used for phase identification and to give a quantitative indication of phase content.

X-ray diffraction may be represented by Bragg's law represented by equation I. From Figure 6.2-2, a beam of X-rays is assumed to be reflected from parallel crystal planes spaced d units apart. Considering rays 1 and 2, ray 2 will travel an additional path of length ABC. From Δ ABD, AB = d.Sinθ. Where d is the interplaner spacing of the crystal (d-spacing) and θ the angle of incidence of the X-ray on the crystal. Consequently, length ABC = 2d.Sinθ. Since the distance between the two rays AD = DC = AB = f(λ) say AB = nλ where n is an integer (1, 2, 3, etc.), and λ the X-ray wavelength, then

$$\mathbf{n\lambda = 2d\sin\theta} \text{ (Bragg's law).}$$

There are certain advantages in using X-ray analysis over many other procedures. Firstly, only small amounts of the substance are required. Secondly the test is non-destructive. The

X-ray method is however limited in application because it is inapplicable to amorphous and glassy substances. Also, structural similarities between many clay minerals, such as cases where the aluminium in the clays is replaced by magnesium and/or iron or where the silicon in the tetrahedral layers is replaced by aluminium, are difficult to distinguish by this method. Saponite, for example, is the clay mineral (with an expanding lattice) formed when there is total replacement of aluminium with magnesium while nontrorite is a similar replacement but with iron. The American society for testing of materials (ASTM) have produced an index method which helps in arriving at identifications using d-spacings. More recently however, computer packages are available to do the same, making the identification of substances (and hence use of X-rays) much easier and quicker.

In the current work, XRD analysis was conducted on both the kaolinite-6wt.%lime-sulphate system using four sulphates - gypsum, magnesium sulphate, sodium sulphate and potassium sulphates, as well as on the kaolinite - lime - GGBS - gypsum system. Work on the kaolinite - lime - sulphate system was conducted (on 26 samples) at the R and D Centre of English China Clays (ECC) International, St Austell, Cornwall, England, using a Philips PW 1825 X-ray generator and CuKα radiation. 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.

XRD work on the kaolinite-lime-GGBS-gypsum system was carried out at the Department of Mechanical, Materials and Manufacturing Engineering, University of Newcastle, Newcastle upon Tyne, *UK.* using a Phillips diffractometer PW1965 and generator PW1730, a graphite monochromator and CuKα radiation of wavelength (λ) of 1.54179Å. The 1 and 4 weeks moist curing periods of specimens used for XRD work were selected to coincide with the curing periods used for the determination of the unconfined compression strength. The work was aimed at establishing the influence of ground granulated blastfurnace slag (GGBS) either as additional to, or as a substitute for the lime present in the system. Specifically, it was aimed at establishing the reasons behind the observed lowering (and sometimes total elimination) of swelling potential with no adverse effects on strength. The work was done with the GGBS progressively substituting the 6wt.% lime and with the gypsum fixed at either 0 or 6wt.%. As this was not a major component of the overall research, samples were cured up to a maximum of 4 weeks only.

6.2.8.3 Scanning electron microscopy (SEM).

Electron microscopy is also a powerful tool for materials analysis and can complement XRD. While X-rays can only confirm and/or identify the presence of crystalline substances, scanning electron microscopy can be used to examine the micro-structure of specimens and to determine particle crystallinity. The method may also be used to characterise as well as (sometimes) identify (though difficult) particular phases and their shape and form. SEM has the advantage of giving 3-dimensional images with superior depth of focus and resolution capabilities as compared to optical micrographs.

SEM mainly uses the secondary electrons released from the specimen. In this method fragments of a specimen are fixed onto sample holders using a conductive adhesive. They are then vacuum dried and coated with another compound, in the current work evaporated gold (≈ 10 - 20 nm thick). Electrons are then generated and accelerated using a potential of 40 - 100 kV in steps of say 20 kV and the electron beam focused onto the specimen. The beam of electrons generally penetrate some distance into the specimen before undergoing a sufficient number of elastic scatterings to reverse the direction of travel and lead to backscattering. A significant fraction of the beam electrons hich strike a target subsequently escape. Those electrons that have been backscattered lose varying amounts of energy depending on their penetration into the specimen. Backscattered electrons provide useful data which is converted into an image in SEM technology. To obtain information about the region of sample near the beam impact area, it is advantageous to select those backscattered electrons which have not lost much energy. These electrons have not penetrated deeply enough into the sample to lose much energy and they give clear SEM images.

6.2.8.4 Electron microanalysis equipment

Figure 6.2-3 shows a very simplified typical modern electron microanalysis system. For the purpose of description, the equipment may be viewed as consisting of three main parts. These parts are, of course, normally intricate and broadly overlapping. They are :-

- the electron gun,
- the lens system, and
- the sample holder and spectrum monitoring system.

The electron gun consists of a filament lamp which is normally electrically heated to release electrons. The electron beam is focused by a series of symmetrically placed lenses to the final spot size of 5 - 200 nm. The specimen holder is a chamber where the sample under study is placed such that it lies in the path of the electron beam. The electron beam normally impacts the stationary sample at a single location, and hence the specimen interaction volume is fixed. The beam impact, as already discussed, produces detectable signals ranging from backscattered electrons, secondary electrons, absorbed electrons and X-rays. To measure the magnitude of this varied mix of signals, suitable detectors are conveniently placed (see Figures 6.2-3 and 6.2-4). In this way all, or at least the desired, signals can then be tapped off from the scattered, absorbed or transmitted electrons. In order to study more than a single specimen location, the electron beam must be moved from place to place by means of a scanning system. This scanning is usually accomplished by electromagnetic scan coils that mobilise the electron beam in a set X-Y grid system. In the current work, the SEM was used to examine the microstructure of lime stabilised material in an attempt to identify the effect that replacement of lime by GGBS in the kaolinite - lime - GGBS - gypsum system has on the microstructure and in particular on ettringite formation. The work was conducted at the University of Glamorgan using a Cambridge Instruments Stereoscan (Model S240) operating at a voltage of 25 kV. The examination was performed on specimens obtained from samples which were moist cured for 1 week and then vacuum dried before being given a coating of evaporated gold $\approx$ 10-20nm thick.

The next two chapters will now report on the results obtained using the instrumentation and experimental procedures prescribed in this chapter. Chapter 7 will report on the consistency limits, compaction and strength development, while Chapter 8 will report on the linear expansion, swelling pressure generation, phase analysis and microstructure.

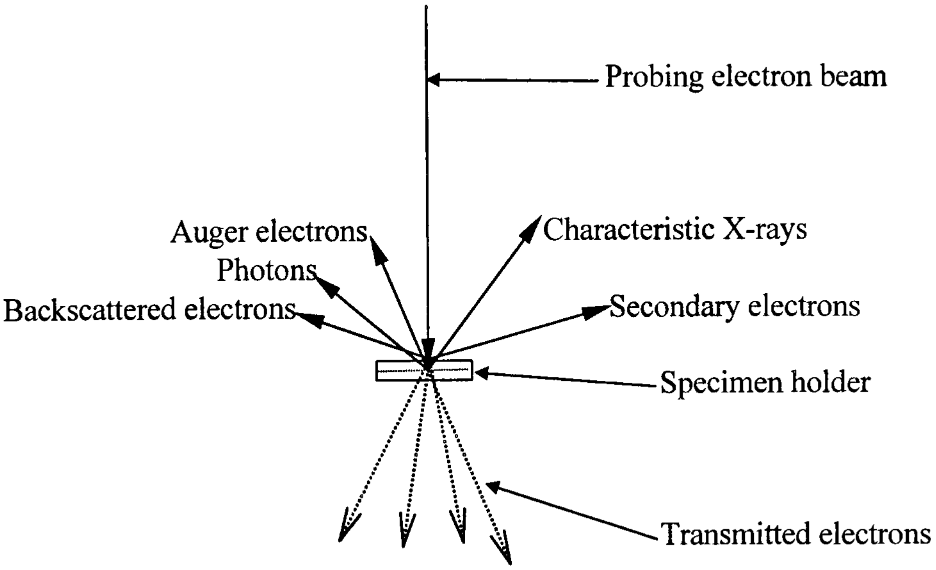


Figure 6.2-1 - Principle of electron microanalysis

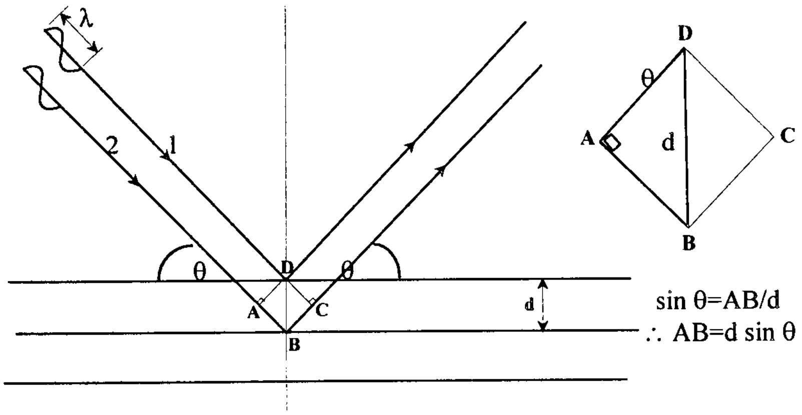


Figure 6.2-2 - X-ray diffraction according to Bragg's law.

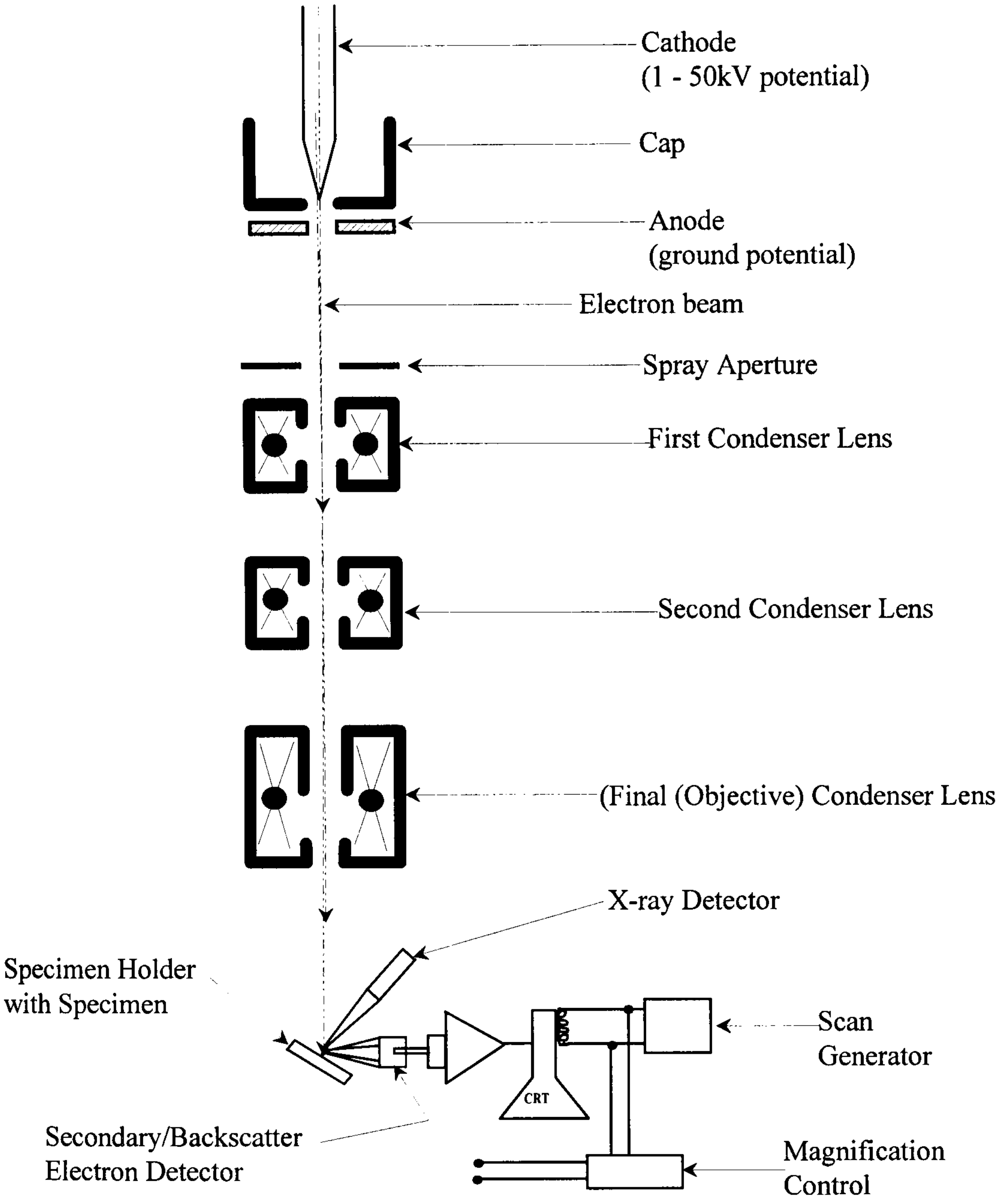
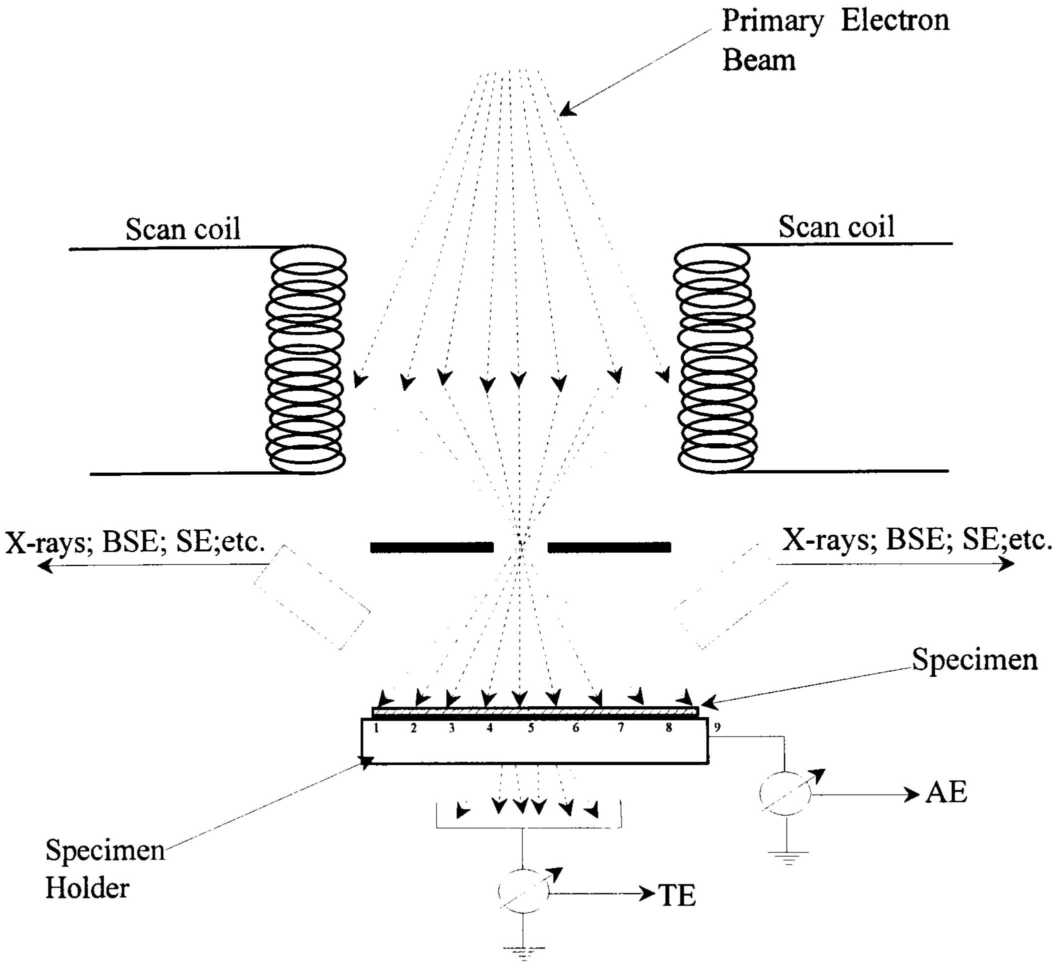


Figure 6.2-3 Simplified typical modern electron microanalysis equipment



BSE - Backscattered Electrons
SE - Secondary Electrons
AE - Absorbed Electrons
TE - Transmitted Electrons
1,2,3, etc. Scanning Beam Incidence
Locations

Figure 6.2-4 Schematic illustration of scanning system of the SEM.

CHAPTER 7 - RESULTS: CONSISTENCY LIMITS, COMPACTION AND STRENGTH DEVELOPMENT

7.1 CONSISTENCY LIMITS

7.1.1 INITIAL CONSUMPTION OF LIME

Figure 7.1-1 illustrates the variation of pH with lime content for various kaolinite - lime solutions containing 0, 1, 2, 3, 4, 5 and 6 wt. % lime as well as the pH of a pure lime solution (Line AB).

BS 1924 recommends a temperature of 25°C for pH determination and reporting, and suggests a pH temperature correction viz:

$$pH_{25} = pH_r + 0.03(T - 25)$$

Where pH_{25} = pH at 25°C

pH_r = pH at the prevailing temperature (°C).

T = Prevailing temperature (°C).

The above temperature correction was applied to all pH readings which were taken at a prevailing temperature of 22°C. A further adjustment was made to bring all data onto the scale on which the pH of a saturated lime solution is 12.4 thus obtaining line AB and the curve shown in Figure 7.1-1 (The full results are shown in Table A3-1 in Appendix 3).

Upon addition of small amounts of lime (of the order of 2wt.%), the pH rose sharply from 4.83 (the pH of pure kaolinite) to 12.11. Further addition of lime resulted in relatively smaller increases in pH. At 6wt.% lime addition, the pH of the kaolinite - lime solution was 12.39, approximately equal to 12.40, the pH observed for pure lime solution.

As the pH of the kaolinite - lime system at 6wt.% lime content was approximately equal to that of pure lime solution, 6wt.% would be the initial consumption of lime required for full modification of the kaolinite used. This initial lime requirement was also indicated by plastic limit tests where the rise in plasticity limit suggested a turning point between 3 and 6wt.% lime addition (Figure 7.1-2). It is worth noting however that the bulk of the changes in pH (≈ 96%) occurred with the addition of only 2% lime ($Ca(OH)_2$). Thus 6wt.% lime was selected as the minimum required hydrated lime content to provide modification and minimal stabilization of this particular kaolinite clay. This is equivalent to 4.5wt.% non-hydrated lime (CaO). Similar work on Kimmeridge Clay suggested a minimum lime requirement of 5wt.% (Table A3-1 in Appendix 3). These minimum hydrated lime contents were used both for the investigation of the effects of the presence of various metal sulphates on the stabilization of the clays, and for the investigation of the effects on clay stabilization of partial and/or total replacement of lime with GGBS. These effects included effects on compaction, swelling and strength properties as well as the nature of the reaction mechanisms.

7.1.2 EFFECTS OF LIME ON ATTERBERG LIMITS OF KAOLINITE AND KIMMERIDGE CLAY

Figure 7.1-3 illustrates the changes in liquid limit, plastic limit and plasticity index of unmellowed kaolinite - lime and mellowed Kimmeridge Clay - lime mixes when various amounts of hydrated lime were added. Data were only obtained for Kimmeridge Clay up to 6wt.% lime addition whereas data for kaolinite were obtained for lime additions of up to 20wt.%.

The liquid limit of "pure" kaolinite increased sharply from 61 % to 72 % with the addition of 3 wt.% lime. Beyond this lime content, the liquid limit remained more or less at this level even at high additions of lime of the order of 14 wt. % where a liquid limit of 73 % was observed, subsequently dropping gradually to 71% at 20wt.% lime addition. The plastic limit increased from 32% for "pure" kaolinite to a stable level of 41% between 6wt.% and 14wt.% lime content, before increasing further to 44% at 20 wt.% lime addition. The liquid limit and plastic limit results resulted in an increase in plasticity index from 29% for "pure" kaolinite to a maximum of 33% at 3wt.% lime. This level of plasticity index was more or less maintained up to 14 wt.% lime addition, before dropping to 27% at 20wt.% lime addition. The stabilization of the plastic limit at 6% lime content, indicated that the initial lime consumption requirement had been satisfied. Generally, between 1-3wt.% lime is needed for modifying soil properties and 2-8wt.% lime for stabilization, depending on clay type and clay content. The apparently high lime content of above 6wt.% required to reduce the PI is attributed to the fact that the kaolinite used was at least 70% clay fraction. Normally, a minimum of 10% clay fraction is required in order that the soil can be effectively modified.

From the experience gained from the work on "pure" kaolinite and the data obtained on the initial consumption of lime on Kimmeridge Clay, it was decided to restrict Atterberg limits work on this clay to a narrower lime addition range of 0 - 6 wt.% (Figure 7.1-3). Over this range, both the liquid limit and the plastic limit showed a general increase with increase in lime, with a slight drop at 5 wt.% lime addition in both cases. The plastic limit had a higher rate of increase than the liquid limit, resulting in a generally reducing plasticity index with increasing lime content.

7.1.3 EFFECTS OF SULPHATES ON CONSISTENCY LIMITS OF LIME-STABILISED KAOLINITE

Figure 7.1-4 illustrates the changes in liquid limit, plastic limit and plasticity index of unmellowed kaolinite - 6wt.% lime mixes when varying amounts of different sulphate types were added. Although sulphates were added in the form of metal salts (i.e. $CaSO_4.2H_2O$, $MgSO_4$, Na_2SO_4 and K_2SO_4), the sulphate content is reported as wt.% SO_3 (expressed as a percentage of the kaolinite (see Appendix 2)) rather than wt.% of the metal salt so that sulphate values are equivalent and are independent of the type of metal salt used. Also studies with the full range of sulphates were only carried out on "pure" kaolinite and work on Kimmeridge Clay was restricted to calcium sulphate because this was a natural contaminant of the clay, not an artificially added component.

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 from 32 % to 22 % as the gypsum content increased from 0-2.79wt.% SO_3 (Figure 7.1-4 (a)).

The effects of the addition of magnesium sulphate were similar to those of the addition of equivalent amounts of gypsum, lowering the liquid limit by a rather similar magnitude by the addition of equivalent amounts of magnesium sulphate. Also, the plastic limit systematically increased, resulting in a gradual decrease in the plasticity index by a marginally higher magnitude than for the case of gypsum additions (from 32 % to 20 % by the addition of 2.79 wt.% SO_3 equivalent).

The addition of a small amount of sodium sulphate (0.93 wt.% SO_3 equivalent) significantly lowered the liquid limit of the lime-treated kaolinite from 73 % to 59 %. Further sulphate additions had no further effect on the liquid limit. The plastic limit behaved in a similar manner, but dropping less sharply but significantly from 41 % to 33 % by the addition of a similar amount of sodium sulphate and remaining at this level on further sulphate addition. Thus, the plasticity index also fell by the addition of small quantities of 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, lowering the liquid limit suddenly from 73 % in the absence of any sulphate to 61 % by the addition of the equivalent of 0.93 wt.% SO_3. 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 slight increase in liquid limit imparted a stabilising effect on the decrease in the plasticity index which after the initial drop by the addition of 0.93 wt.% SO_3 potassium sulphate increased gently by further sulphate addition. The main feature of the four set of curves in Figure 7.1-4 is the marked similarity in behaviour between the two divalent metal sulphates and between the two monovalent metal sulphates.

7.1.2.1 Comparative effects of different sulphate types

Figure 7.1-5 emphasizes the effects that different metal cations have on the three Atterberg limits, when added as metal sulphates. Increases in sulphate content generally lowered the liquid limit, the magnitude of decrease increasing in the order:

$$\mathbf{CaSO_4 < MgSO_4 < K_2SO_4 < Na_2SO_4},$$

the sulphate to the left decreasing the liquid limit by a smaller magnitude than the one to the right. It should be noted that the cation order (i.e. Ca < Mg < K < Na) is the same as that in the lyotropic series (see section 3.2.2). The sulphates containing Ca^{2+} and Mg^{2+} cations displayed similar liquid limit trends as did those containing Na^+ and K^+ although the trends were different in each case. Ca^{2+} and Mg^{2+} cation containing sulphates produced a continuous reduction in liquid limit with increasing sulphate content while the Na^+ and K^+ cation containing sulphates produced a much steeper initial fall but with no further significant drop beyond 0.93% SO_3 content. Indeed, K^+ containing sulphates displayed an increasing liquid limit beyond this sulphate level.

The two groups of sulphates (containing monovalent and divalent metals) also showed pairing trends with respect to their effects on the plastic limit. Ca^{2+} and Mg^{2+} 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^{+} and K^{+} cations containing sulphates exhibited sharp decreases in plastic limit at low sulphate levels and subsequently showed only small increases in plastic limit at higher sulphate levels.

The resulting changes in both liquid limit and plastic limit resulted in decreased plasticity with increasing sulphate content in all cases. Ca^{2+} and Mg^{2+} cations containing sulphates recorded substantial decreases in plasticity over the entire sulphate range. Increasing the SO_3 content from 0wt.% to 2.79wt.% reduced the plasticity index by approximately a third in both cases. Na^{+} and K^{+} cations containing sulphates reduced the plasticity by greater amounts than did Ca^{2+} and Mg^{2+} sulphates at low sulphate levels, but at higher sulphate levels the plasticity index either increased (K^{+}) or showed little change (Na^{+}). Thus up to about 0.93% SO_3 content, the effect of the cation in reducing plasticity index was in the order:

$\mathbf{Ca^{2+} < Mg^{2+} < K^{+} < Na^{+}}$, where sodium caused the largest

reduction, but at high SO_3 contents (3%) the order was

$\mathbf{K^{+} < Na^{+} < Ca^{2+} < Mg^{2+}}$

A comparison of Figures 7.1-4 (c) and 7.1-4 (d) indicated that the difference in plasticity reduction by the two sulphates of sodium and potassium was due to the fact that although both Na^+ and K^+ cation containing sulphates had comparable effects on plastic limit reduction, Na^+ cation containing sulphates reduced the liquid limit by a bigger margin from 73% without sulphate to 59% with sulphate, as compared to from 73% to 61% for K^+ cations containing sulphates.

In summary, the sulphates of calcium and magnesium produced a decrease in liquid limit and a gradual increase in plastic limit, resulting in a declining plasticity index. The sulphates of sodium and potassium lowered the plastic limit from 41% to a stable level at about 34%. This stability in plastic limit imparted a similar stability on the plasticity index, which was lowered from 32% to a stable level of 28% for potassium sulphate and of 24% for sodium sulphate.

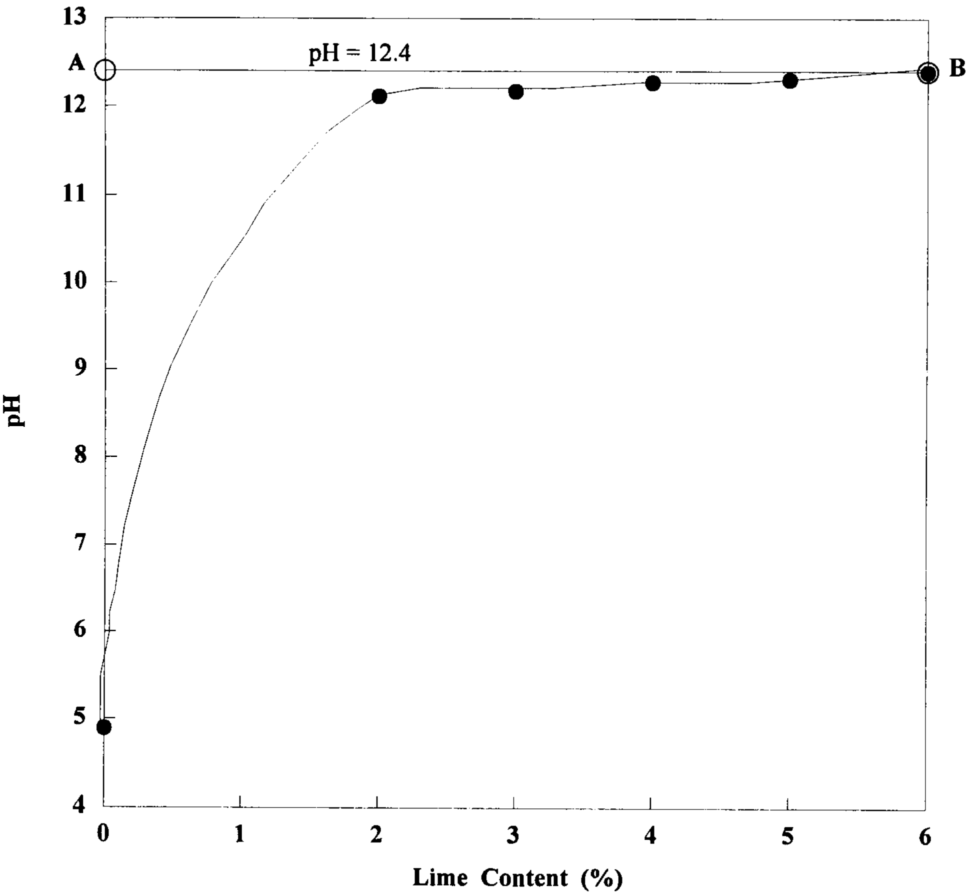


Figure 7.1-1 - pH vs. Lime content of kaolinite-lime solutions at 22°C

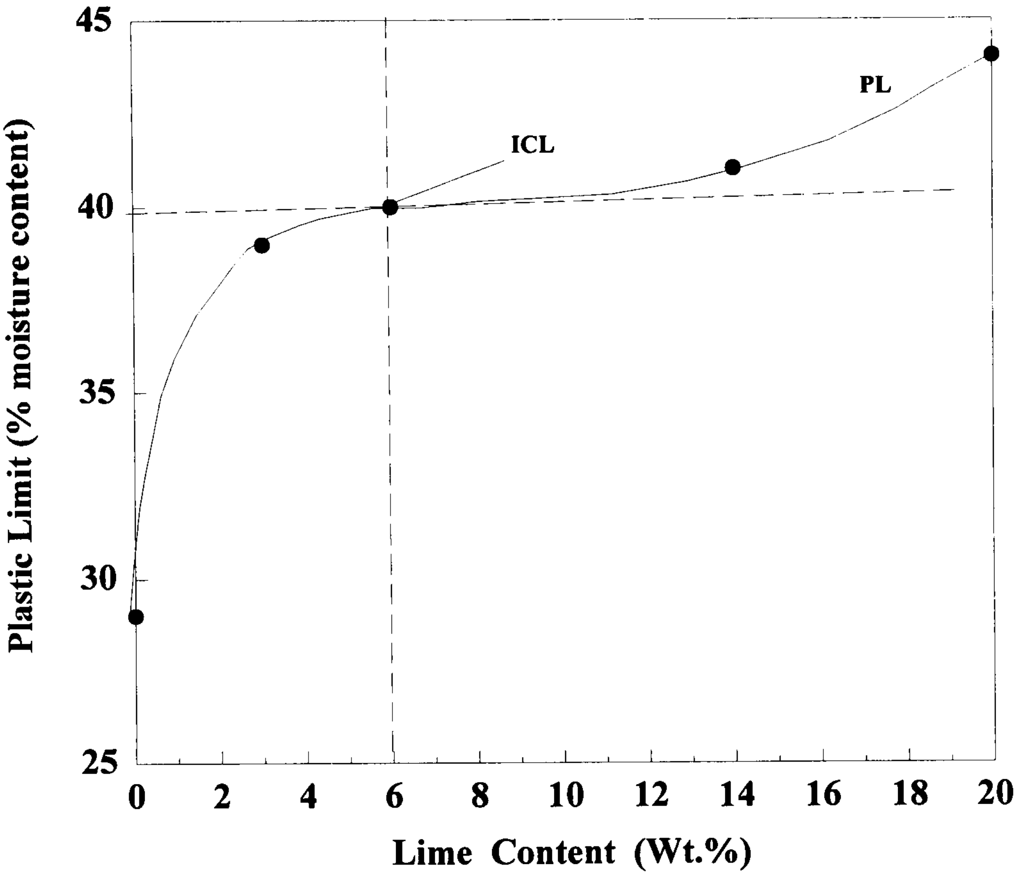


Figure 7.1-2 - Plastic limit vs. Lime content of kaolinite-lime mixes.

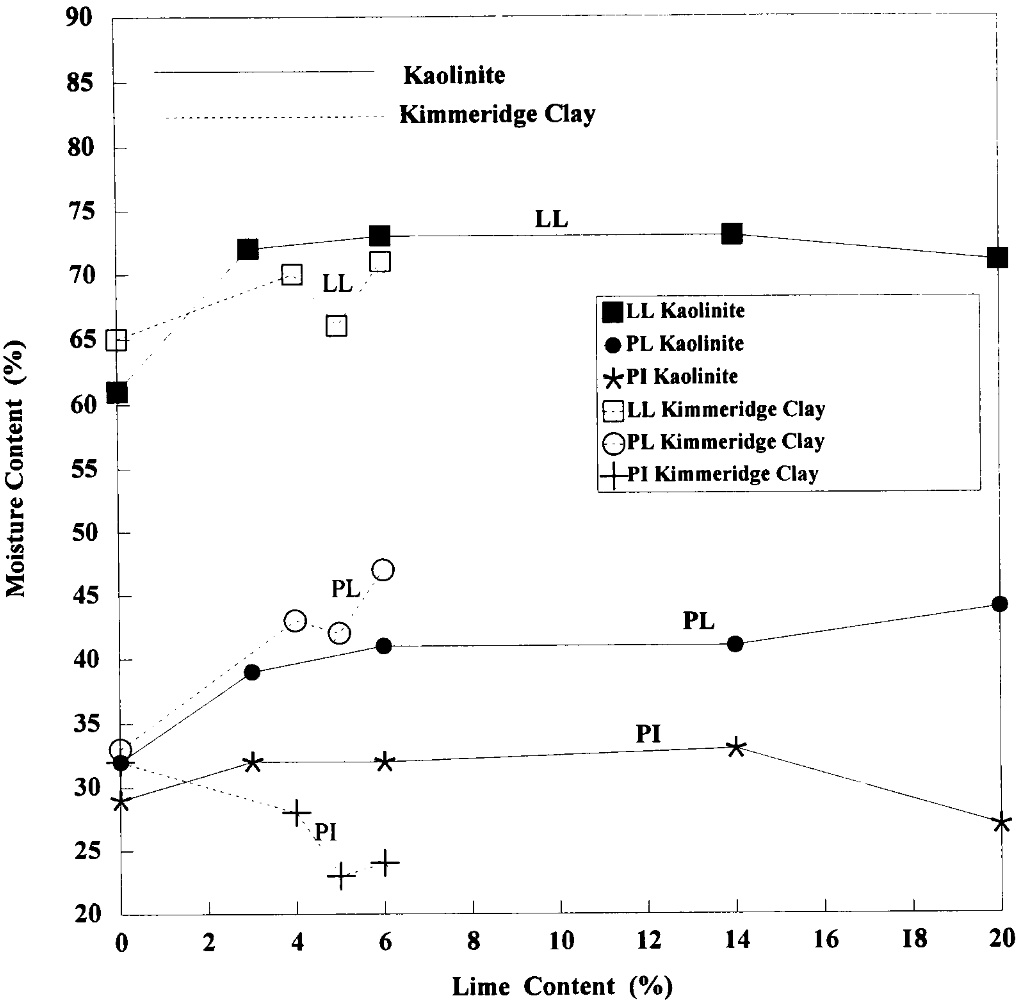
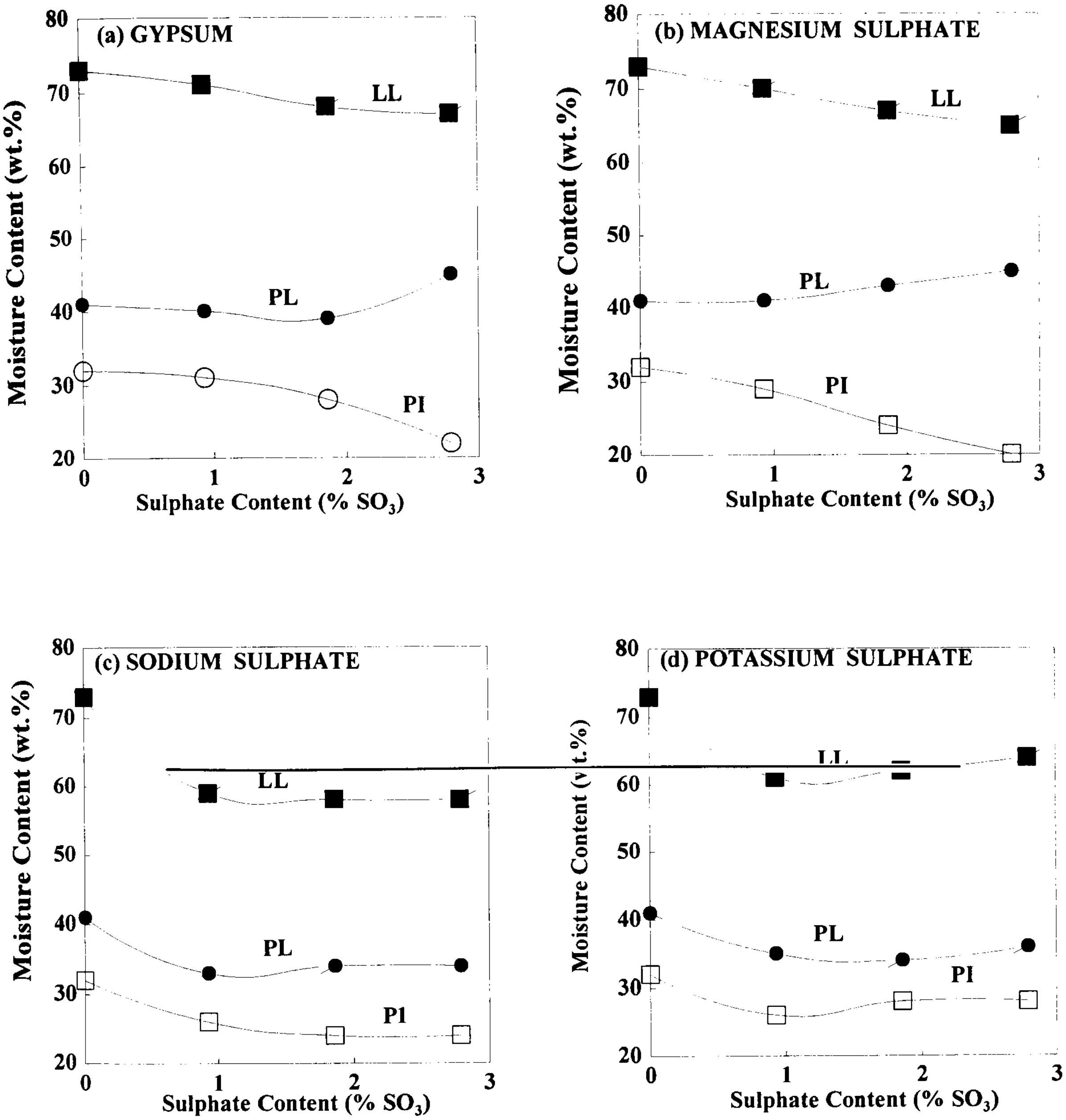


Figure 7.1-3 Atterberg Limits vs. Lime Content for kaolinite and Kimmeridge clays with various amounts of lime.



KC - Kimmeridge Clay with 6wt.% lime

Figure 7.1-4 - Atterberg limits moisture contents vs. Sulphate content for kaolinite-6wt.% lime mixes with varying additions of individual metal sulphates

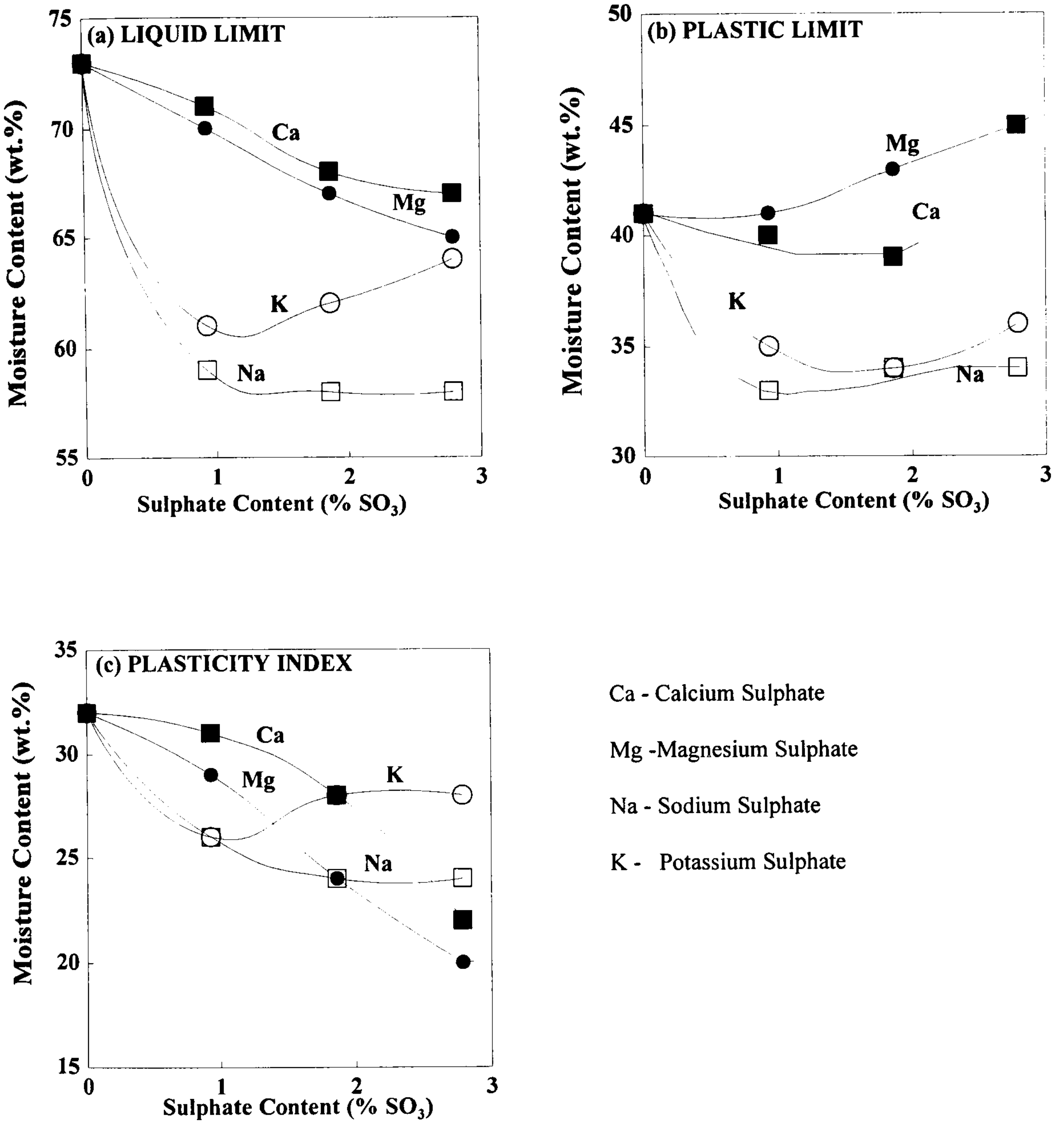


Figure 7.1-5 - Atterberg limits moisture contents vs. Sulphate content for kaolinite-6wt.% lime mixes with varying additions of various metal sulphates

7.1.4 EFFECTS OF THE SUBSTITUTION OF LIME BY SLAG ON THE ATTERBERG LIMITS OF THE STABILISED CLAYS

7.1.4.1 Kaolinite

Figures 7.1-6 and 7.1-7 (and Tables A3-3 (a) and (b) in Appendix 3) illustrate the effects on the Atterberg limits, of lime-stabilised kaolinite, of partially or fully replacing the lime with GGBS both immediately and after 72 hours of mellowing. Figure 7.1-6 gives the Atterberg limits of kaolinite-lime-slag without gypsum and Figure 7.1-7 gives similar data for mixes containing 8wt.% gypsum (3.72% SO_3). Calcium sulphate was selected as the sulphate for this particular study because this is the sulphate present in the Kimmeridge Clay. The level selected was the highest level used in any subsequent tests.

In the absence of gypsum (Figure 7.1-6), the effect of 72 hours mellowing on each of the Atterberg limits is relatively small, particularly in the case of the liquid limit where the 'unmellowed' and 'mellowed' values are identical within the limits of error. Also substitution of lime by slag has very little effect on the Atterberg limits up to a slag:lime ratio of 5:1, beyond which there is a sharp drop. At the stabiliser composition 6% slag-0% lime (i.e. 6(0)) the values of the liquid limit, plastic limit and plasticity index are very similar to the values for kaolinite alone (respectively A, B and C in Figure 7.1-6). This clearly indicates that the slag has negligible effect on the Atterberg limits whereas the lime has a significant effect as long as sufficient is present to produce modification.

When gypsum is present (Figure 7.1-7) the change in Atterberg limits with replacement of lime by slag is more complex. Firstly, 72 hours of mellowing produces a significant increase in liquid limit, and also produces increases in plastic limit and plasticity index. Secondly the liquid limit shows a general increase with substitution level reaching a maximum at a slag to lime ratio of 4:2 and then falls very sharply. The plastic limit for the unmellowed material is however less sensitive to substitution level, thus the trend in plasticity index for the unmellowed material is very similar to that for the liquid limit. At the stabiliser composition 6% slag - 0% lime the results are very similar to those where no gypsum is present. The observations of the relative effects of mellowing on the Attereberg limits suggest that sulphate has a marked influence on the initial clay-lime reactions.

7.1.4.2 Kimmeridge Clay

Figure 7.1-8 shows the effects of lime substitution by slag for mellowed Kimmeridge Clay. In common with kaolinite containing gypsum but unlike kaolinite without gypsum, the liquid limit gradually increases, with increase in slag level. The plasticity index shows very little change up to a substitution level of 2slag - 3lime and then shows a sharp increase. The plastic limit thus increases, up to a slag/lime ratio of unity beyond which it decreases with further increase in slag.

7.1.5 EFFECTS OF MELLOWING

The magnitude and behaviour of the Atterberg limits of the unmellowed kaolinite - lime - GGBS mixes were similar both with and without the presence of gypsum, except that in the presence of gypsum, substitution of lime was more sensitive to both liquid and plastic limits (and hence to the plasticity index). When 72 hours mellowing period was allowed in kaolinite - lime - GGBS mixes, small reductions in liquid limit were observed, in the absence of sulphates, but those were not significant and the trend was very similar to that without mellowing. As for the plastic limit and the plasticity index, mellowing for 72 hours again only produced minor modifications to the curve. However in the presence of 3.72wt.% SO_3 equivalent of gypsum, mellowing produced marked changes in all Atterberg limits. Both liquid and plastic limits were generally significantly increased, resulting in similar increases in the plasticity index. The general trends were however similar to those obtained under unmellowed conditions.

7.1.6 SUMMARY

1. Lime generally increases the liquid limit and plastic limit of both kaolinite and Kimmeridge Clay. The plasticity indices of both clays are generally reduced by the addition of lime
2. Metal sulphates generally lower the liquid limit and plasticity index of lime stabilised kaolinite. The plastic limit may increase or decrease, depending on the

type of sulphate, the sulphates containing divalent cations raising it while those containing monovalent ones lowering it.

3. In the absence of gypsum, substitution of lime with GGBS has no effect on both mellowed and unmellowed Atterberg limits of lime-stabilised kaolinite until a slag:lime ratio of 5:1 beyond which further substitution of lime results in reduced limits.
4. In the presence of gypsum, substitution of lime marginally raises the LL of lime - stabilised kaolinite up to a slag:lime ratio of 5:1 1 beyond which further substitution of lime results in reduced LL. The PL is generally reduced throughout the substitution. The PI is thus increased in a pattern similar to that of LL.
5. In the presence of gypsum, the effects of mellowing on lime - stabilised kaolinite are much more pronounced; the LL and PL increasing up to a slag:lime ratio of 5:1 and PI decreasing throughout the substitution
6. The effects of substitution of lime with GGBS for Kimmeridge Clay on LL and PL are generally similar to those of kaolinite clay in the presence of gypsum.

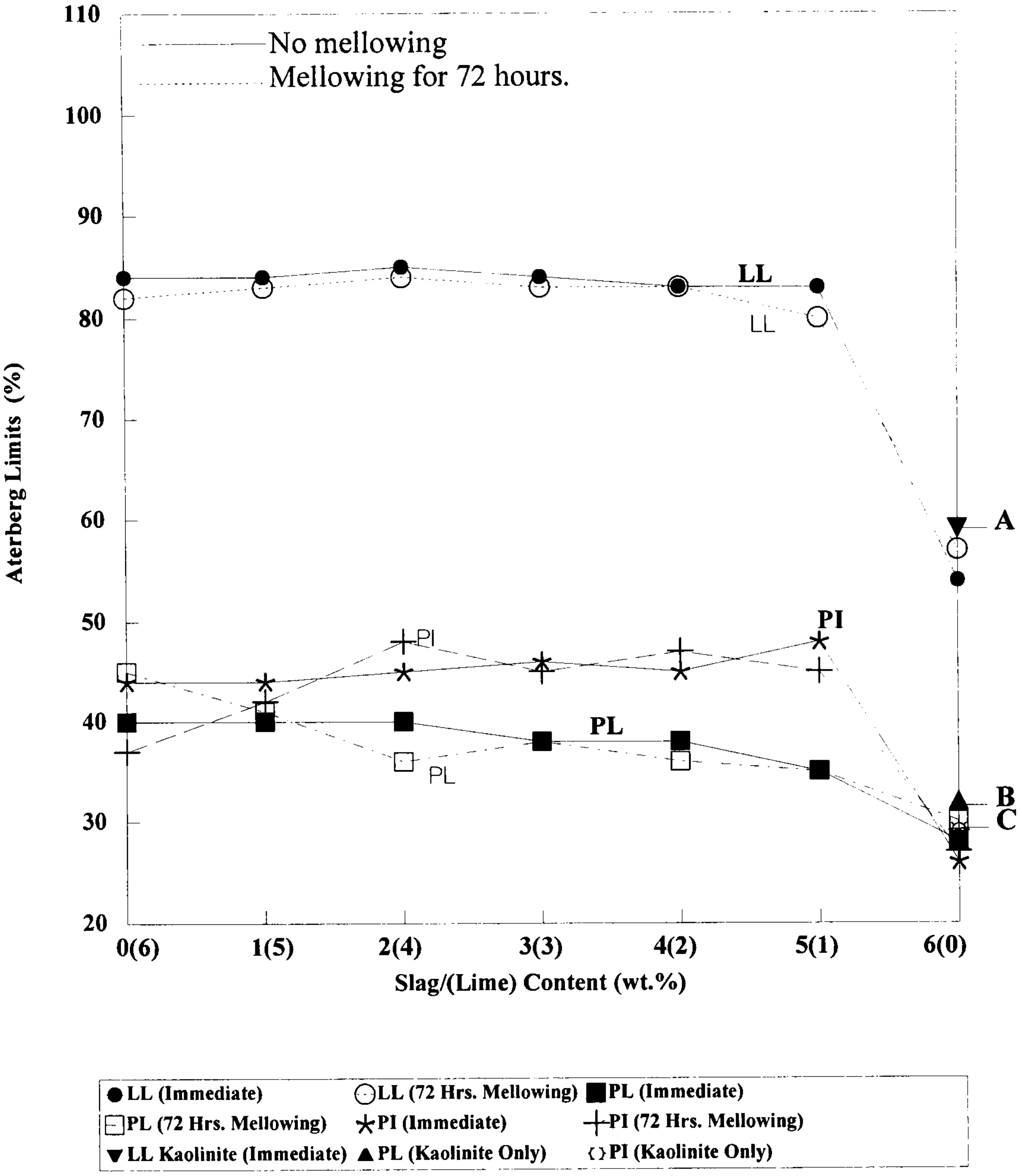


Figure 7.1-6 - Atterberg Limits vs. Slag/Lime Content (wt.%) for Kaolinite-lime-ggbs composites

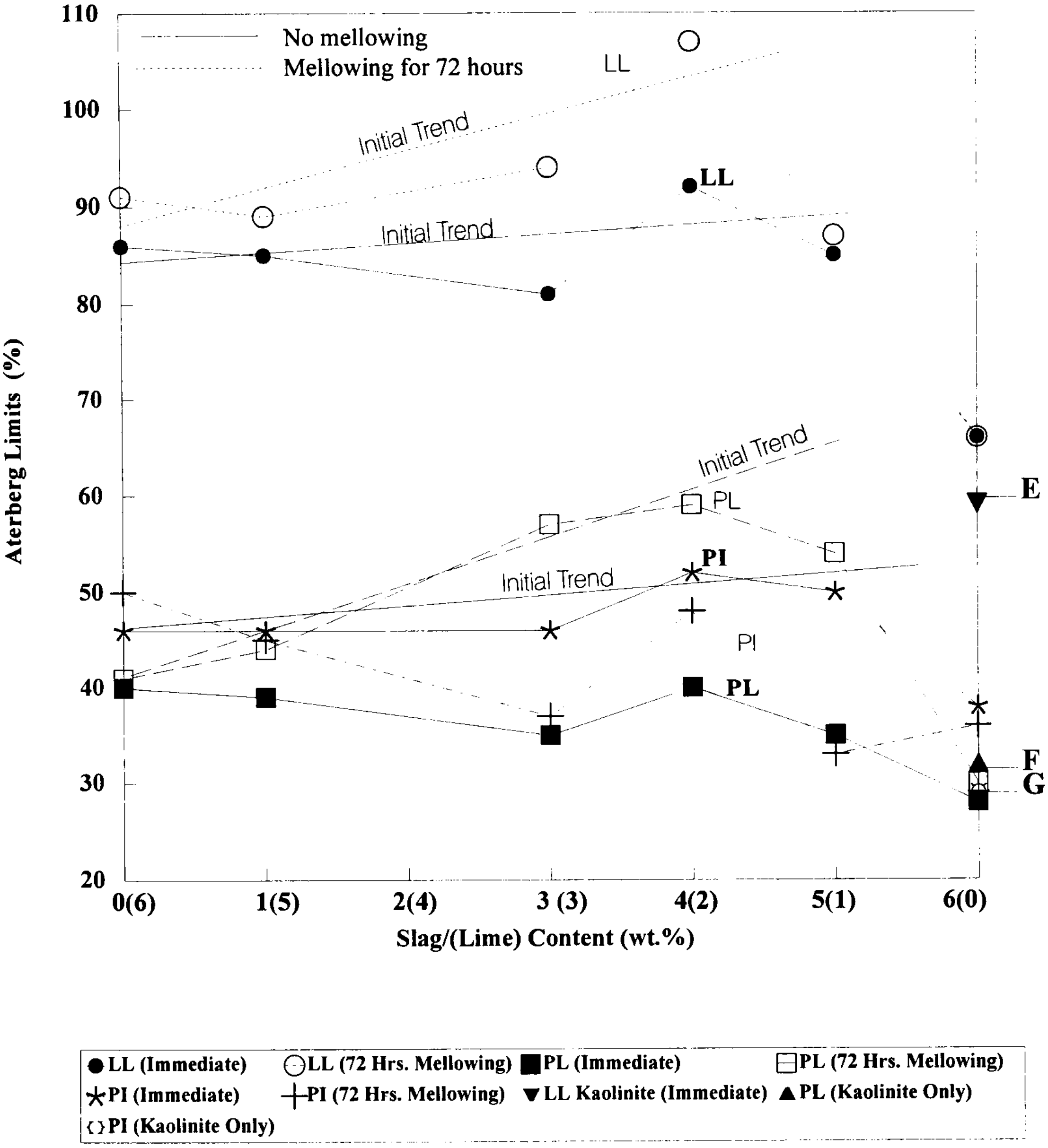


Figure 7.1-7-Atterberg limits vs. Slag/Lime content (wt.%) for kaolinite-lime-ggbs-8wt.% gypsum (3.72% SO_3) composites.

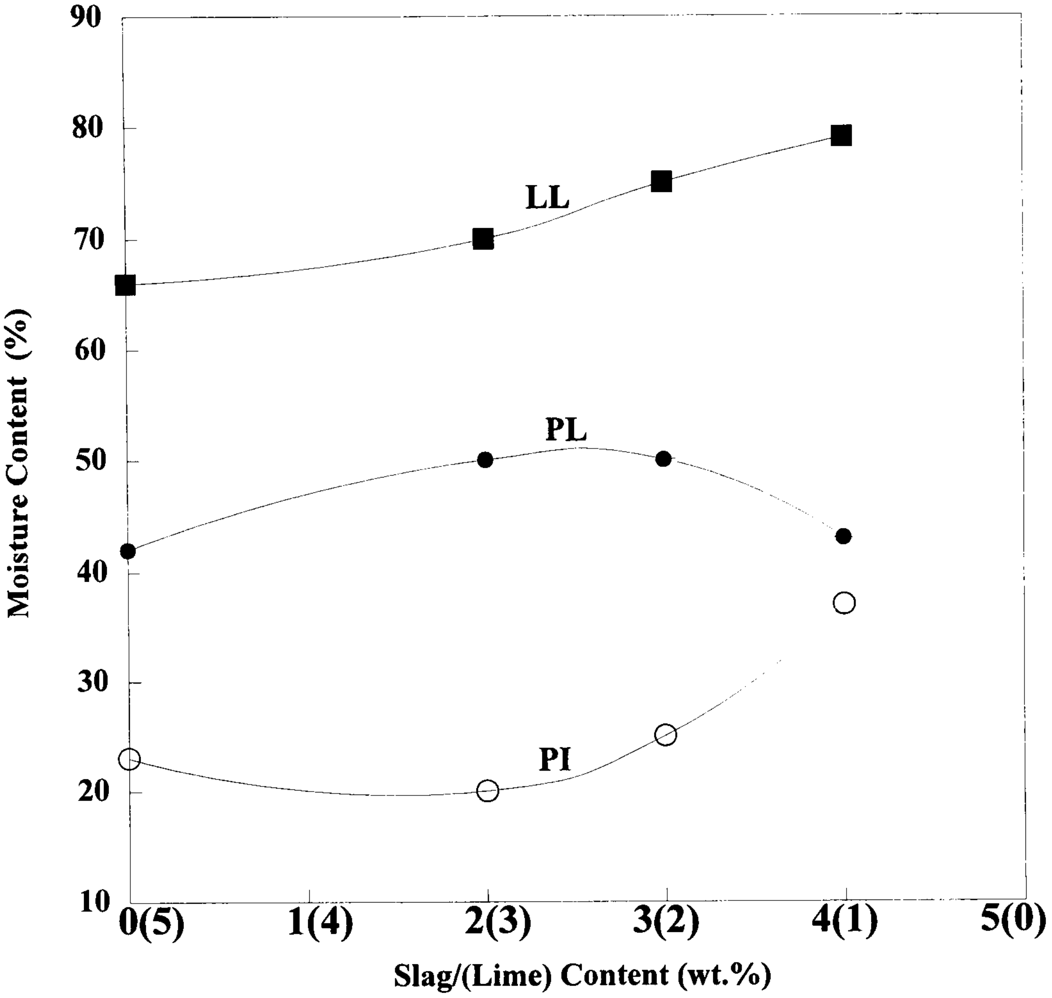


Figure 7.1-8 - Atterberg Limits vs. Slag/Lime Content (%) for Kimmeridge clay-lime-ggbs mixtures after 72 hours mellowing..

7.2 DRY DENSITY - MOISTURE CONTENT RELATIONSHIP

7.2.1 INTRODUCTION

The primary reason why the Proctor tests were conducted was to establish, the approximate, maximum dry density and optimum moisture content to be generally adopted during the preparation of specimens for unconfined compression tests, swelling pressure generation tests and linear expansion tests. The second objective was to establish the variation in Proctor compaction properties on the addition of various amounts of metal sulphates to kaolinite - lime mixtures. In the kaolinite - lime - sulphate system, four sulphates were used - calcium sulphate, magnesium sulphate, sodium sulphate and potassium sulphate. For each of these, the sulphate content was varied from 0 to 0.93, 1.86, 2.79 and 3.72 % SO_3 (see Appendix 1 for sulphate SO_3-SO_4 conversion).

For the Kimmeridge Clay which inherently contained 1.73 % SO_3 (approximately 4wt%) gypsum, 5% lime was the approximate initial lime requirement for the modification of this clay, and Proctor tests for the investigations into the effects of progressive substitution of lime with GGBS were therefore done at this lime content.

7.2.2 EFFECTS OF LIME

Addition of lime had the overall effect of lowering the maximum dry density (MDD) and raising the optimum moisture content (OMC) for both unstabilised kaolinite and

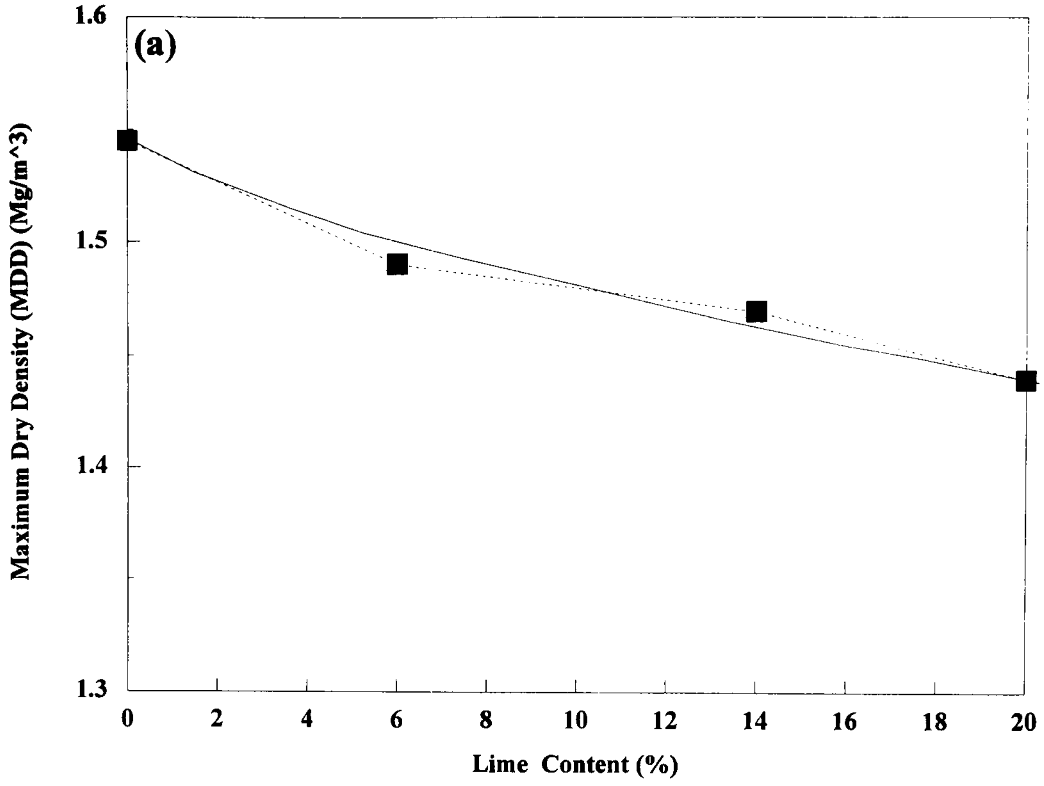
Kimmeridge Clay (Figures 7.2-1, and 7.2-2). In both cases, the MDD decreased substantially upon the introduction of lime, but showed relatively minor variation on further increase in lime content beyond 6wt.% for kaolinite and 4wt.% for Kimmeridge Clay. The OMC showed a general increase with increase in lime content for both clays although the changes were much less systematic for Kimmeridge Clay. This anomalous behaviour of Kimmeridge Clay has also been observed at slightly higher lime contents (although still within a comparable range with the current work) by Littleton and Willavise (1992). Littleton and Willavise worked on lime treatment of Kimmeridge Clay obtained from the west of Swindon. They used 0, 4, 5 and 6wt.% quicklime (CaO) (equivalent to 0, 5.3, 6.6 and 7.9 $Ca(OH)_2$) and observed a minimum MDD at 4 wt.% CaO. The MDD then increased suddenly at 5wt.% CaO before dropping again at 6 wt.% CaO. Similarly for the OMC, they observed a drop in OMC between 4 and 5wt.% CaO addition and resumed increase between 5 and 6 wt.% CaO addition. Normally, the maximum dry density of most soils is generally decreased and the optimum moisture content generally increased by the addition of lime as clearly demonstrated with kaolinite - lime mixes. Although there may be changes in the rates of decrease in MDD and increase in OMC, usually there is no complete reversal in these trends, and therefore the Kimmeridge Clay, is showing none standard behaviour. This is almost certainly related to specific chemical components present in the Kimmeridge Clay and their chemical reaction as will be discussed later in Chapter 9.

7.2.3 EFFECTS OF SULPHATES ON COMPACTION OF KAOLINITE

Figure 7.2-3 shows the effect of different metal sulphate additions on the MDD and OMC, of the kaolinite-6wt.%lime mixes. Sulphate content (SO_3) is expressed as weight percent of kaolinite and the metal sulphates considered are calcium, magnesium, sodium and potassium. The introduction of sulphates to the kaolinite in addition to the lime, particularly at low sulphate concentrations (of the order of the equivalent of 0.93wt.% SO_3), further lowered the MDD for all sulphates except sodium sulphate which had little effect on it (Figure 7.2-3 (a). Also, the sulphates further raised the OMC of the lime stabilised kaolinite except (again), sodium sulphate where sulphate addition had in general little effect on the OMC. The other sulphates therefore, had effects similar to the addition of more lime especially those of calcium and magnesium (Compare Figure 7.2-3 (a) and (b) with Figure 7.2-1 (a) and (b)). Addition of sodium sulphate in minor quantities had effects similar to decrease in lime.

Increasing the sulphate content beyond 0.93% SO_3 had little effect on MDD for the sulphates of calcium and magnesium. At these high sulphate contents, potassium sulphate tended to behave in a similar manner to sodium sulphate. At the high SO_3 concentration, the sulphates of calcium and magnesium continued to raise the OMC while those of sodium and potassium tended to lower it. These results seem to suggest that at high sulphate contents, the cation exchange reaches a level where further cation addition has no further change on flocculation (hence constant density). The effects of the addition of sulphates to the compaction characteristics seem to be determined mainly by the cation part of the sulphate through cation exchange.

The change in OMC with sulphate content for magnesium and calcium sulphates showed a diametrically opposite effect to that of MDD. Thus, Figure 7.2-3 (a) is effectively an inverted mirror image of Figure 7.2-3 (b) with magnesium sulphate emerging as the most powerful in the cation exchange process that leads to flocculation and agglomeration.



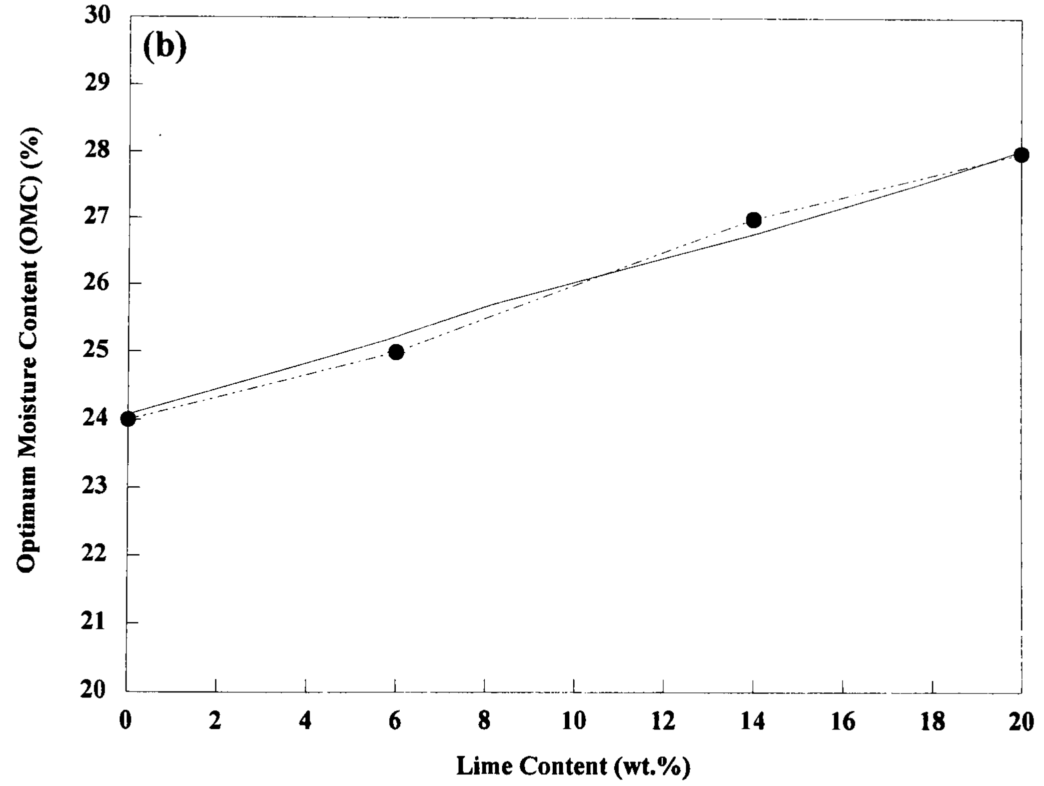
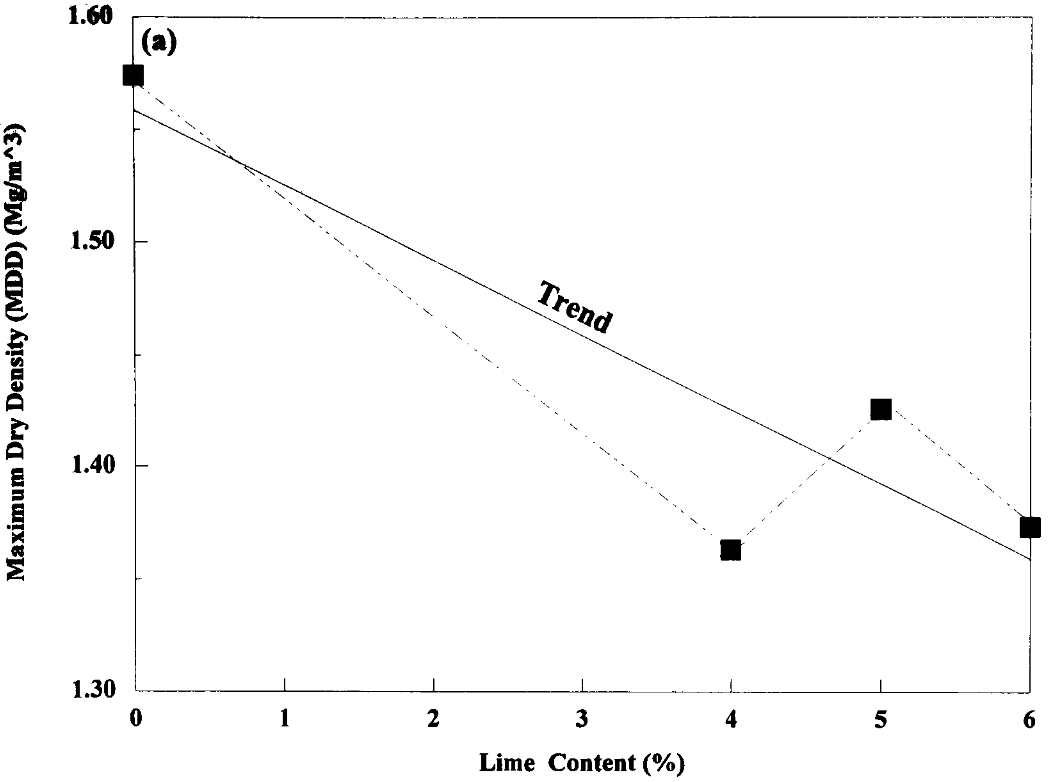


Figure 7.2-1- (a) Maximum Dry Density (MDD) vs. Lime Content and (b) Optimum Moisture Content vs. Lime Content for Kaolinite



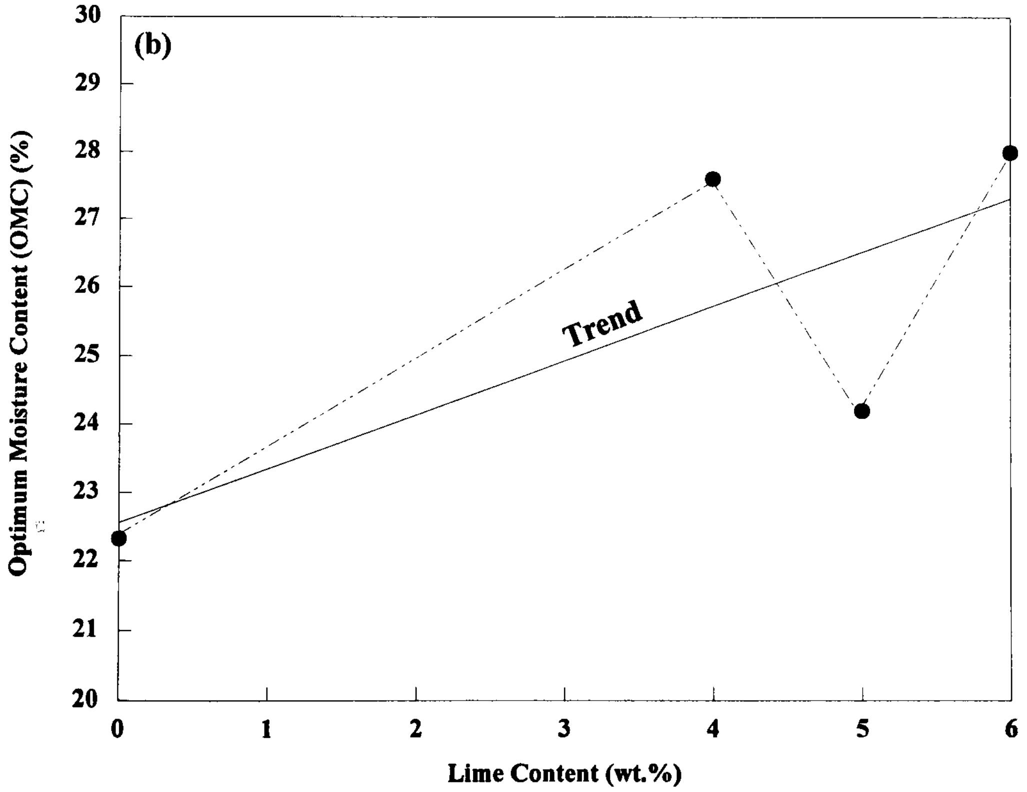
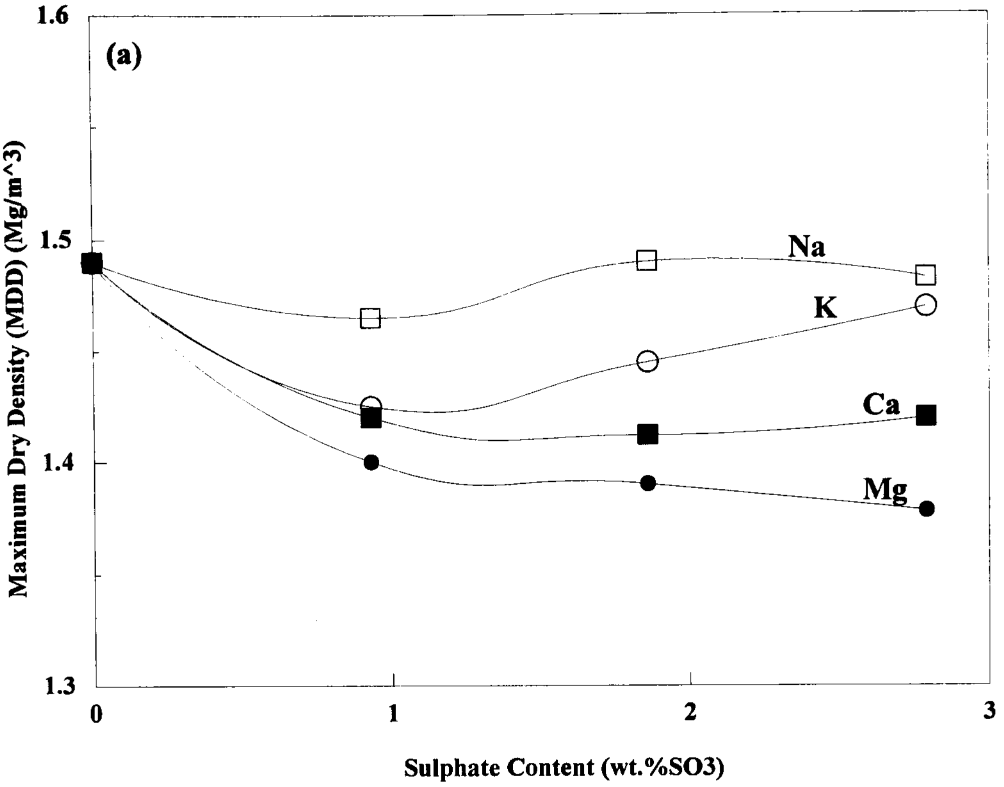


Figure 7.2-2– (a) Maximum Dry Density (MDD) vs. Lime Content and (b) Optimum Moisture Content vs. Lime Content for Kimmeridge clay.



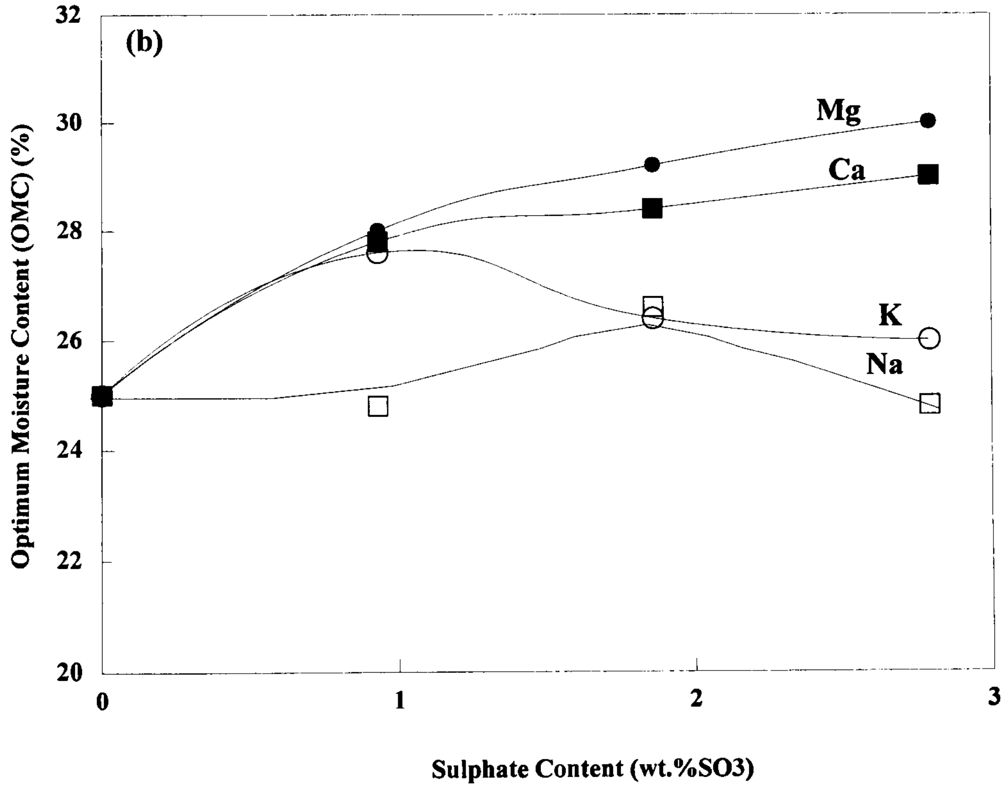


Figure 7.2-3– (a) Maximum Dry Density (MDD) vs. Sulphate Content and (b) Optimum Moisture Content vs. Sulphate Content for Kaolinite-6wt.% Lime mixes containing varying amounts of various sulphate types.

7.2.4 EFFECTS OF VARYING THE SLAG:LIME RATIO ON PROCTOR PARAMETERS OF STABILISED KAOLINITE AND KIMMERIDGE CLAY

Figures 7.2-4 (a) and 7.2-5 (a) show the change in MDD for respectively kaolinite-6% lime-6% gypsum (2.79% SO_3) and Kimmeridge Clay - 5%lime when, in both cases, the lime is systematically replaced with GGBS (See also Figure A4-1 in Appendix 4). Figures 7.2-4 (b) and 7.2-5 (b) give the equivalent OMC data for these compositions. Substitution of lime by slag up to the substitution levels indicated has very little influence on the MDD for either kaolinite (with or without gypsum) or for Kimmeridge Clay, other than for a small fall in MDD for kaolinite without sulphate at the initial substitution level (1% slag - 5% lime). The MDD for both treated clays is of course much less than that for clays alone because of the flocculating effect of the lime and although MDD data were not obtained for 100% substitution of lime with slag, the MDD values might be expected to be similar to clay alone for these compositions. The change in OMC with lime substitution by slag does not show the same common trends between the two clays. The OMC for treated kaolinite with gypsum increases by a small but decreasing rate with increasing substitution. When gypsum is absent the initial increase (at 1% slag - 5% lime) is much sharper. For Kimmeridge Clay although there is a small initial increase in OMC with substitution (2% slag - 3% lime) the OMC then systematically decreases to the extent that the OMC is actually below that for clay alone.

7.2.5 SUMMARY

1. Lime lowers the MDD of both kaolinite and Kimmeridge Clay. On the other hand it raises the OMC.
2. Kimmeridge Clay displays non-typical behaviour in the MDD and OMC trends with the addition of lime.
3. Metal sulphates further lower the MDD and further raise the OMC of lime stabilised kaolinite. These effects are higher for the sulphates containing divalent cations than for those containing monovalent ones. Sodium has the least effect in these changes.
4. Substitution of lime with GGBS has little effect on the MDD of both lime-stabilised kaolinite and lime-stabilised Kimmeridge Clay
5. Substitution of lime with GGBS has an insignificant increase in the OMC of lime-stabilised kaolinite either with and without gypsum. However the substitution significantly lowers the OMC of lime-stabilised Kimmeridge Clay.

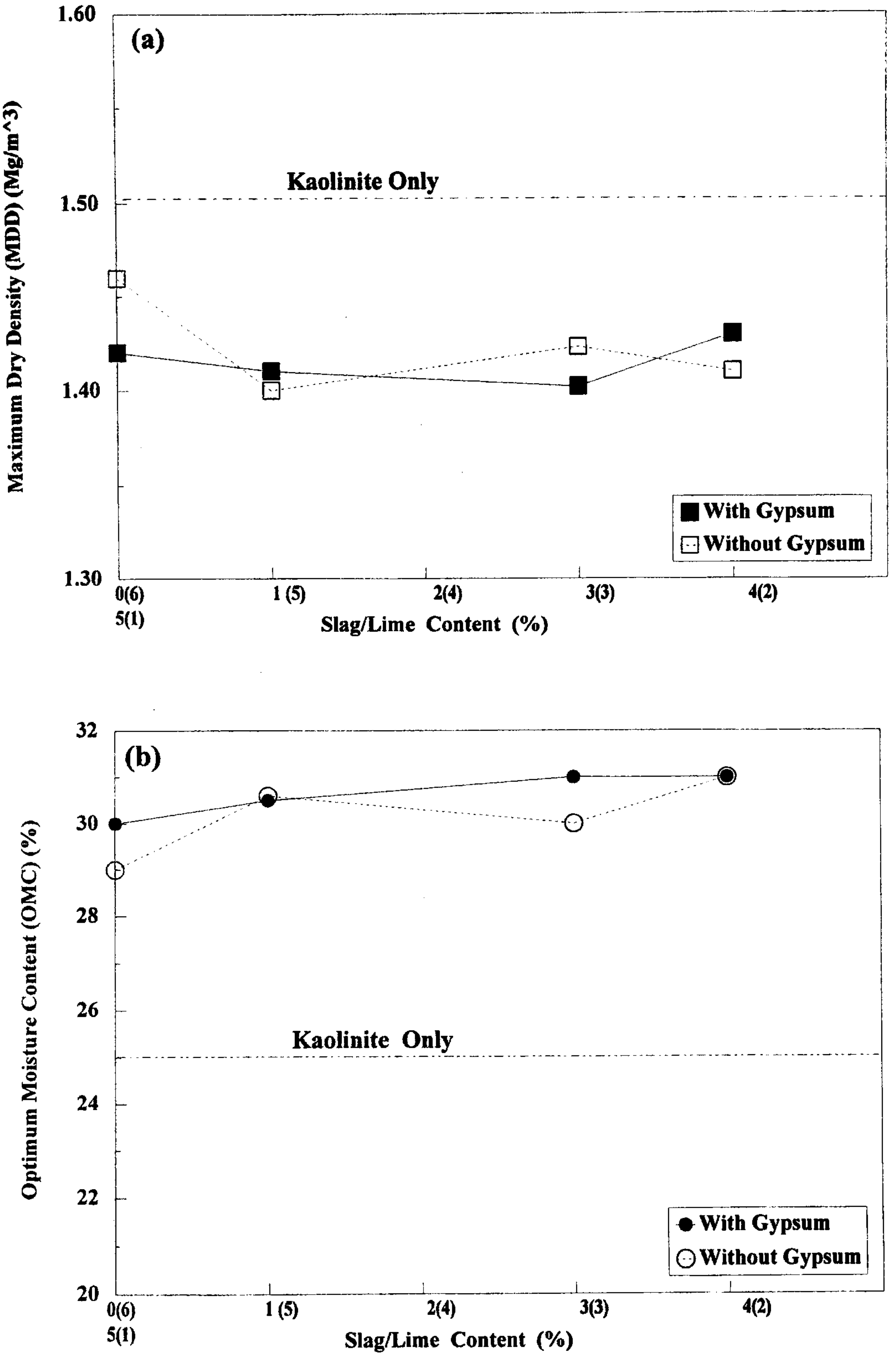
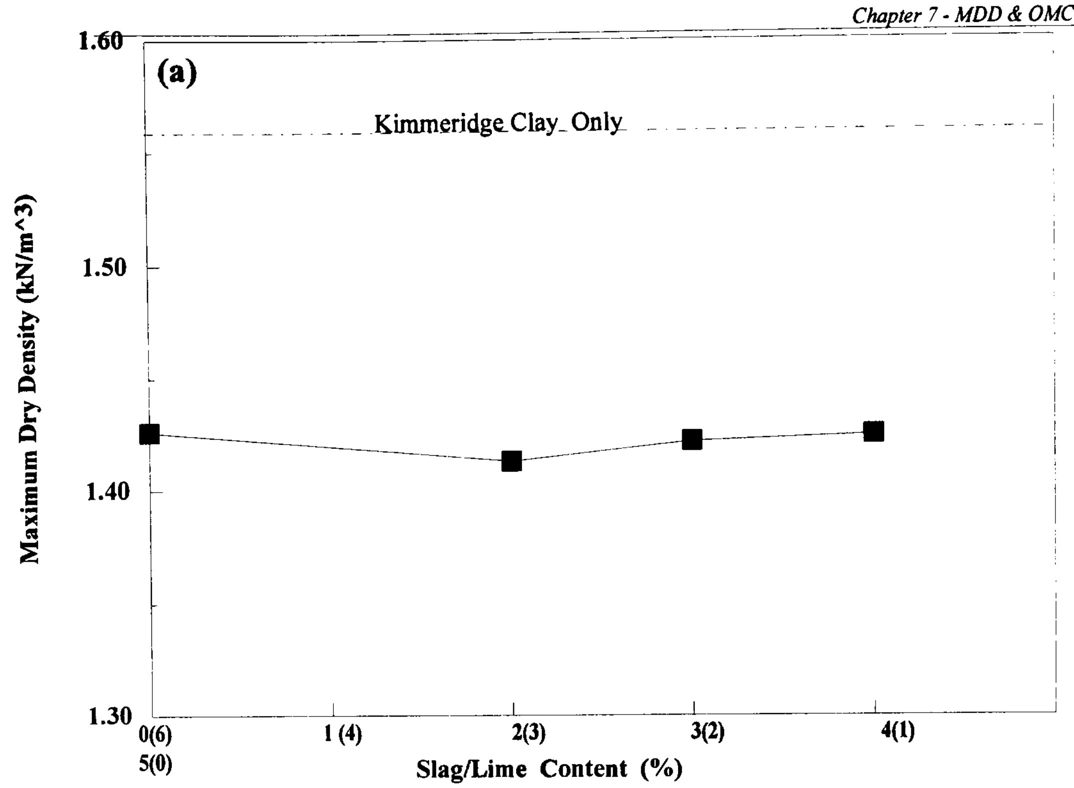


Figure 7.2-4-(a) Maximum Dry Density (MDD) vs. Slag/(Lime) content (b) Optimum Moisture Content (OMC) vs. Slag/(Lime) content for kaolinite-lime-slag-gypsum (2.79% SO_3) mixes.



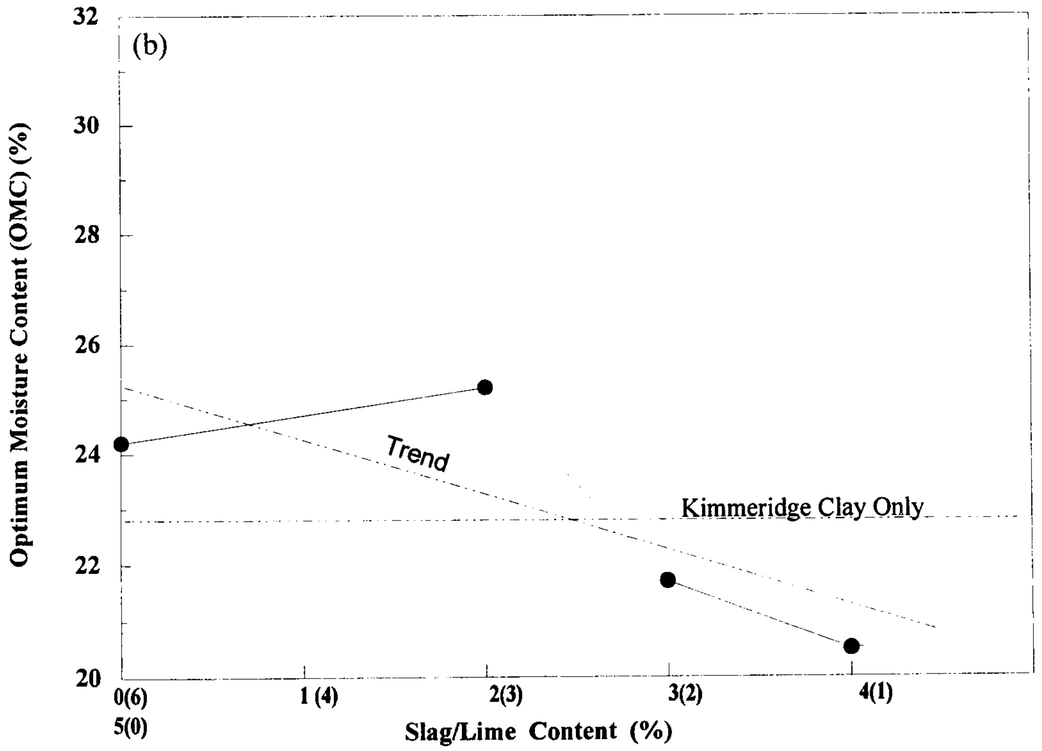


Figure 7.2-5- (a) Maximum Dry Density (MDD) vs. Slag/(Lime) content (b) Optimum Moisture Content vs. Slag/(Lime) content for Kimmeridge clay-lime-slag mixes.

7.3 UNCONFINED COMPRESSIVE STRENGTH OF LIME - STABILISED KAOLINITE AND KIMMERIDGE CLAY

7.3.1 INTRODUCTION

During the first phase of work on the unconfined strength of lime-stabilised clays, samples of kaolinite stabilised with 6 wt.% lime (Control mix) and containing varying amounts of the sulphates of calcium, magnesium, sodium and potassium were cured for various periods up to a maximum of 20 weeks. Four levels of sulphate additions were used such that any addition would provide a sulphate ion concentration equivalent to the addition of either 2, 4, 6 or 8 wt.% gypsum (i.e. 0.93, 1.86, 2.79 and 3.72 % by mass of SO_3 (see Appendix 1)).

The second phase was intended to study the effects on strength development of the addition of ground granulated blastfurnace slag (GGBS) on lime-stabilised clays. For this phase, the lime content in the kaolinite - 6 wt. % lime (control) mix and in Kimmeridge Clay - 5 wt. % lime (also control mix) was gradually replaced with GGBS. Gypsum was selected as the source of sulphate for this study, in preference to the other sulphates, for three main reasons. Firstly, it has a much more widespread occurrence in natural clays. Secondly, the Kimmeridge Clay used in this work as a typical natural sulphate bearing clay contains this type of sulphate, making gypsum a better choice for comparison of results with those obtained with the "pure" kaolinite. Finally, research on strength and swelling properties where gypsum is the source of sulphate is more widespread and hence makes comparison more meaningful. In addition, due to time considerations, it was not possible to study all the possible effects of all the sulphate types. For this reason (and in order to reasonably reduce the number of possible mix material combinations), samples for the study of lime substitution with GGBS were cured for one and four weeks only. No gypsum was added to Kimmeridge Clay as it already inherently contained a substantial amount of gypsum in the form of selenite crystals (1.73 % SO_3 equivalent to about 4 wt.% gypsum). Greater amounts of gypsum (3.72% SO_3) were used during the first phase of the work using kaolinite in order to study the extreme effects on swelling of very high sulphate levels. Higher amounts of gypsum would not only give a better indication of the extremes of any detrimental swelling effects but also the limit to strength development likely to occur at high sulphate contents.

7.3.2 EFFECTS OF DIFFERENT SULPHATE TYPES ON UCS

7.3.2.1 Gypsum

Figure 7.3-1 (a) illustrates the effects of curing on the strength development of kaolinite - 6wt% lime (control mix) samples containing various amounts of gypsum cured for various periods up to a maximum of twenty weeks. At all curing periods, the addition of gypsum at levels higher than the SO_3 equivalent addition of 0.93% resulted in enhanced strength development. A peak in strength developed with increased sulphate content (see Figure 7.3-1 b)), the position of this peak shifting to higher SO_3 levels at increased curing times of up to about 5 weeks. The maximum strength occurred after 10 weeks at an optimum gypsum content of 2.79 % SO_3. The dotted line in Figure 7.3-1 (b) clearly shows the emergence of this optimum gypsum content from lower gypsum levels and its movement with prolonged curing. Ultimately at 20 weeks of curing, the strength attained in order of sulphate content was:-

$$\mathbf{2.79 > 3.72 > 1.86 > 0.93 \approx 0 \text{ (control) } \% \; SO_3}$$

(i.e. at 20 weeks all samples containing gypsum gave strengths in excess of that of the control mix).

7.3.2.2 Magnesium Sulphate

Figure 7.3-2 (a) shows the strength development of the kaolinite control mix upon addition of various amounts of magnesium sulphate. Below curing periods of approximately five weeks, all levels of $MgSO_4$ addition resulted in strength increase relative to the control mix. This strength increase however reached an early maximum at curing periods of only two weeks for samples containing relatively higher sulphate contents (above 1.86 % SO_3) and then the samples started to deteriorate and lose strength. After this initial strength development, samples containing high sulphate levels recorded low strengths (lower than the control) throughout the curing period. Those that continued to record appreciable strengths (those containing 0.93 and 1.86% SO_3) also started to deteriorate beyond 10 weeks of curing. Figure 7.3-2 (b) shows that although up to ten weeks of curing a peak in strength emerges at 1.86% SO_3, the general trend as curing period increases is for strength to decrease with increase in SO_3 content. Thus, unlike the case for gypsum, no clearly defined optimum $MgSO_4$ content was observed. Also at 20 weeks all specimens containing $MgSO_4$ gave strengths below that of the control mix.

7.3.2.3 Sodium Sulphate

The strength development with curing for kaolinite - 6 wt.% lime containing various amounts of sodium sulphate is illustrated in Figures 7.3-3 (a) and (b). As was the case for both gypsum and $MgSO_4$ additions, all levels of Na_2SO_4 addition resulted in enhanced strength during the initial curing period of less than six weeks. For Na_2SO_4 levels up to 2.79 % SO_3, strength continued to increase with age up to 10 weeks beyond which there was no further significant strength gain whereas specimens containing 3.72% SO_3 showed no further increase after 3 weeks. Also, only the specimens containing 1.86 % SO_3 had strengths in excess of the control at 20 weeks. Figure 7.3-3 (b) shows the emergence of an optimum sulphate content of 1.86 % SO_3 from an early curing period of one week. This optimum sulphate content does not change with curing time.

7.3.2.4 Potassium Sulphate

Figure 7.3-4 (a) shows strength development for Kaolinite - 6 wt. % lime - K_2SO_4 samples. Most of the strength development occurred during the first 6 weeks of curing and, as with the other sulphate types all levels of sulphate addition produced enhanced strength during this period. Beyond this period, the control mix continued to increase in strength (up to 20 weeks) but samples containing the various levels of K_2SO_4 showed little further strength gain. Thus at 20 weeks all specimens containing K_2SO_4 had strengths below that of the control. Figure 7.3-4 (b) does not indicate a clear optimum sulphate level but shows that the early strength did tend to increase with increase in SO_3 content, up to 2.79 % SO_3. As was the case for magnesium sulphate, and in contrast to calcium sulphate, all samples containing potassium sulphate had strengths at 20 weeks below that of the control.

7.3.3 COMPARISON OF THE EFFECTS OF THE DIFFERENT SULPHATE TYPES ON UCS

It is very difficult to compare the effects on UCS of the different sulphate types without specifying other related variables which include curing time and sulphate content as all these factors are interrelated. In this section therefore, the headings are used as a convenient way to emphasize the most significant effects under each heading.

7.3.3.1 Curing Time

Figure 7.3-1 - 7.3-4 show that the initial rate (up to 10 weeks) of strength development of the control mix (kaolinite - 6wt.% lime) was fairly constant. Beyond 10 weeks, the strength increase was slower up to the maximum observed curing period of 20 weeks. The addition of metal sulphates in all cases accelerated the initial rate of strength development during the first 3 weeks, the accelerating effect being generally of comparable magnitudes for all the sulphate types. After this initial curing period (of up to three weeks), there was a general tendency in the case of sulphates of Mg, Na and K for the rate of strength development to decline, and in the case of sodium and particularly magnesium sulphate, high sulphate concentrations (> 2.79% SO_3) actually produced a reduction in strength. The effect of calcium sulphate additions on strength was intrinsically different from that of the other sulphates in that (particularly at high concentrations of sulphate (2.79 and 3.72% SO_3)), the strength continued to show substantial increases beyond 6 weeks. This effect was particularly pronounced at 2.79% SO_3. Also within 6 weeks the strength change with time exhibited a step function (indicated by the dotted line in Figure 7.3-1), an effect observed by Wild *et al.,* (1990) in a study of the effect of gypsum on the strength development of lime - PFA mixes. This indicated that the reaction of lime with kaolinite in the presence of gypsum was fundamentally different from that of the other sulphates. In fact in the case of sodium, potassium and magnesium sulphates, most of the strengths fell below that of the control at extended curing periods (between 10 and 20 weeks) and especially at high sulphate concentrations (Figures 7.3-2 (a) - 7.3-4 (a)). In fact in the case of magnesium sulphate addition, the strengths of specimens with high sulphate contents (2.79 - 3.72% SO_3) fell below the control at ages as early as 6 weeks.

7.3.3.2 Sulphate Type and Content

The effects of increasing the sulphate concentration on strength for the four different metal sulphates at different curing periods between 1 week and 20 weeks are further illustrated in Figures 7.3-5 (a) - (d). As already noted there was, in particular cases, a maximum in the observed strength at a particular (or a range of) optimum sulphate concentration. The change in this maximum strength with increase in curing time and SO_3 content was represented (in cases where a clear pattern emerged), by a dotted line as in Figures 7.3-1 (b) and 7.3-3 (b). For the case of the addition of sulphate containing Ca^{2+} cations, the magnitude of this maximum strength increased with both increase in curing time and also increase in SO_3 content up to a curing time of 10 weeks and a sulphate content of 2.79 % SO_3 (see Figure 7.3-5 (a) - (d)). For the case of Na_2SO_4 addition, the maximum strength at each curing time occurred (and increased with curing time) at an optimum SO_3 content of 1.86% which emerged as early as at one week of curing.

After 10 weeks of curing, the value of the maximum strength was greatest for calcium sulphate and generally decreased in the cation order :-

Ca^{2+} > Na^{+} > K^{+} > Mg^{2+} ....(See Figure 7.3-5 (c) and (d))

All sulphates showed decrease in strength beyond 2.79% SO_3 content with prolonged curing (See Figure 7.3-5 (b) - (d)). After curing for one week (Figure 7.3-5 (a)), the different sulphates do not show very pronounced difference in their effects on strength but differences do become very marked at extended curing times, particularly after ten weeks (Figure 7.3-5 (c)). In particular calcium sulphate additions produce a very strong strength peak at 2.79% SO_3. It should be noted that for a 6% $Ca(OH)_2$ addition to the kaolinite, the SO_3 level from gypsum required to fully consume that lime in ettringite formation is 6.49% SO_3 and in monosulphate formation 2.16% SO_3.

7.3.3.3 Effects of Sulphate Type

The effect of the different metal sulphates on the strength of cured 6% lime - kaolinite cylinders is presented, for short and long curing periods and for different SO_3 levels, in Table 7.3-1. All the different metal sulphate additions produce strengths in excess of the control at short curing periods, confirming the accelerating effect of sulphate additions on strength development. Magnesium has the strongest effect on strength gain and potassium the weakest. Sodium is also very effective at low sulphate concentrations (< 3.72 % SO_3). However at long curing periods the relative performance of the metal sulphates with regard to strength is very different. Magnesium sulphate has a clearly deleterious effect on strength particularly at high sulphate concentrations where strengths are substantially less than the control. This suggests that although magnesium sulphate may initially accelerate the cementitious reactions, the ultimate reaction products contribute to a fall in strength. At high sulphate concentrations, only calcium sulphate produces strengths in excess of the control and the strength enhancement achieved is substantial. This suggests that the long term reaction products produced with calcium sulphate make a significant contribution to strength. It should also be noted that sodium sulphate when at low concentrations is also quite effective in producing strength enhancement up to extended curing periods.

Table 7.3.1 - Order of strength development for kaolinite - lime mixes containing varying amounts of various sulphates.

SO_3 CONTENT	SHORT CURING PERIOD (0-3 WEEKS)	LONG CURING PERIOD (20 WEEKS)
0.93%	$Mg^{2+} > Na^{+} > Ca^{2+} > K^{+} >$ Kao.	$Na^{+} \geq Ca^{2+} \geq$ Kao $> Mg^{2+} > K^{+}$
1.86%	$Na^{+} > Ca^{2+} > Mg^{2+} > K^{+} >$ Kao	$Ca^{2+} \approx Na^{+} >$ Kao $> K^{+} > Mg^{2+}$
2.79%	$Na^{+} > Mg^{2+} \approx Ca^{2+} > K^{+} >$ Kao.	$Ca^{2+} >$ Kao. $> K^{+} > Na^{+} > Mg^{2+}$
3.72%	$Mg^{2+} > Ca^{2+} \approx Na^{+} \geq K^{+} >$ Kao.	$Ca^{2+} >$ Kao. $> K^{+} > Na^{+} > Mg^{2+}$

Kao. = Kaolinite-6wt.% lime, without sulphate addition.

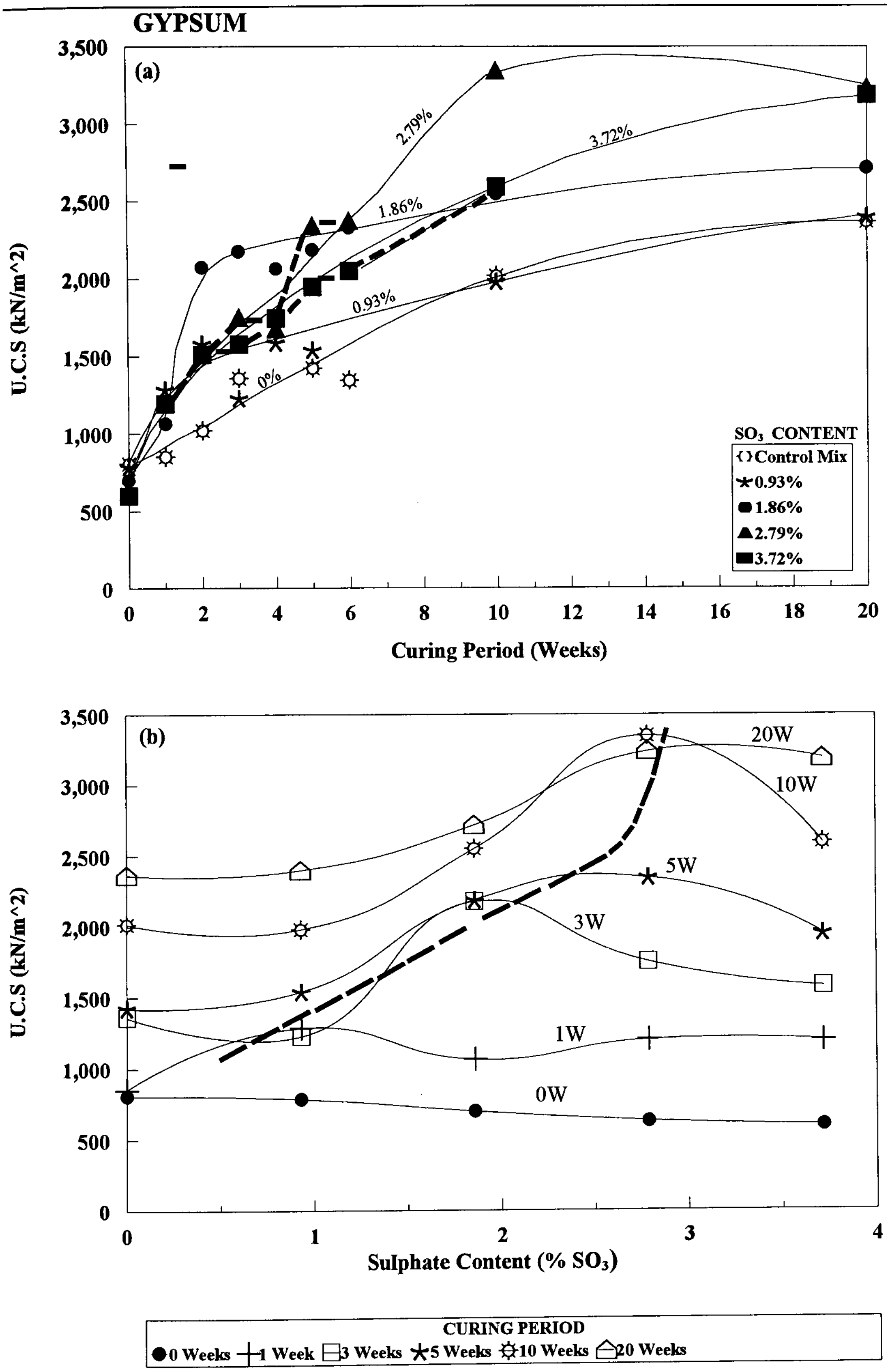


Figure 7.3-1-UCS vs. Curing time for kaolinite-6wt.% lime cylinders with additions of varying amounts of gypsum, cured at 30°C and 100% relative humidity *(MDD=1.41 Mg/m^3; OMC=27.4%).*

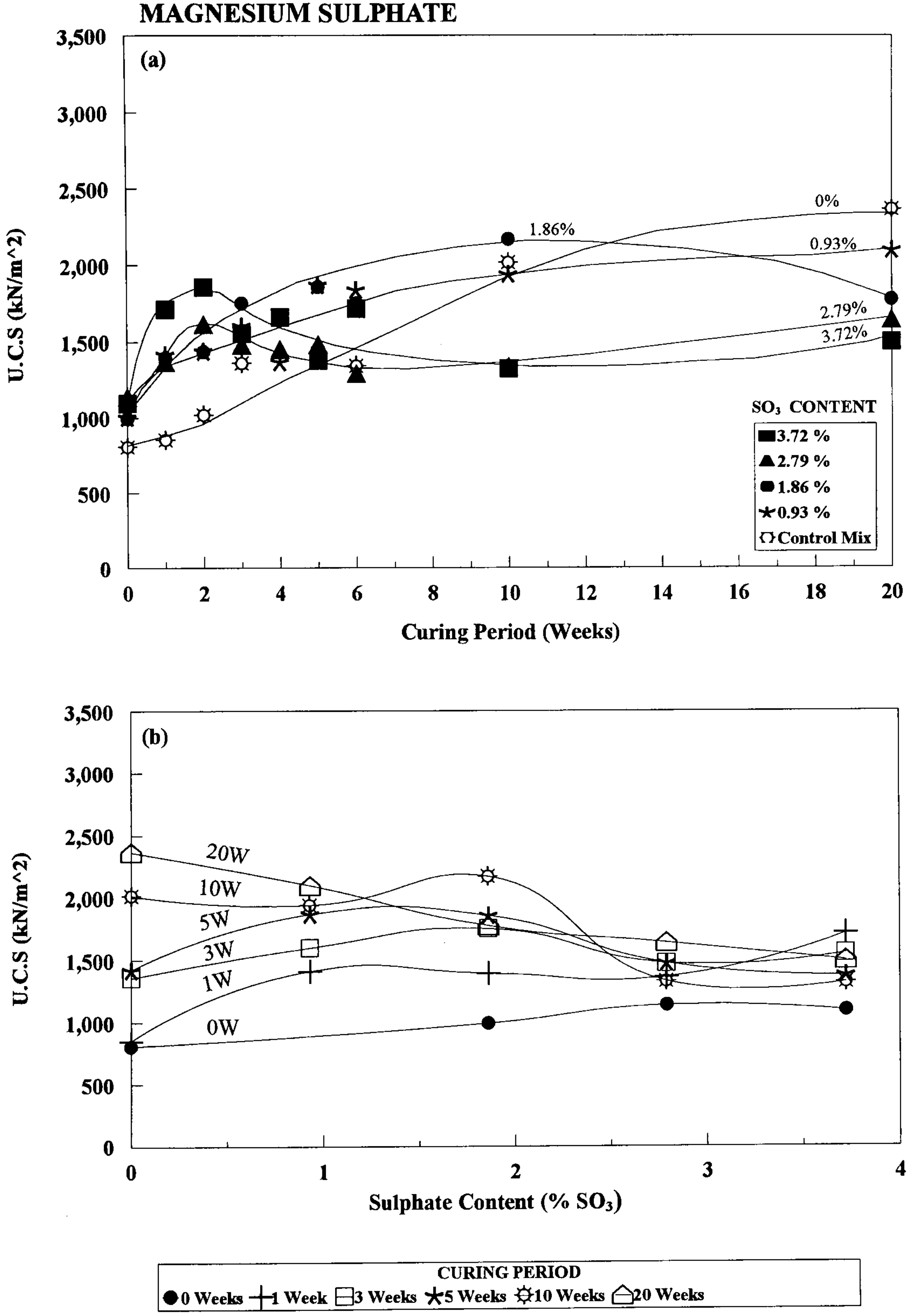


Figure 7.3-2-UCS vs. Curing time for kaolinite-6wt.% lime cylinders with additions of varying amounts of magnesium sulphate, cured at 30°C and 100% relative humidity *(MDD=1.41 Mg/m^3; OMC=27.4%)*

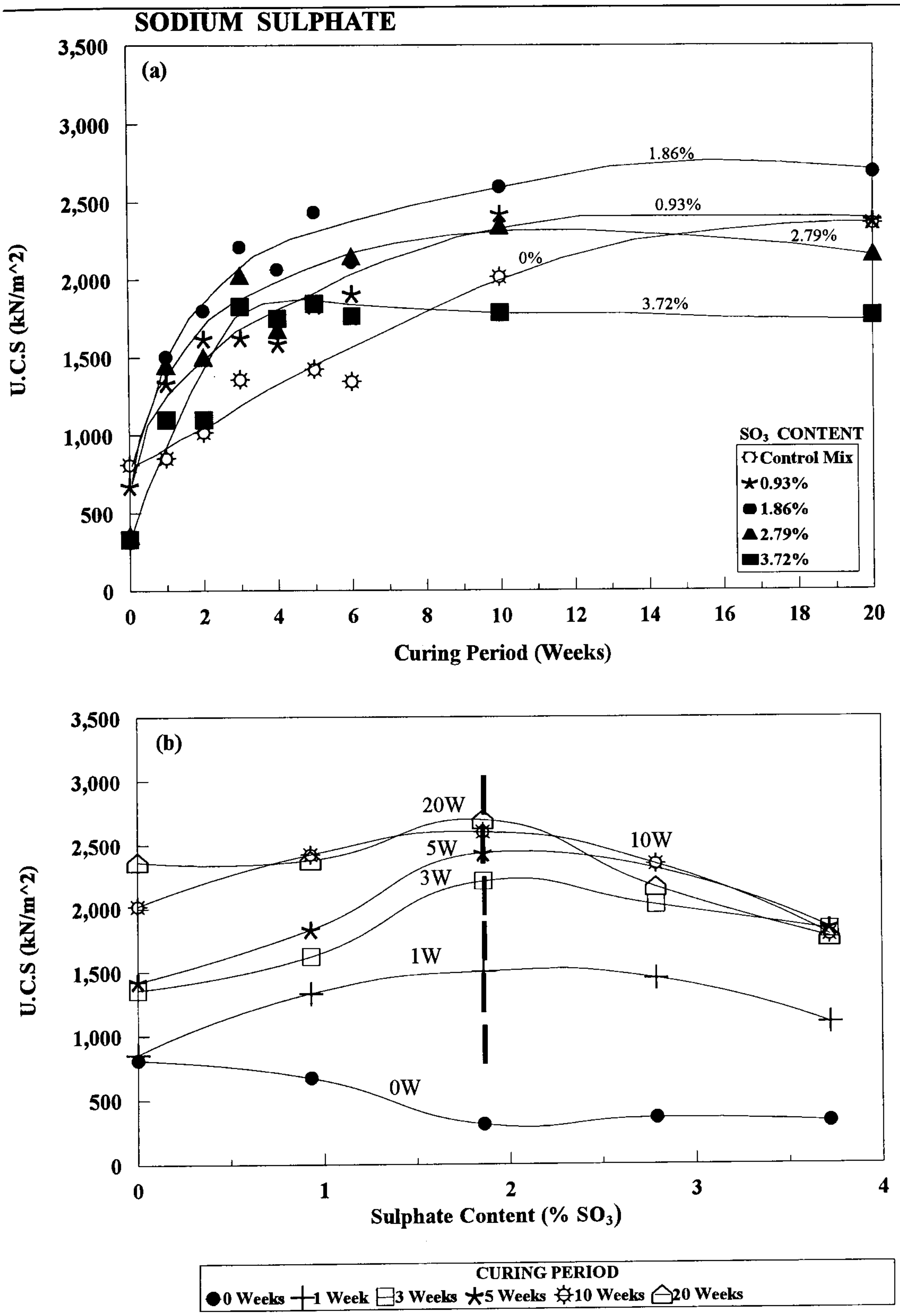


Figure 7.3-3-UCS vs. Curing time for kaolinite-6wt.% lime cylinders with additions of varying amounts of sodium sulphate, cured at 30°C and 100% relative humidity. *(MDD=1.41 Mg/m^3; OMC=27.4%)*

POTASSIUM SULPHATE

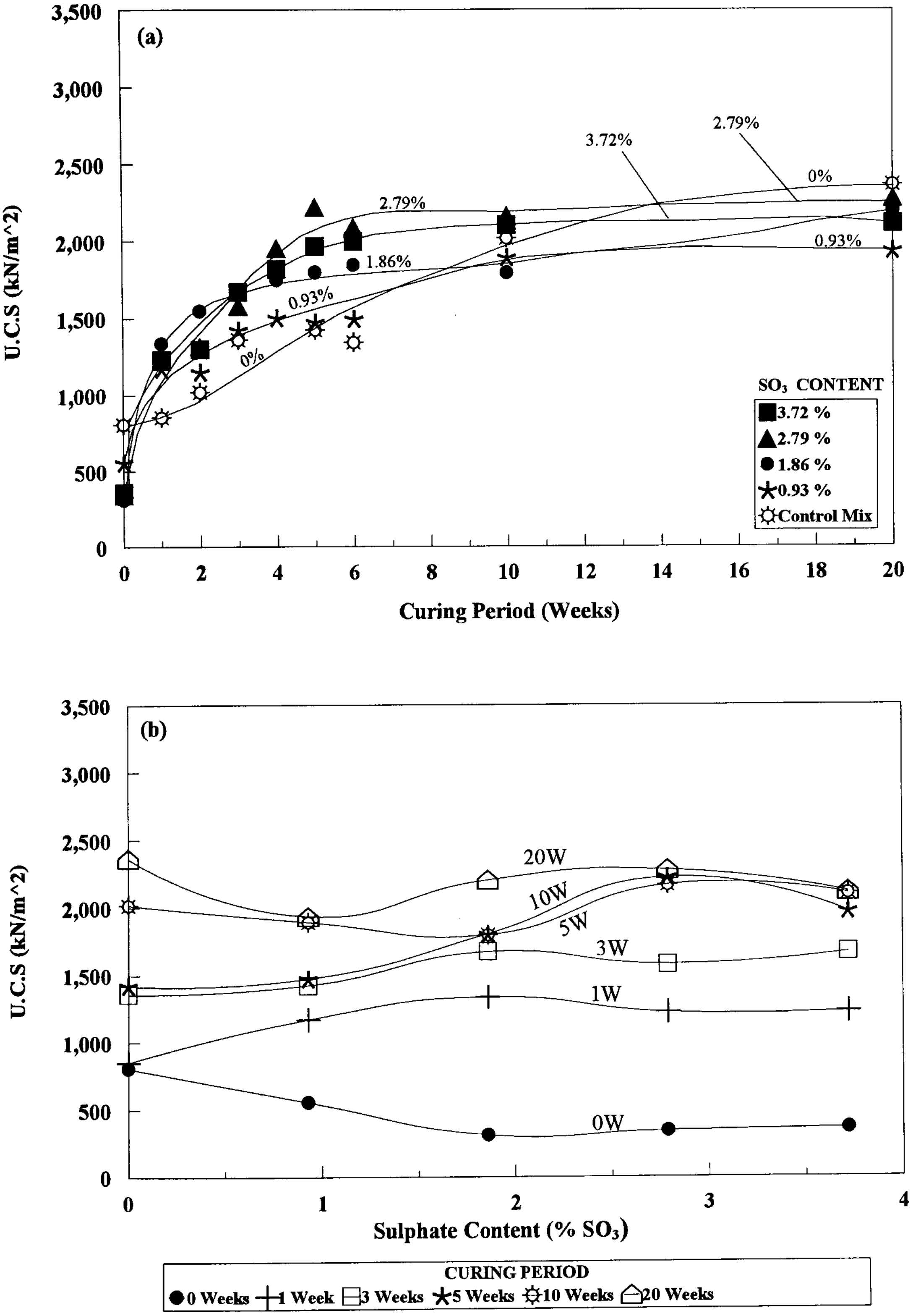


Figure 7.3-4-UCS vs. Curing time for kaolinite-6wt.% lime cylinders with additions of varying amounts of potassium sulphate, cured at 30°C and 100% relative humidity *(MDD=1.41 Mg/m^3; OMC=27.4%)*

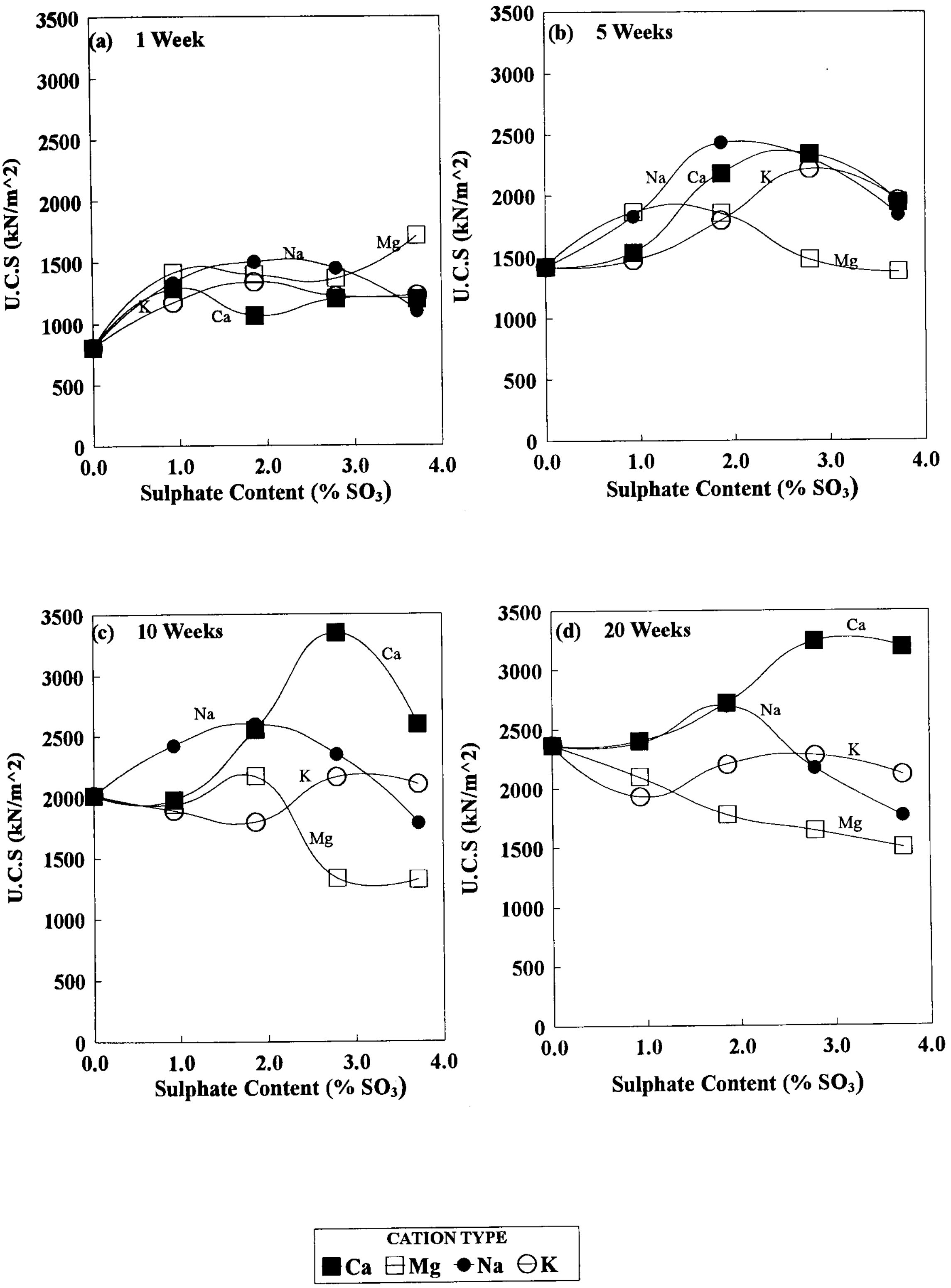


Figure 7.3-5-UCS vs. Sulphate content for kaolinite-6wt.% lime cylinders with additions of varying amounts of various sulphates, cured at 30°C and 100% for (a) 1 Week, (b) 5 Weeks, (c) 10 Weeks and (d) 20 Weeks *(MDD=1.41 Mg/m^3; OMC=27.4%)*

7.3.4 EFFECTS OF PARTIAL SUBSTITUTION OF LIME WITH GROUND GRANULATED BLASTFURNACE SLAG (GGBS) ON UCS

7.3.4.1 Kaolinite system

Figures 7.3-6 (a), (b) and (c) illustrate the effects (on the 7-day and 28-day UCS) of progressive substitution of lime with GGBS in kaolinite - 6 wt.% lime (control) samples with and without added gypsum. Three levels of gypsum were used 2, 4 and 6 wt.%, based upon the clay and stabilizer combined. This is equivalent to 0.93, 1.86 and 2.79% by mass of SO_3 (see Appendix 2).

When no gypsum is present, then for the 7 day curing period (Figure 7.3-6) partial substitution of lime with slag has very little effect on strength, producing only a slight increase in strength with increasing substitution. However after 28 days the level of substitution has a significant effect on strength, producing continuously increasing strength with increasing substitution of lime with slag. This indicates that by 28 days the hydration of the slag is at a much more advanced stage with regard to its contribution to strength than is the pozzolanic reaction between the lime and the kaolinite.

When gypsum is present, for the 7 day curing period there is increasing strength enhancement, relative to the sulphate free material, with increasing substitution of lime with slag. This suggests that the presence of gypsum not only accelerates the cementitious reactions with lime and kaolinite (as previously observed in section 7.3.3) but also even more effectively accelerates the hydration of the slag. After 28 days curing, there is further strength enhancement by the gypsum but in this case the strength enhancement is much greater at low substitution levels and decreases as the lime is substituted with slag. Thus at a 5:1 slag to lime ratio there is virtually no difference in the 28 day strengths of specimens with gypsum and without gypsum, irrespective of the SO_3 level. This indicates that the accelerating effect of the gypsum on the slag hydration is complete. However at 0:6 slag to lime ratio there is at 28 days substantial strength enhancement when gypsum is present particularly at the higher SO_3 levels, which suggests that the effect of gypsum on the cementitious reaction between lime and kaolinite is more pronounced at this later stage. It should also be noted that if only slag is present and no lime (6:0), then strengths are extremely low. There is no strength development, and gypsum has no influence whatsoever on strength (point B on graphs in Figure 7.3-6). This suggests that gypsum will only accelerate slag hydration if the slag is activated with lime, and will not activate the slag on its own.

Figure 7.3-7 presents the same 7 day and 28 day strength data but in this case plotted against gypsum content (as % SO_3) rather than slag/lime ratio. This again emphasizes the increasing strength enhancing effect of the sulphate additions with increasing substitution of lime with slag. In addition it shows that there is an optimum sulphate content of 0.93% SO_3 for maximum 7 day strength which is principally a result of acceleration of the slag hydration reactions. For the composition 6L0S, sulphate content has little beneficial effect on strength at 7 days. After 28 days however sulphate content has a very marked effect on the strength of this composition (6L0S) which increases steeply from 0% SO_3 to 1.86% SO_3 , emphasizing as previously suggested that the reaction product resulting from the lime - clay - gypsum reaction contributes significantly to strength at these later periods. Conversely specimens containing a small amount of lime and a large amount of slag (1L5S) show negligible variation in strength with increase in sulphate level simply because the initial accelerating effect of the sulphate on slag hydration is complete and the hydration level of specimens without sulphate has reached that of specimens with sulphate.

The way in which different levels of sulphate influence the rate of strength development is clearly illustrated in Figure 7.3-8 (a), (b), (c) and (d). When no sulphate is present (Figure 7.3-8 (a)) strength development of high lime-low slag material (e.g. 6L0S0G) is very limited emphasizing the very slow pozzolanic lime - clay reaction. In contrast strength development of the low lime - high slag material is substantial confirming the much more rapid activated slag hydration reaction. When sulphate is introduced (See 7.3-8 (b)) the 7 day strengths of low lime-high slag compositions increase substantially whereas those of high lime-low slag compositions show much smaller increases emphasizing the much greater accelerating effect of sulphate on activated slag hydration compared with its influence on the lime-clay reaction. The effect of sulphate on lime - kaolinite activity is much more pronounced at higher sulphate concentrations and at longer curing time (28 days) (See Figure 7.3-8 (c)). Here the strength increase between 7 and 28 days for the high lime-low slag compositions is substantial particularly when compared to that where no sulphate is present (Figure 7.3-8 (a)). This strength increase is attributed to formation of a cementitious reaction product which is not formed in the absence of sulphate. It is suggested that this product is ettringite.

7.3.4.2 Kimmeridge clay

Figures 7.3-9 to 7.3-11 illustrate the effects (on UCS) of progressive substitution of lime with GGBS in Kimmeridge Clay - lime cylinders at various magnitudes of total stabilizer (TS) content (i.e. lime + GGBS = 5%, 6%, 8% and 10%). In contrast to the kaolinite - lime - gypsum system, where the SO_3 level was artificially varied, in Kimmeridge Clay the sulphate content is fixed at its natural level of 1.73 % SO_3. Thus for purposes of comparison with the kaolinite - lime - gypsum system, Figure 7.3-6 (b) is the nearest equivalent (1.86 % SO_3). Also in the case of the Kimmeridge Clay the total stabilizer content was varied from 5% to 10% in order to establish from a practical and engineering aspect, what an appropriate level of stabilizer would be. There are clear similarities in behaviour between the clay systems. Comparison of Figure 7.3-9 (b) with 7.3-6 (b) show parallel behaviour in the relationship between 7 day and 28 day strength in that at low slag to lime ratios (6L0S) the 28 day strength is much greater than the 7 day strength and at high slag to lime ratios (1L5S) the 7 day and 28 day strengths move closer to each other. Also in both cases the 7 day strength initially increases as the slag to lime ratio increases, reaches a maximum, and then decreases although the maximum occurs earlier with Kimmeridge Clay. However in the case of the 28 day strength there is a general reduction in strength with increasing slag to lime ratio, particularly at high slag low lime contents (1L4S), which is not observed in the kaolinite - lime - gypsum system other than when there is zero lime present. The 28 day strength developed at high slag low lime compositions is attributed principally to the hydration of the slag which is activated by lime and initially accelerated by the presence of sulphate. The fact that at high slag and low lime compositions (1L4S) the strength falls significantly both at 7 and particularly 28 days of curing suggests that there is insufficient total lime in the system to fully activate the slag. This interpretation is supported by the results obtained with increased stabilizer contents (Figures 7.3-9 (b) and 7.3-10 (a) and (b)) where strengths at high slag - low lime compositions are markedly increased relative to those at low slag high lime compositions. Figure 7.3-11 suggests an optimum slag/lime ratio of 1.0 - 2.0.

Another factor observed with Kimmeridge Clay not present with kaolinite is that compositions containing slag but no lime do show small strength gains with time (points B and B' on the curves in Figures 7.3-9 and 7.3-10). This suggests that the Kimmeridge Clay contains some component(s) which can produce partial and limited activation of the slag. However, this was not observed to occur in the kaolinite - lime - gypsum system which suggests that the component producing this effect is something other than gypsum alone.

7.3.5 SUMMARY

The following principal points may be deduced from the results, with regard to the influence of sulphates and GGBS on kaolinite and Kimmeridge Clay when stabilised with lime.

1. Of all the metal sulphates tested, gypsum has the greatest effect on the strength development of lime-stabilised kaolinite.
2. Magnesium and potassium sulphates emerge as the most deleterious of the sulphates under study in the long-term. However, magnesium does appear to accelerate the initial cementitious reactions.

3. Sodium sulphate at low concentrations (below 1.86% SO_3) has both short-term and long-term strength enhancing effects.
4. All sulphates record a reduction in the rate of strength development at sulphate concentrations beyond 2.79% SO_3.
5. Substitution of lime with GGBS gives improved 7 day and 28 day strength for both kaolinite and Kimmeridge Clay. In the case of kaolinite, the effects are more pronounced in the presence of gypsum.
6. The most significant strength enhancement due to lime replacement with GGBS over the first 28 days was either for i) high lime-low slag mixes with gypsum, due to the contribution of gypsum to the longer term kaolinite - lime - gypsum reaction, or for ii) low lime - high slag without gypsum due to the lime activated slag hydration (see Figure 7.3-6).
7. The greatest short-term strength enhancement was for low lime - high slag with gypsum due to the accelerating effect of gypsum on the lime/gypsum activated slag hydration.
8. Slag alone has no effect on both short-term and long-term strength effects of kaolinite while it does provide limited but significant strength enhancement in the case of Kimmeridge Clay.
9. Substitution of lime by slag for Kimmeridge Clay provides a maximum in 28 day strength at a specific replacement level whereas for kaolinite the 28 day strength continues to increase gradually up to a replacement level of at least 5S1L although at 6S0L strength falls sharply.

The next chapter will report on the linear expansion, swelling pressure generation, phase analysis and microstructure.

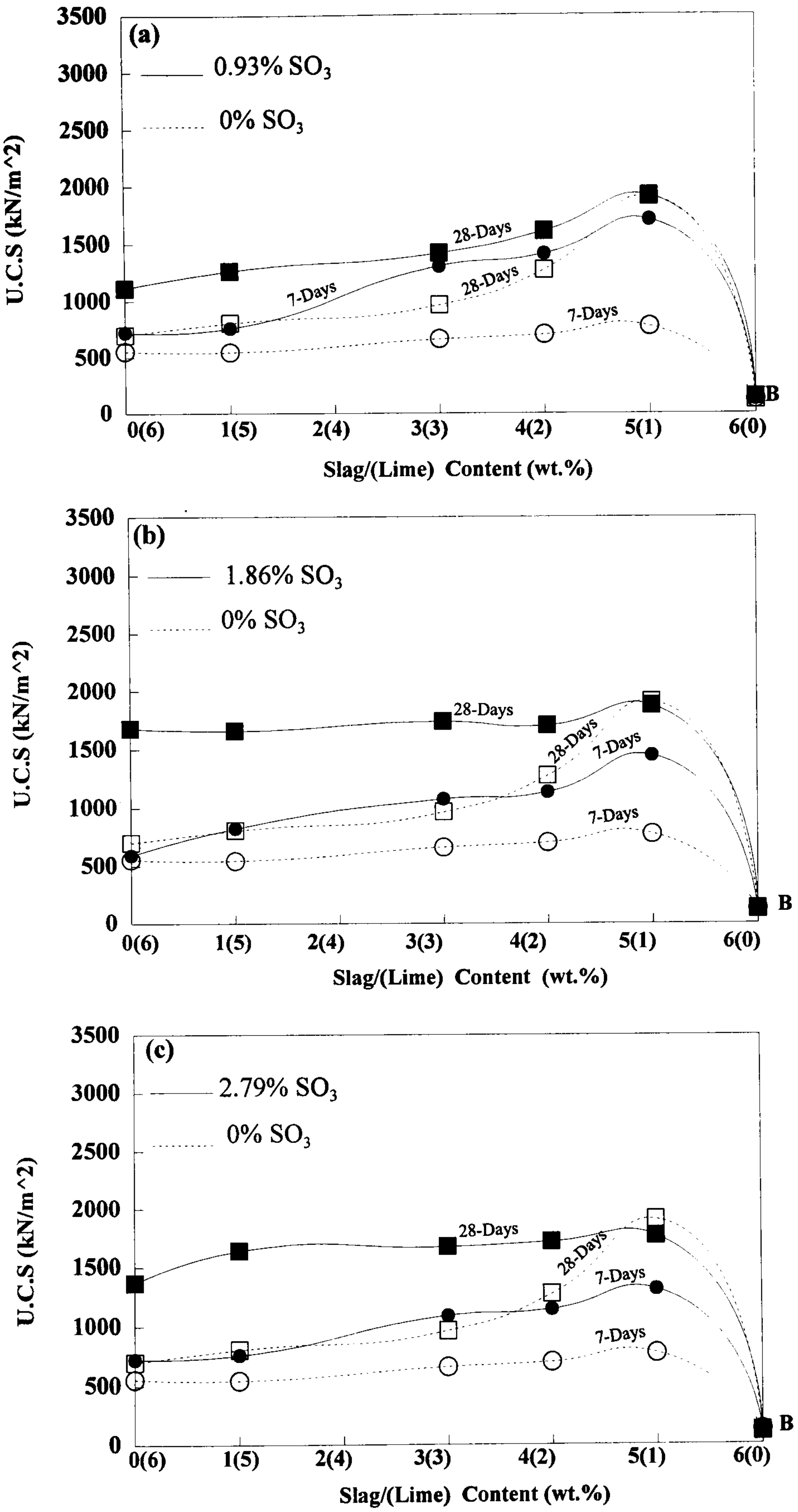


Figure 7.3-6 UCS vs. Slag/(Lime) content for kaolinite-lime-ggbs cylinders with and without (a) (0.93) (b) 1.86 & (c) 2.79% SO_3 equivalent of gypsum and moist cured for 7 and 28 days at 30°C and 100% relative humidity *(MDD=1.41 Mg/m^3; OMC=30.55)*

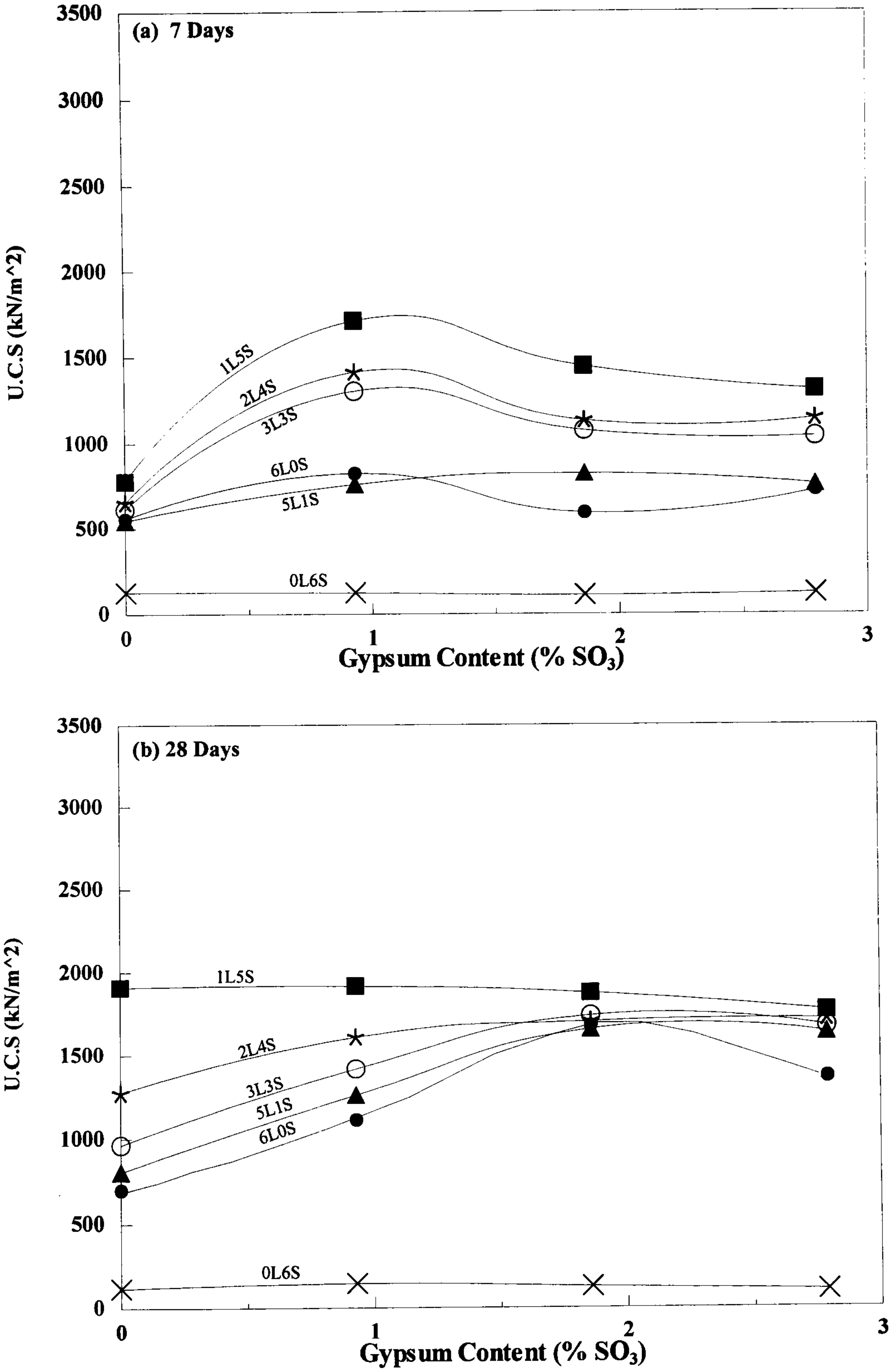


Figure 7.3-7 UCS vs. Gypsum content (% SO_3) for kaolinite-lime-ggbs cylinders with additions of varying amounts of gypsum, moist cured for (a) 7 & (b) 28 days at 30°C and 100% relative humidity *(MDD=1.41 Mg/m^3; OMC=30.55%).*

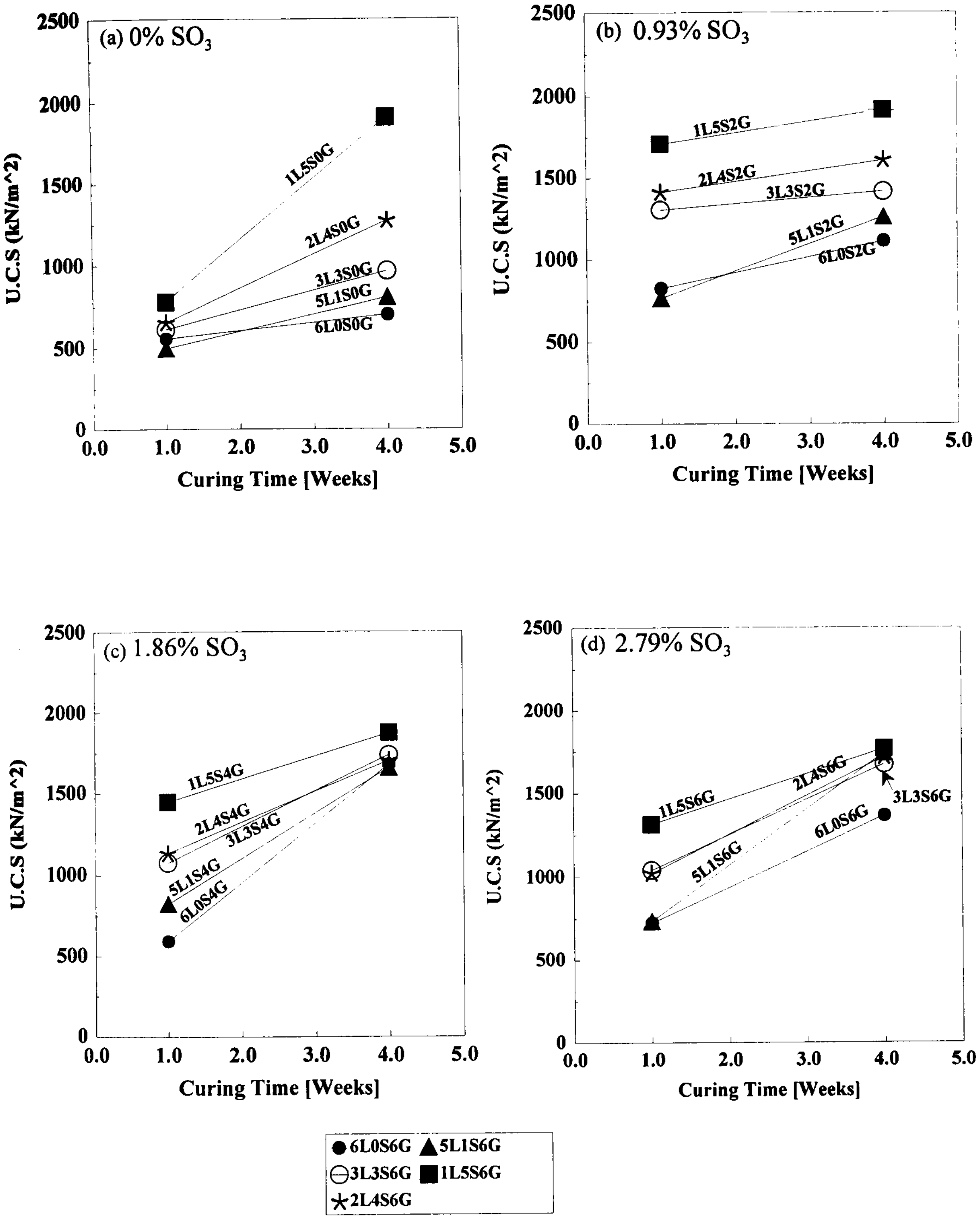


Figure 7.3-8 UCS vs. Curing time for kaolinite-lime-ggbs cylinders with additions of varying amounts of gypsum, moist cured at 30°C and 100% relative humidity *(MDD=1.41 Mg/m^3; OMC=30.55%).*

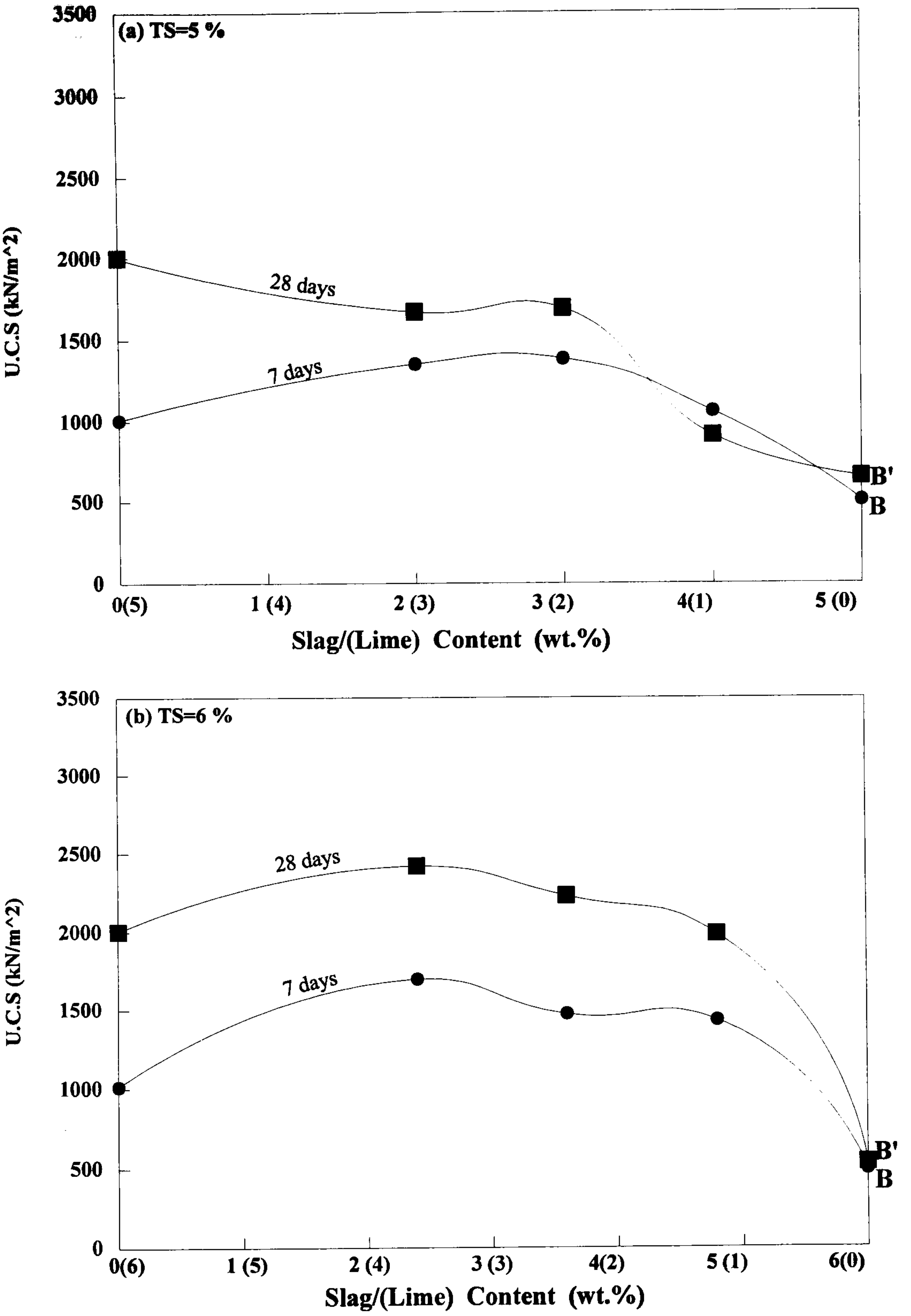
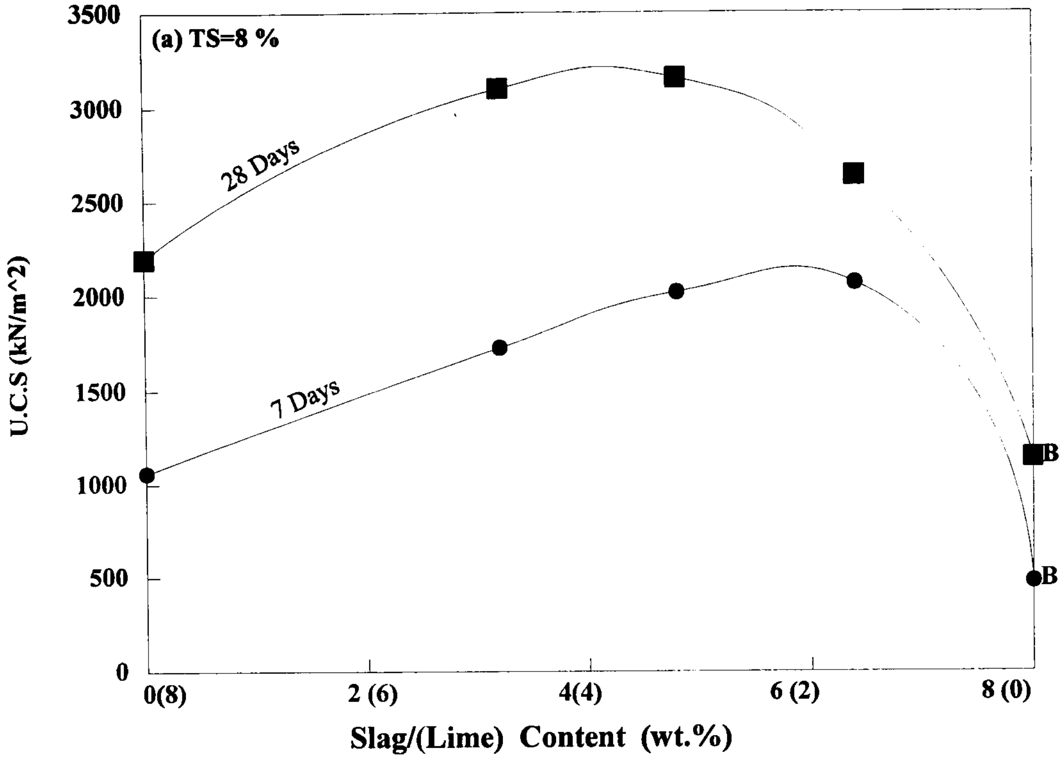


Figure 7.3-9 UCS vs. Slag/(Lime) content for Kimmeridge clay-lime-ggbs cylinders containing a total stabiliser content (Lime + ggbs) of (a) 5 and (b) 6 wt.%, and moist cured for 7 and 28 days at 30°C and 100% relative humidity.
(MDD=1.41 Mg/m^3; OMC =24.22%).



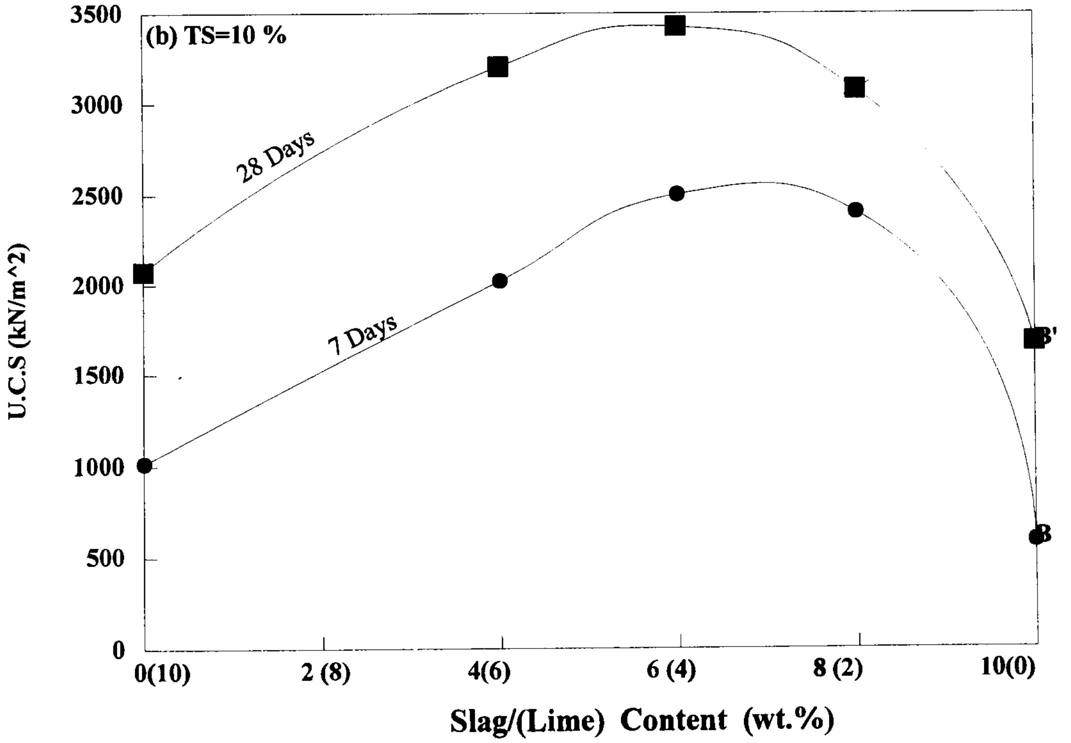


Figure 7.3-10 UCS vs. Slag/(Lime) content for Kimmeridge clay-lime-ggbs cylinders containing a total stabiliser content (Lime + ggbs) of (a) 8 and (b) 10 wt.%, and moist cured for 7 and 28 days at 30°C and 100% relative humidity.
(MDD=1.41 Mg/m^3; OMC =24.22%).

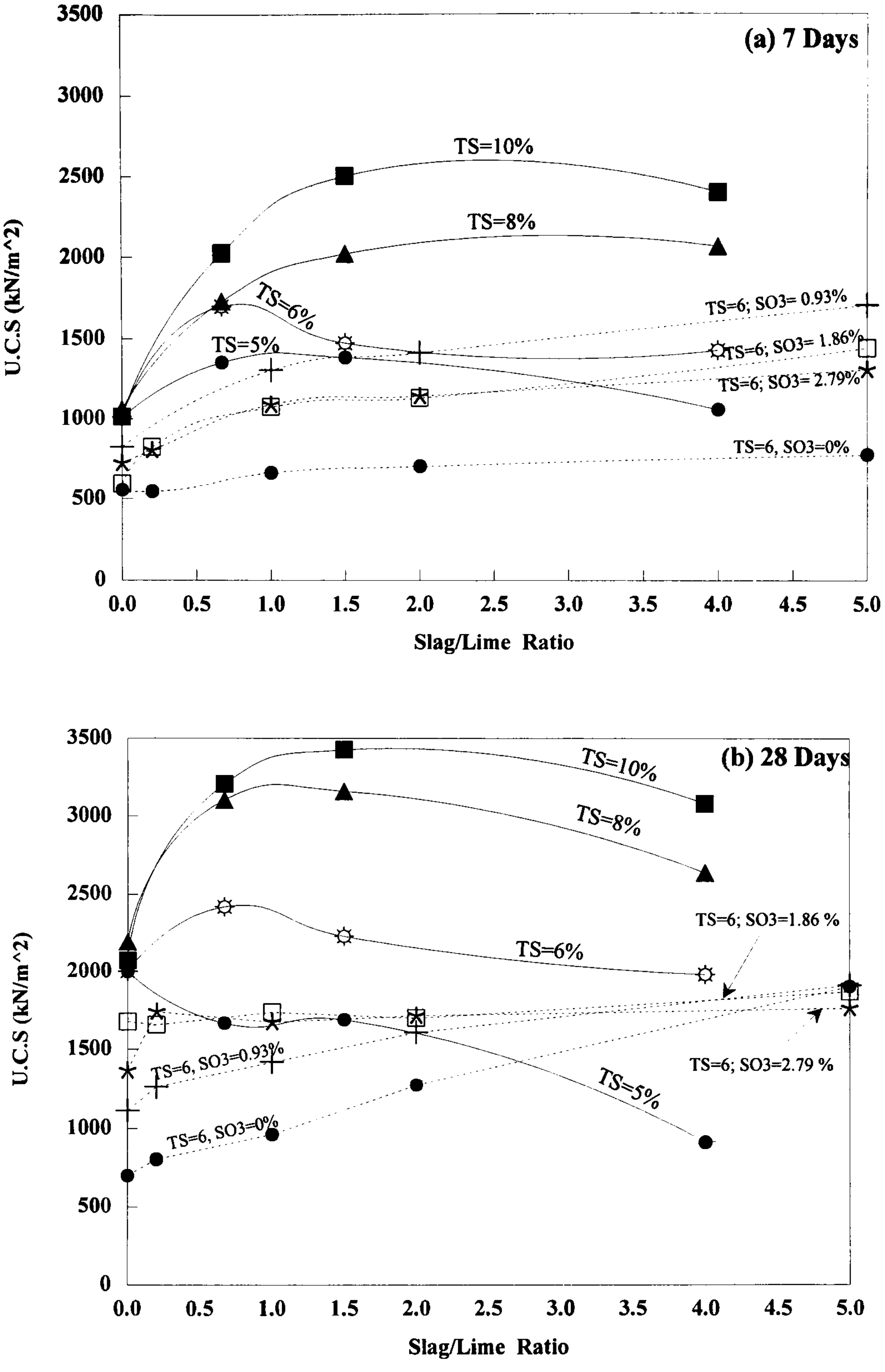


Figure 7.3-11 UCS vs. Slag/(Lime) ratio for Kimmeridge clay-lime-ggbs cylinders moist cured for 7 and 28 days at 30°C and 100% relative humidity.
(TS = total stabiliser content (Lime + ggbs); Dotted lines = work using kaolinite) (MDD=1.41 Mg/m^3; OMC =24.22%).

CHAPTER 8 - LINEAR EXPANSION, SWELLING PRESSURE, PHASE ANALYSIS AND MICROSTRUCTURE

8.1 SWELLING TESTS

8.1.1 INTRODUCTION

The first phase of the swelling tests was intended to study the expansive effects, during moist curing at 30°C and 100% relative humidity, of kaolinite - lime mixtures containing different metal sulphates. In the first phase, the linear expansion of cylinders immediately after compaction was monitored during moist curing at the above mentioned temperature and humidity conditions until no further significant expansion was observed.

The second and third phases were intended to study the effects of excessive water ingress after the crucial initial 7-day moist curing period normally specified in most construction projects. In the second phase, the linear swelling of kaolinite - 6wt.% lime cylinders, containing various amounts of the sulphates of calcium, magnesium, sodium and potassium, was determined.

The third phase combined the first two phases and determined the linear expansion of cylinders in one continuous process, that is during the initial 7-day moist curing period (as in the first phase) and followed by subsequent soaking (as in the second phase), until no further significant linear expansion was observed.

In order to study the effects of ground granulated blastfurnace slag (GGBS) on the swelling behaviour, tests were also conducted, on cylinders in which slag had been introduced either in addition to or (as was done in most cases,) as a substitute for part or all of the lime used in the control mixes (i.e. kaolinite-6wt.% lime or Kimmeridge Clay - 5wt.% lime). Where kaolinite was used, tests were done in which the kaolinite also contained various amounts of gypsum. Due to time constraints, not all possible combinations of materials could be investigated for all the possible effects of curing time, soaking time and composition. Thus the following systems were chosen:-

Phase I - Kaolinite-6wt% lime mixes containing the sulphates of calcium, magnesium, sodium and potassium in amounts equivalent to 0.93, 1.86, 2.79 or 3.72 % by mass of SO_3.

Phase II and III - System 1: Kaolinite - 6wt% lime mixes containing the sulphates of calcium, magnesium, sodium and potassium in amounts equivalent to 0.93, 1.86, 2.79 or 3.72 % by mass of SO_3; System 2: Kaolinite - 6wt% lime mixes with various amounts of GGBS substituting for or added to the lime content. The kaolinite contained gypsum additions equivalent to 0, 0.93, 1.86, 2.79 or 3.72 % by mass of SO_3; System 3: Kimmeridge Clay - 5wt.% lime with various amounts of GGBS substituting for the lime content. During the third phase, the effects on expansion of varying initial moisture content were also investigated using an adaptation of system 2 above by compacting the cylinders at varying water contents at OMC, wetter of optimum (1.2 OMC), and drier of optimum (0.6 OMC and 0.8 OMC).

Figures 8.1-1 - 8.1-22 illustrate all the linear expansion effects observed in all the three phases of testing. The expansion of the control mix (kaolinite - 6wt.% lime) is also included in most cases for the purpose of comparison. The figures illustrate that the control mix recorded a small amount of shrinkage during moist curing and limited swelling during soaking. In both cases, the bulk of the changes in expansion occurred within 3 days of curing and/or soaking. For specimens containing sulphates, these changes occurred over a comparatively longer duration, depending on the amount of sulphate added, with mixes containing higher amounts of sulphate generally taking longer for the ultimate expansions to be achieved.

8.1.2 LINEAR EXPANSION DURING MOIST CURING

8.1.2.1 Effects of Gypsum

Figure 8.1-1 (a) illustrates the expansive effects during moist curing of adding various amounts of gypsum to the kaolinite - 6wt.% mixes, for curing periods up to a maximum of 79 days (approximately 11 weeks). During the initial curing stages (less than 10 days), samples containing low SO_3 content (1.86% and below,) recorded higher linear expansions than those containing high SO_3 concentrations. The linear expansion increased with both curing time and increasing SO_3 content, reaching the highest expansion with 3.72% SO_3 content after 6 weeks of curing. As the SO_3 content increased, the ultimate linear expansion reached an initial peak, (shown by the dotted line A-A in Figure 8.1-1 (b)) and further increase in SO_3 concentration resulted in reduced ultimate expansion (giving a minimum point (line B-B in Figure 8.1-1 (b)). Expansion then showed a further increase with further increase in SO_3 to 3.72 %. Ultimate expansion refers to expansion levels where further increase in expansion with increased curing time may be considered insignificant.

The rate of expansion decreases with increasing curing time (Figure 8.1-1 (a)) and is higher for the lower SO_3 concentrations than for the high ones and there is an abrupt decrease in rate between 1.86% SO_3 content and 2.79% SO_3 content. It was also relatively high initially for all SO_3 contents during the first 1-3 weeks of curing, before suddenly reducing to very little or no further increase (or even shrinkage at 0.93 % SO_3) beyond certain curing stages unique for each SO_3 level and sulphate type. These expansion termination times (ETTs) shown in Figure 8.1-1 (a)) are proportional to SO_3 content. They occur at approximately 9, 18, 27 and 40 days for 0.93, 1.86, 2.79 and 3.72 % SO_3 respectively. A very clear pattern emerged relating the ETTs to the SO_3 content viz:-

$$\mathbf{ETT \approx 10 \times SO_3}$$

where ETT = Expansion Termination Time (in days)

and SO_3 = SO_3 content (%).

Thus, the lower a sample is in its SO_3 content, the lower will be its expected expansion termination time. This suggests that some physico-chemical process is taking place which has a completion time in direct proportion to the sulphate concentration in the sample. Also the fact that the amount of expansion does not increase directly with increase in sulphate content but shows a maximum at about 2% SO_3, and a minimum at about 2.8% SO_3 and then a further increase indicates that the products of the chemical process may change with change in sulphate concentration.

8.1.2.2 Effects of Magnesium Sulphate

Figure 8.1-2 illustrates the influence of the addition of various amounts of magnesium sulphate on the linear expansion of kaolinite - 6wt.% lime cylinders. The cylinders behaved to some extent in a similar manner to those containing gypsum in that there is a peak expansion at 1.86 % SO_3 content (Figure 8.1-2 (b)). This peak is marginally higher than the one recorded in the case of gypsum (although it was also observed at the same SO_3 content). Also, there was again an abrupt decrease in the initial rate of expansion in going from 1.86% SO_3 to 2.79% SO_3. There was reduced expansion thereafter with increased SO_3 concentration. However, unlike in the case of gypsum, there was no further increase in expansion with increasing SO_3 concentration beyond the peak expansion. At 3.72 % SO_3 content, all samples cured for 3 weeks and above recorded the same expansion (Point C in Figure 8.1 -2 (b)). There was also a well defined expansion termination time within 5-30 days of curing. At 0.93% SO_3 content after the initial expansion a small shrinkage occurred similar to that observed for gypsum additions. The ETTs were 5, 20, 30 and 20 days for 0.93, 1.86, 2.79 and 3.72 % SO_3 respectively and therefore did not show a simple proportional relationship to SO_3 content as was the case for gypsum.

8.1.2.3 Effects of Sodium Sulphate

Sodium sulphate demonstrated a similar expansion pattern to gypsum with respect to sulphate concentration, reaching an initial peak expansion at 1.86 % SO_3 although at a much lower level of expansion (Line D-D in Figure 8.1-3 (b)). Subsequently, the expansion dropped to a minimum at 2.79 % SO_3 content (Line E-E in Figure 8.1-3 (b)) and then expansion continued to increase on further increase in SO_3 concentration.

Expansion levels were however much less (≈ 50%) than those observed for both gypsum and magnesium sulphate. In addition, there was again an abrupt drop in initial expansion rate in going from an SO_3 content of 1.86% to one of 2.79%.

8.1.2.4 Effects of Potassium Sulphate

In the case of potassium sulphate, the ultimate expansion increased with SO_3 content to a peak (of approximately equal magnitude to that in the case of Na_2SO_4 addition) at 1.86 % SO_3 concentration (Figure 8.1-4). Beyond this SO_3 level, further increase in SO_3 content resulted in reduced levels of expansion, similar to the pattern which was observed for magnesium sulphate. There was however, as in all the other cases of sulphate addition, a significantly faster initial rate of linear expansion at low SO_3 concentrations (up to 1.86%) and a much slower rate at high SO_3 concentrations. Also in common with magnesium sulphate, the highest sulphate level (3.72 % SO_3), produced the smallest expansion (with the exception of the control) at all curing times (Point F in Figure 8.1-4(b)).

8.1.2.5 Summary of the effects of sulphates

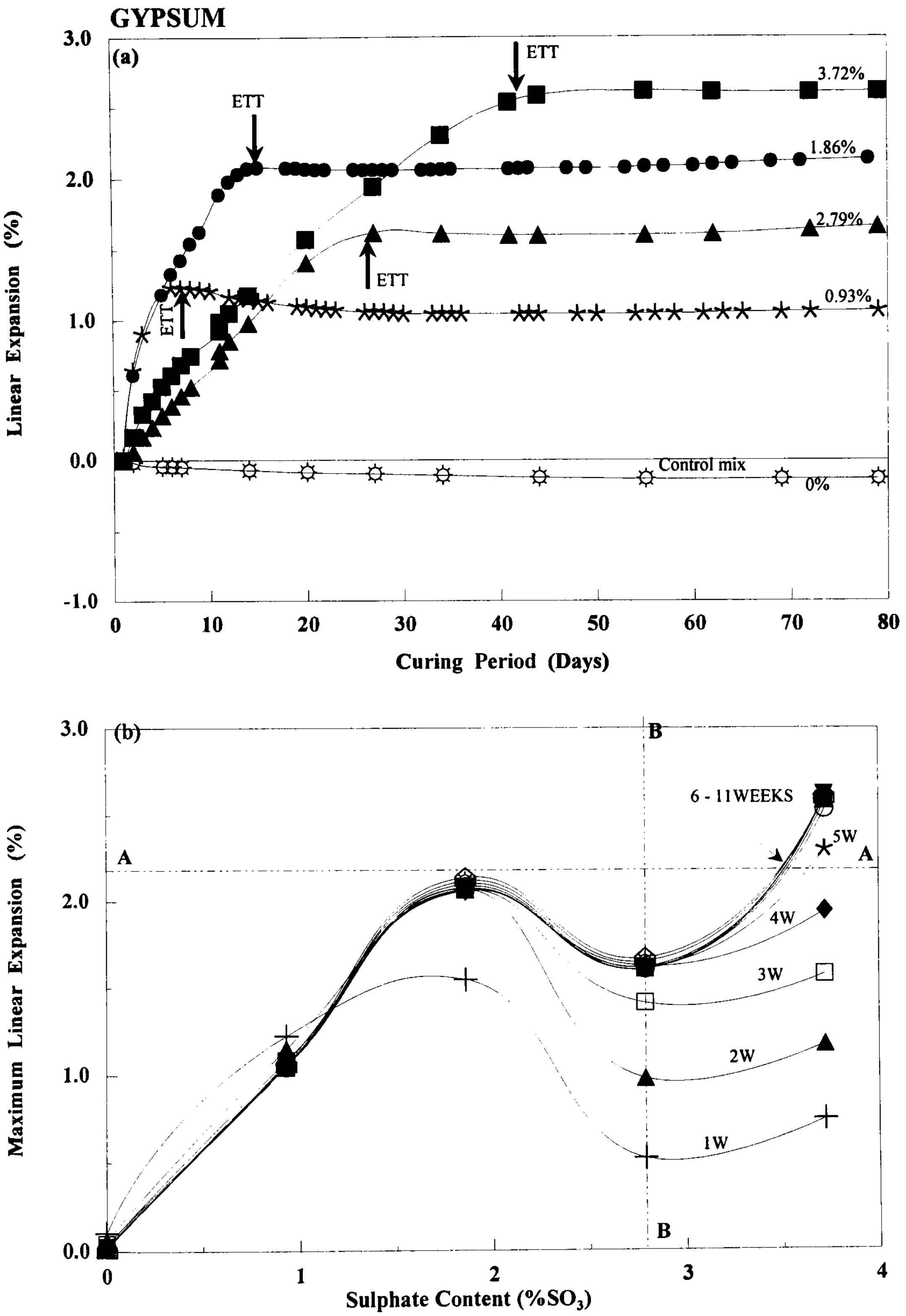
Figure 8.1-5 illustrates the relative effects of the addition of the different sulphate types with respect to curing period and sulphate level. At low levels of SO_3 (0.93% and 1.86%) the monovalent metal sulphates behave in a similar manner to each other as do the divalent metal sulphates. The monovalent metal sulphates produce a more rapid initial rate of expansion than the divalent metal sulphates (1-2 days) but subsequently the expansion rate of the monovalent metal sulphates reduces much more than that for the divalent metal sulphates (2-16 days) (compare Figures 8.1-1 (a) and 8.1-2 (a) with Figures 8.1-3 (a) and

8.1-4 (a) at low SO_3 levels). Thus the ultimate expansions of the samples containing divalent metal sulphates are greater than those containing monovalent metal sulphates. At higher sulphate levels this distinction disappears primarily because the expansions of specimens containing calcium sulphate (and sodium sulphate) show further increases with increasing sulphate content and specimens containing magnesium sulphate (and potassium sulphate) show decreased expansions (See Figure 8.1-5).

With increasing SO_3 content (See Figure 8.1-5), the expansions for cylinders containing Mg and K increased up to a peak at 1.86 % SO_3 content after which expansion showed a general decline. For those containing Ca and Na, the expansion also reached a peak at 1.86% SO_3 content followed by a drop at 2.79 % SO_3 but expansion then showed a further increase at 3.72 % SO_3. It is interesting to note that the well defined minimum in the expansion versus sulphate content plots for gypsum containing samples (See Figure 8.1-1 (b)) occurs at exactly the same SO_3 content as the maximum in strength in Figure 7.3-5 (c). Samples containing the monovalent cations reached ultimate expansions within 1-2 weeks while the samples containing divalent cations had increasing expansions up to 2-6 weeks, depending on SO_3 content. At curing periods in excess of one week, cylinders containing gypsum generally maintained high expansions at high sulphate contents while those containing magnesium sulphate showed the highest overall expansions at intermediate sulphate contents (Figure 8.1-5 (b) - (d)). In brief, the following points may be noted for the effects of the various sulphates during moist curing:

1. Gypsum levels display a clear pattern in relation to the time taken for the termination of expansion during moist curing relative to the sulphate content.

2. Gypsum and magnesium sulphate produce the highest overall linear expansions. Gypsum is dominant at high sulphate content (3.72% SO_3) while magnesium sulphate is dominant at intermediate (1.86-2.79% SO_3) levels.
3. Gypsum and sodium sulphate produce similar linear expansion patterns - a peak expansion at 1.86% SO_3, a minimum at 2.79% SO_3 and resumed expansion beyond this sulphate content.
4. Magnesium and potassium sulphates display similar linear expansion patterns - a peak expansion at 1.86% SO_3 and reduced expansion beyond this sulphate content.



ETT - EXPANSION TERMINATION TIME

Figure 8.1-1 (a) Linear expansion during moist curing vs. Curing time and (b) Linear expansion vs. Sulphate content, for kaolinite-6wt.% lime cylinders with additions of varying amounts of gypsum, during moist curing at 30 °C and 100% relative humidity. *(MDD=1.41 Mg/m^3; OMC=27.4%).*

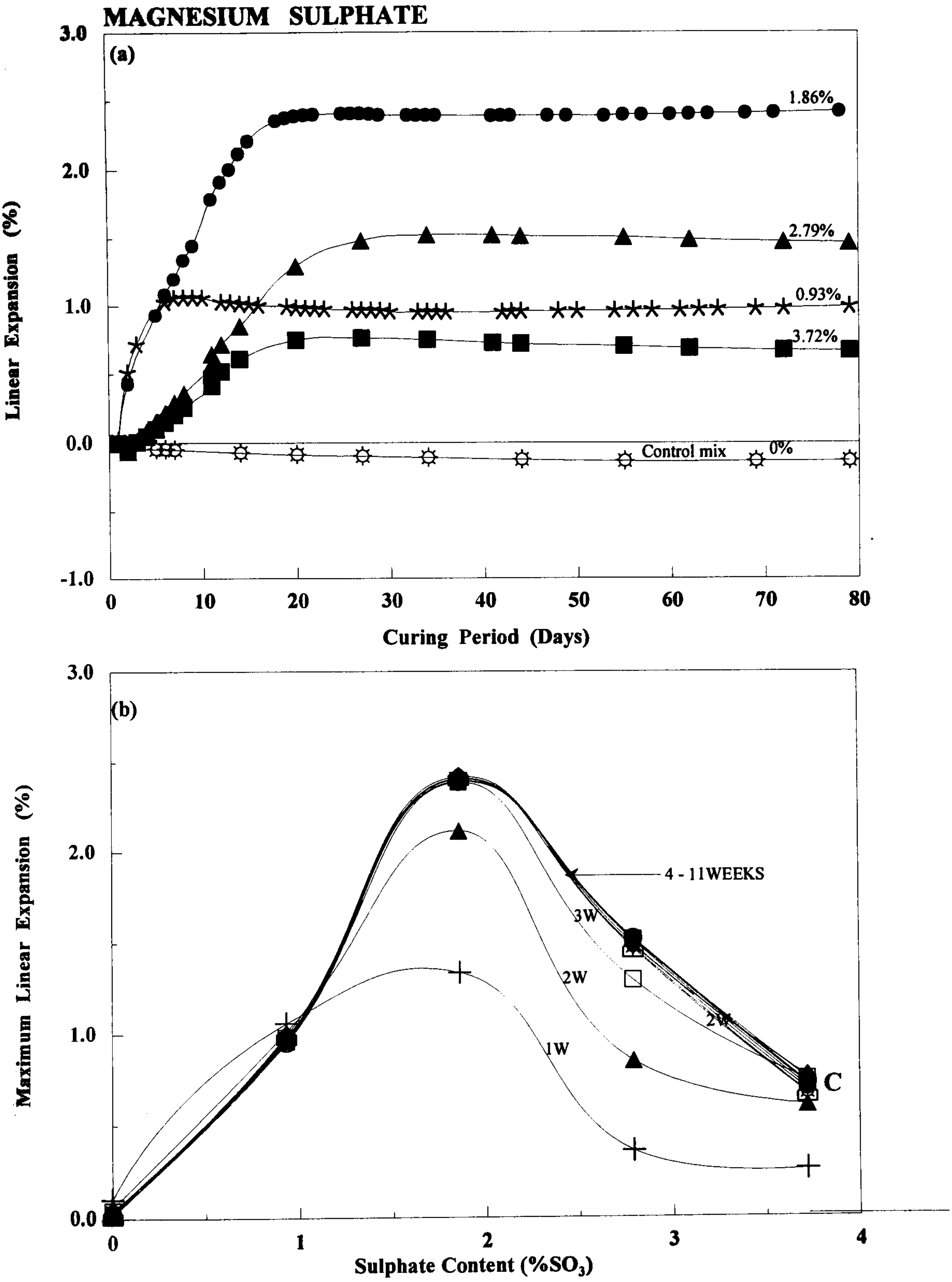


Figure 8.1-2 (a) Linear expansion during moist curing vs. Curing time and (b) Linear expansion vs. Sulphate content, for kaolinite-6wt.% lime cylinders with additions of varying amounts of magnesium sulphate, during moist curing at 30°C and 100% relative humidity. *(MDD=1.41 Mg/m^3; OMC=27.4%).*

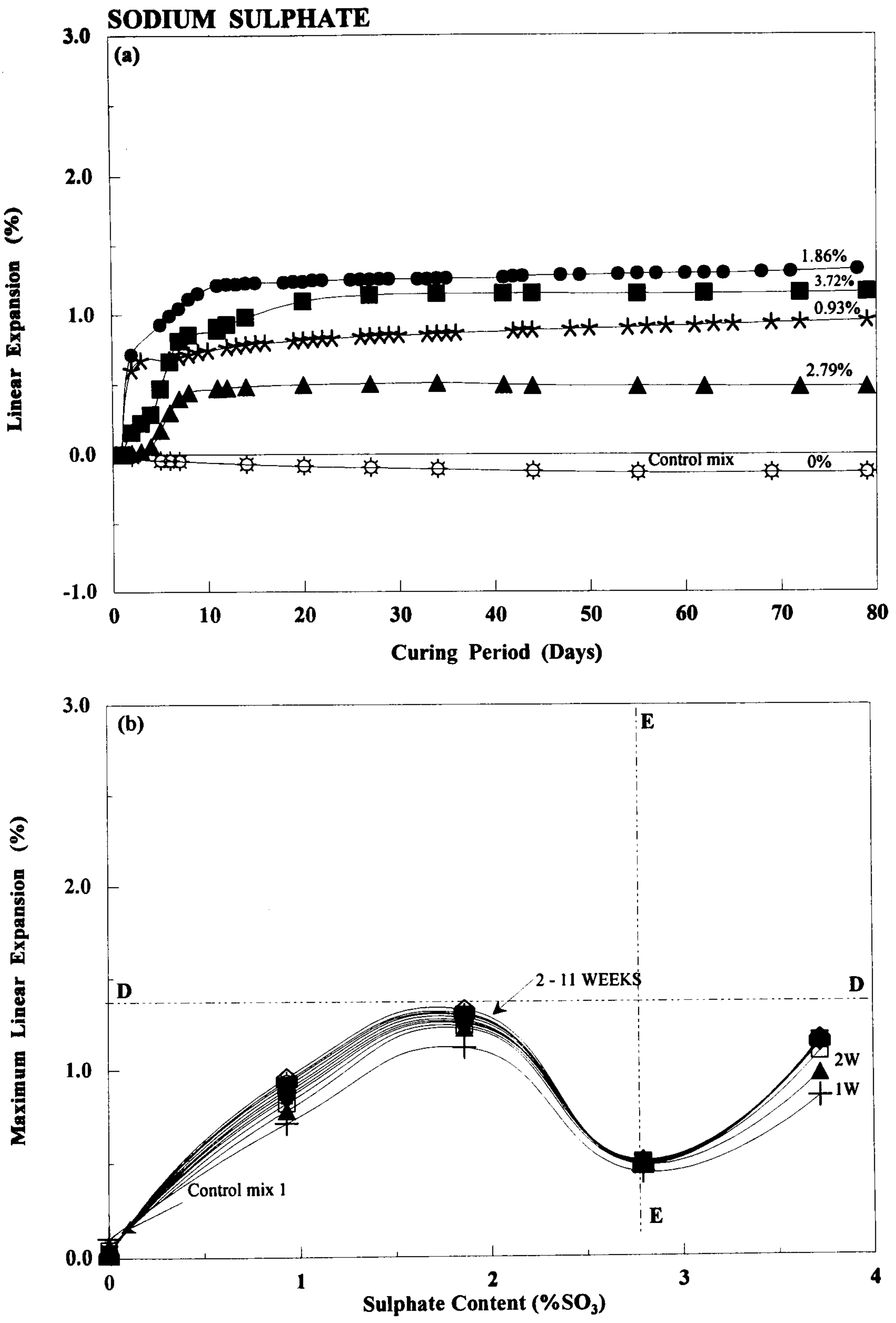


Figure 8.1-3 (a) Linear expansion during moist curing vs. Curing time and (b) Linear expansion vs. Sulphate content, for kaolinite-6wt.% lime cylinders with additions of varying amounts of sodium sulphate, during moist curing at 30°C and 100% relative humidity. *(MDD=1.41 Mg/m^3; OMC=27.4%).*

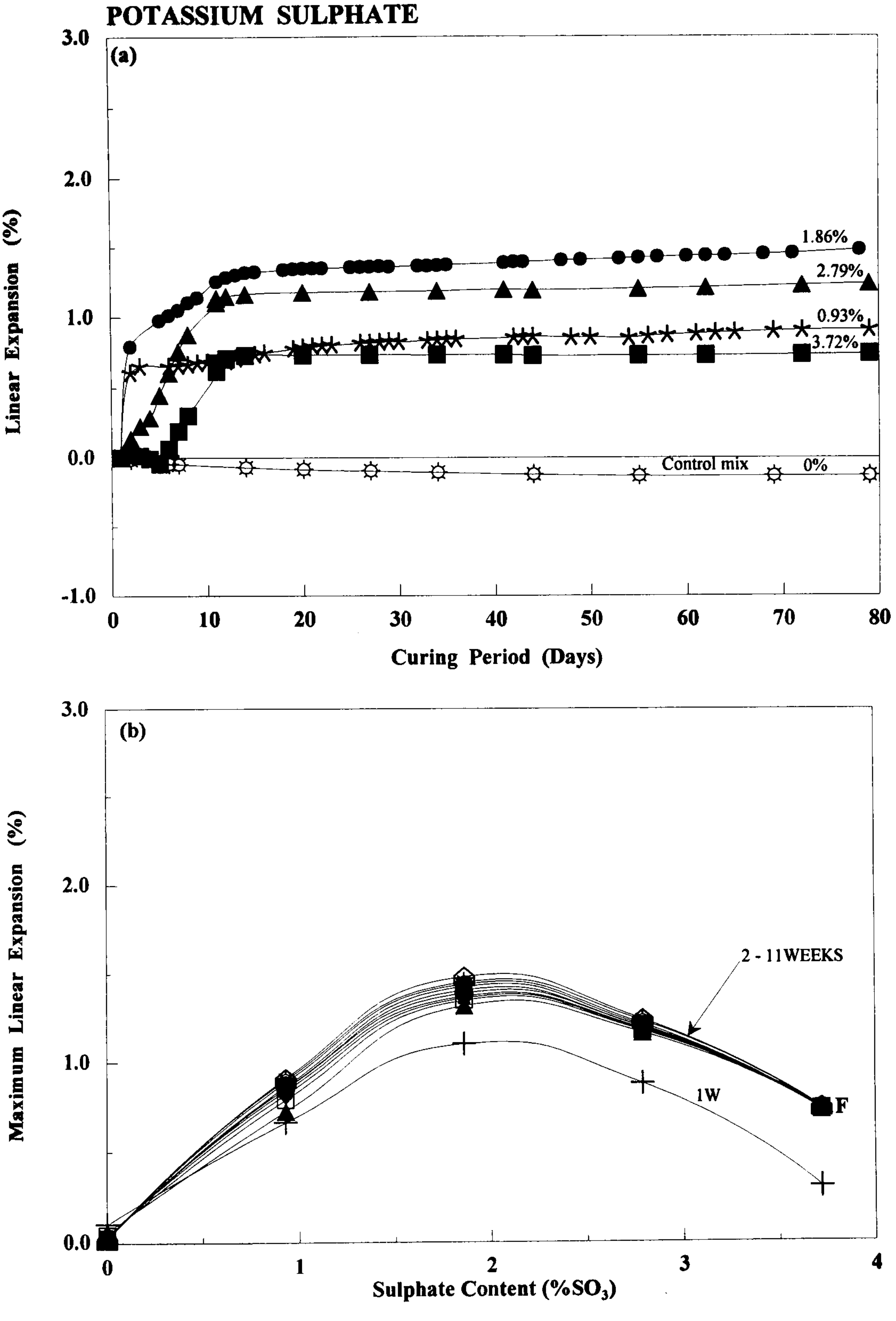


Figure 8.1-4 (a) Linear expansion during moist curing vs. Curing time and (b) Linear expansion vs. Sulphate content, for kaolinite-6wt.% lime cylinders with additions of varying amounts of potassium sulphate, during moist curing at 30°C and 100% relative humidity. *(MDD = 1.41 Mg/m^3; OMC = 27.4%).*

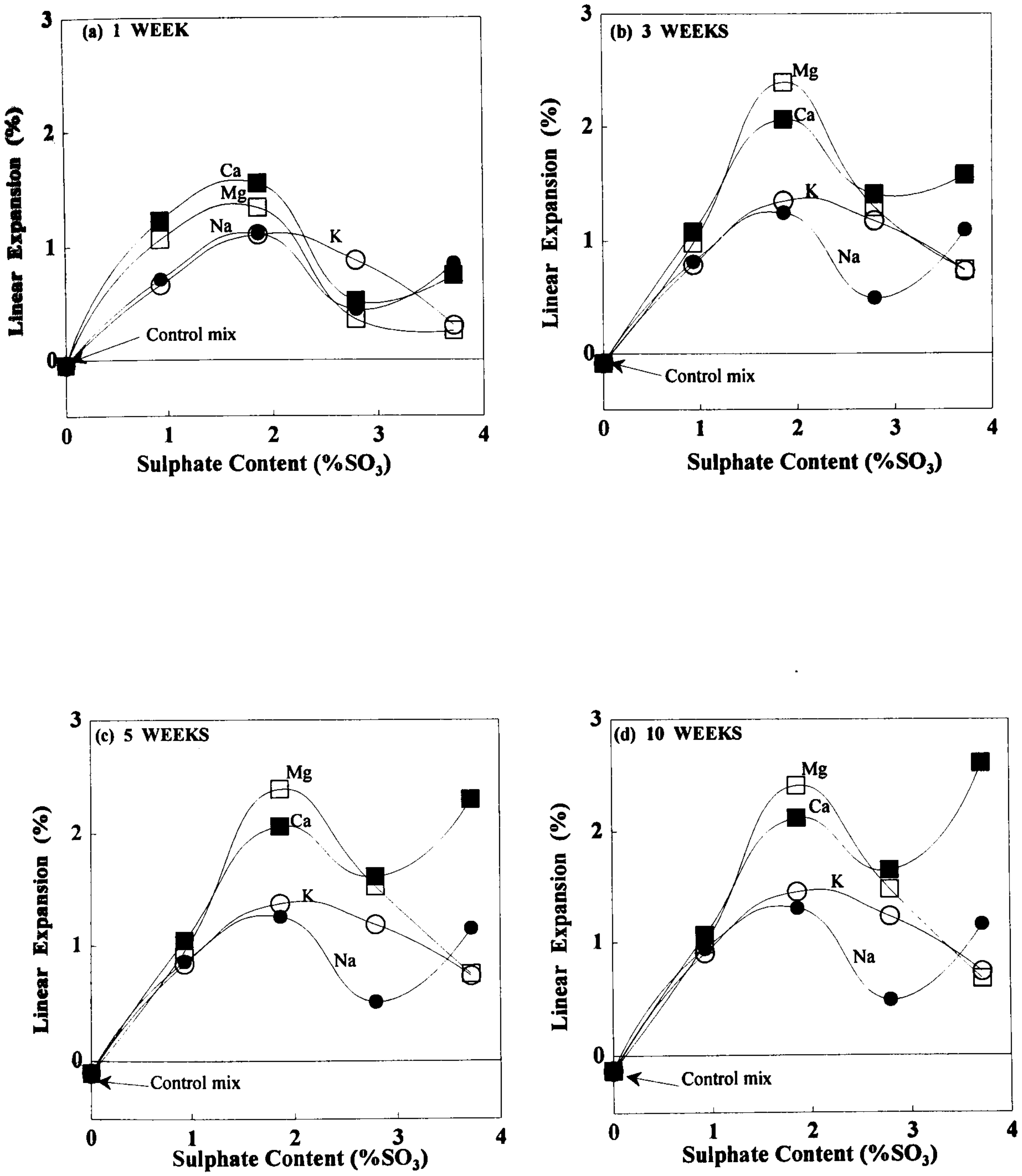


Figure 8.1-5 Linear expansion during moist curing vs. SO$_3$ content for kaolinite-6wt.% lime cylinders with varying additions of various metal sulphates moist cured at 30°C and 100% relative humidity, presented at (a) 1, (b) 3, (c) 5 and (d) 10 weeks of moist curing. *(MDD=1.41 Mg/m^3; OMC=27.4%).*

8.1.2.6 Effects of substitution of lime with ground granulated blastfurnace slag (GGBS)

Figures 8.1-6 (a) and (b), 8.1-7 (a) and (b) and 8.1-9 (a) illustrate the effects of increasing replacement of lime with GGBS on the 7 day expansive behaviour of kaolinite-lime-gypsum mixes (compacted at OMC) with gypsum contents varying from 0 to 8wt% (0 - 3.72% SO_3). Figures 8.1-8 and 8.1-9 illustrate the effects of varying the initial (compaction) moisture content. Cylinders without gypsum recorded very little or no expansion (Figure 8.1-6 (a)). Also, those without lime but with gypsum showed very little or no expansion (e.g. samples 0L0S2G, 0L0S4G, 0L0S6G and 0L0S8G) and by 7-days most of these samples exhibited significant shrinkage. The shrinkage was generally greater at high gypsum levels. The small expansion that did occur, occurred within the first 2 days of moist curing. Samples to which only slag was added also recorded shrinkage (sample 0L6S0G in Figure 8.1-6 (a)). Among the most expansive samples during moist curing were those containing high amounts of both lime and gypsum and little or no GGBS (samples of composition 5L1S4G, 6L0S4G, 6L0S6G, 6L0S8G and 5L1S8G in Figures 8.1-7 - 8.1-9) and the trend generally was that as the lime content decreased and the slag content increased the amount of expansion decreased.

For samples containing 0.93% SO_3 (see Figure 8.1-6 (b)), the expansion stopped at between 1 and 2 days and the samples subsequently contracted. The same phenomenon occurred with 1.86 % SO_3 (see Figure 8.1-7(a)) but in this case shrinkage began at a later time ($\approx$ 4 days) and was less pronounced. In contrast specimens containing 2.79%

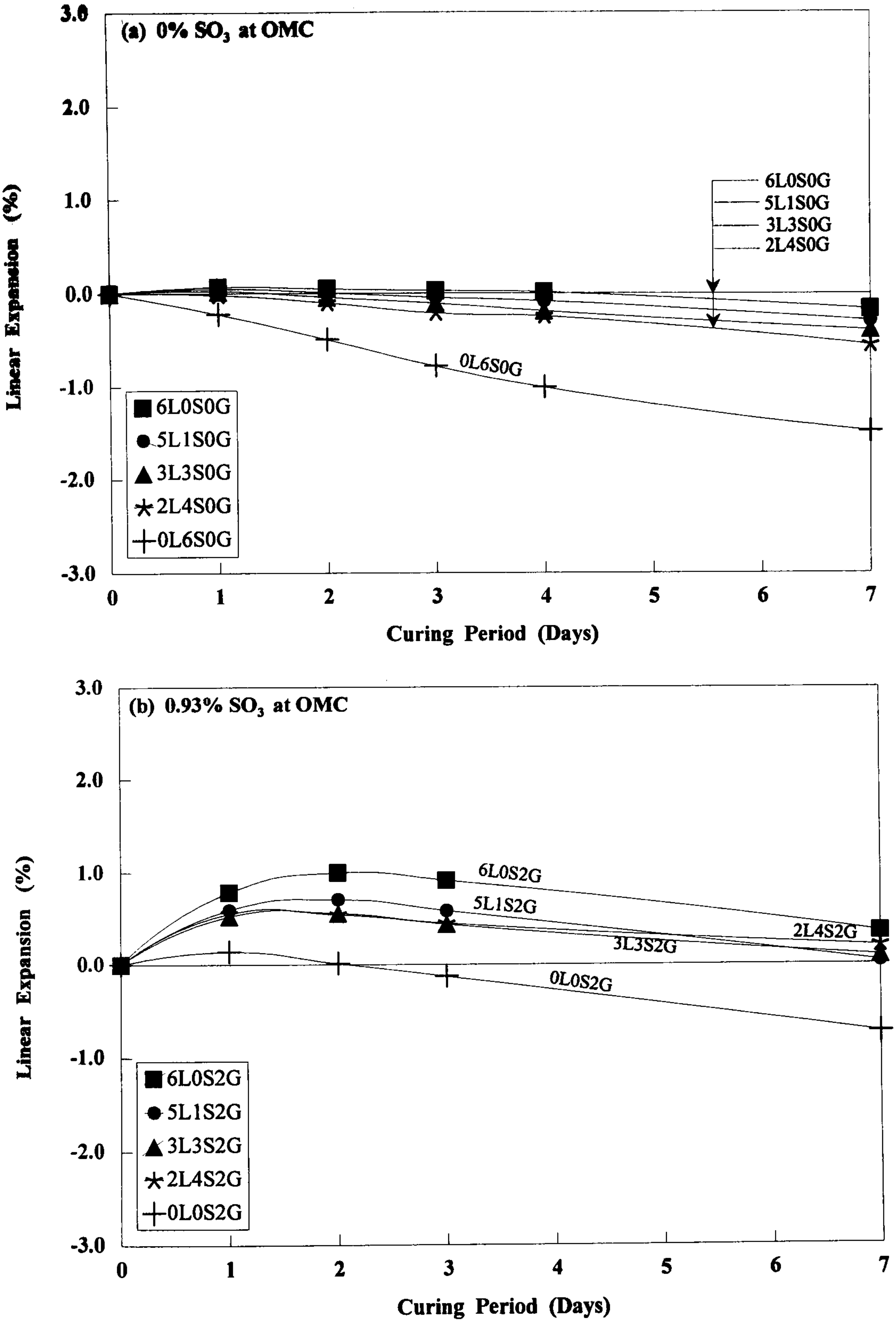
SO_3 equivalent of gypsum and a high proportion of lime (i.e. samples of composition 6L0S6G and 5L1S6G in Figure 8.1-7 (b)) recorded sustained expansion throughout the 7 days of moist curing. At 3.72 % SO_3 (Figure 8.1-9 (a)), expansion tended to be slightly lower than at the other three gypsum contents (i.e. 0.93, 1.86 and 2.79% SO_3) and again specimens with high lime contents (6L0S8G, 5L1S8G) continued to expand up to 7 days.

Overall, significant shrinkage was displayed by samples without lime which contained gypsum and/or GGBS, with the magnitude of shrinkage increasing with increasing gypsum and/or GGBS. For the samples that showed significant expansion, the expansion generally decreased with increasing slag content and reducing lime content. It is therefore apparent from these observations that significant expansion occurs during moist curing only if both lime and gypsum are present and that if only one component is present there is shrinkage rather than expansion. Also when both gypsum and lime are present the amount of expansion can be considerably reduced by replacing some of the lime by slag. This indicates that the reaction product formed during reaction of kaolinite with lime and gypsum, is responsible for the expansion.

Figures 8.1-8 and 8.1-9 show the effect of varying the moisture content on the expansive behaviour of the kaolinite - 6wt.% lime - 8wt.% gypsum samples in which lime is partially replaced by GGBS. In general as the moisture content increases the 7 day expansion decreases. Also for specimens compacted at 1.2OMC (Figure 8.1-9 (b)) contraction occurred in all cases after curing times of between 1 and 2 days. This effect is opposite to what might be expected, in that increasing moisture should produce increased swelling. However, the moist cured system is a closed system in which water neither enters nor leaves the specimens. It is suggested that as the specimen moisture content is increased the thickness of the films of water around the clay particles is greater, thus providing more space for formation of surface reaction products. At very low moisture contents where surface water films are very thin the reaction products formed at particle - particle contact regions force particles apart. However at high moisture contents where thick films of water separate the particles the effect is much less. Also the removal of some of this water by the chemical hydration reactions actually results in a small amount of shrinkage over time.

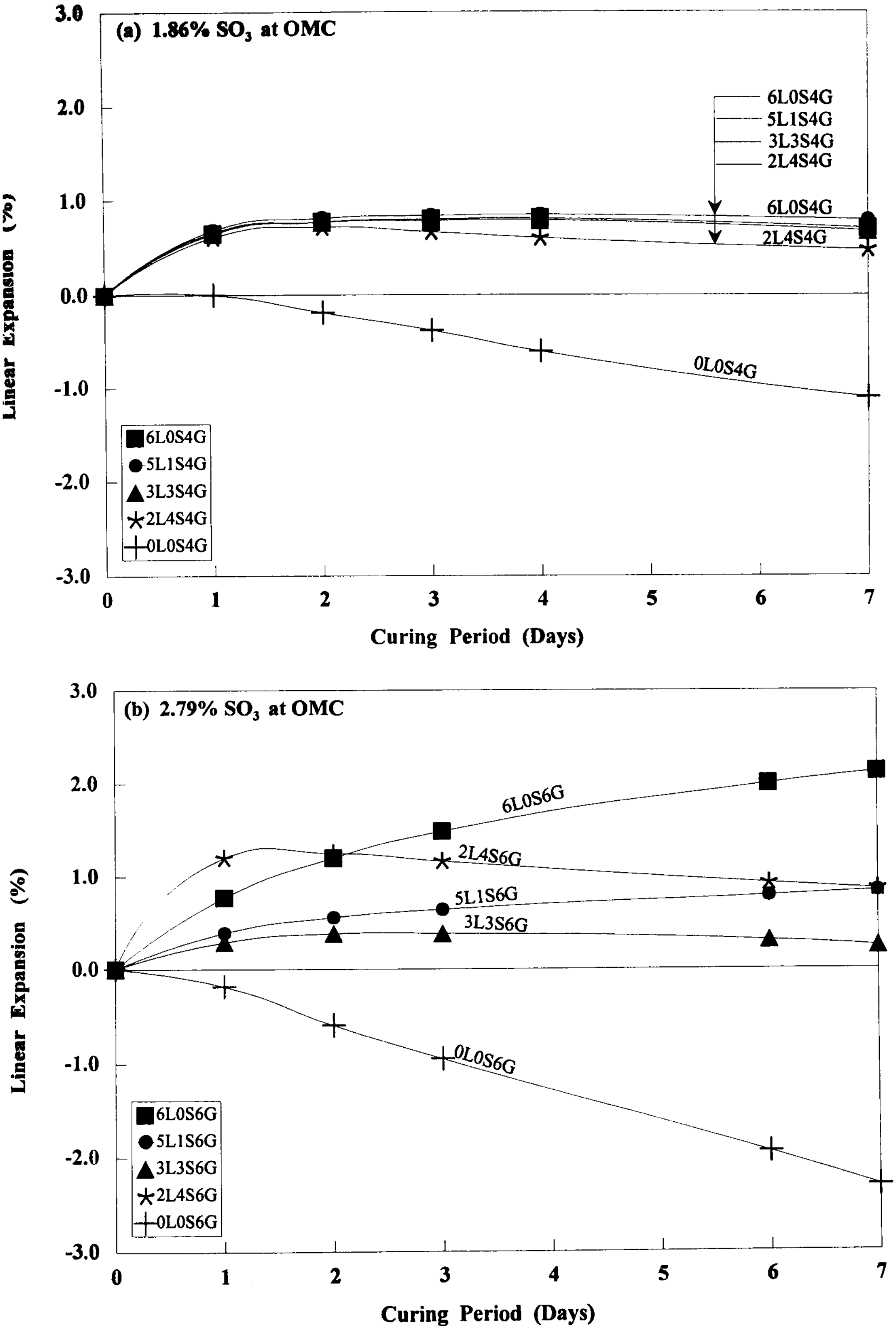
8.1.2.7 Summary of the effects of slag during moist curing

1. Specimens without gypsum but containing either lime and/or slag record no 7 day expansion. They record shrinkage.
2. Specimens containing gypsum only also record no expansion. They record shrinkage in proportion with the gypsum content.
3. As the gypsum content is increased, specimens containing lime and/or low slag recorded increasing sustained expansion. This expansion reduced with :- i) excess gypsum ($SO_3 > 3.72\%$) and ii) increase in moisture content beyond OMC.



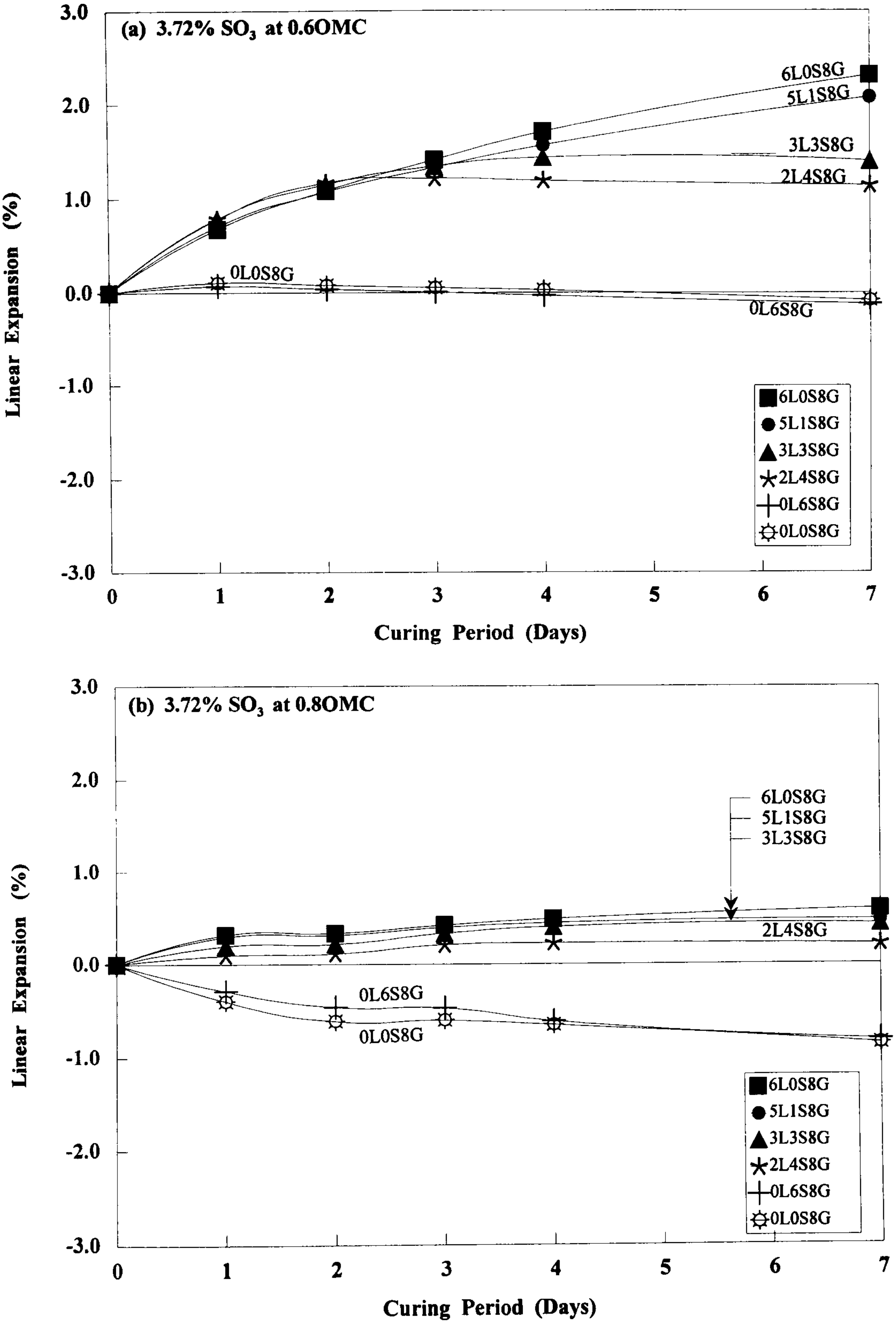
L - Lime
S - Slag
G - Gypsum
6 - 6Wt.%

Figure 8.1-6 Linear expansion during moist curing vs. Curing time for kaolinite-6wt.% lime cylinders containing (a) 0 and (b) 0.93% SO_3 additions of gypsum at 30°C and 100% relative humidity *(MDD=1.41 Mg/m³; OMC=30.55%).*



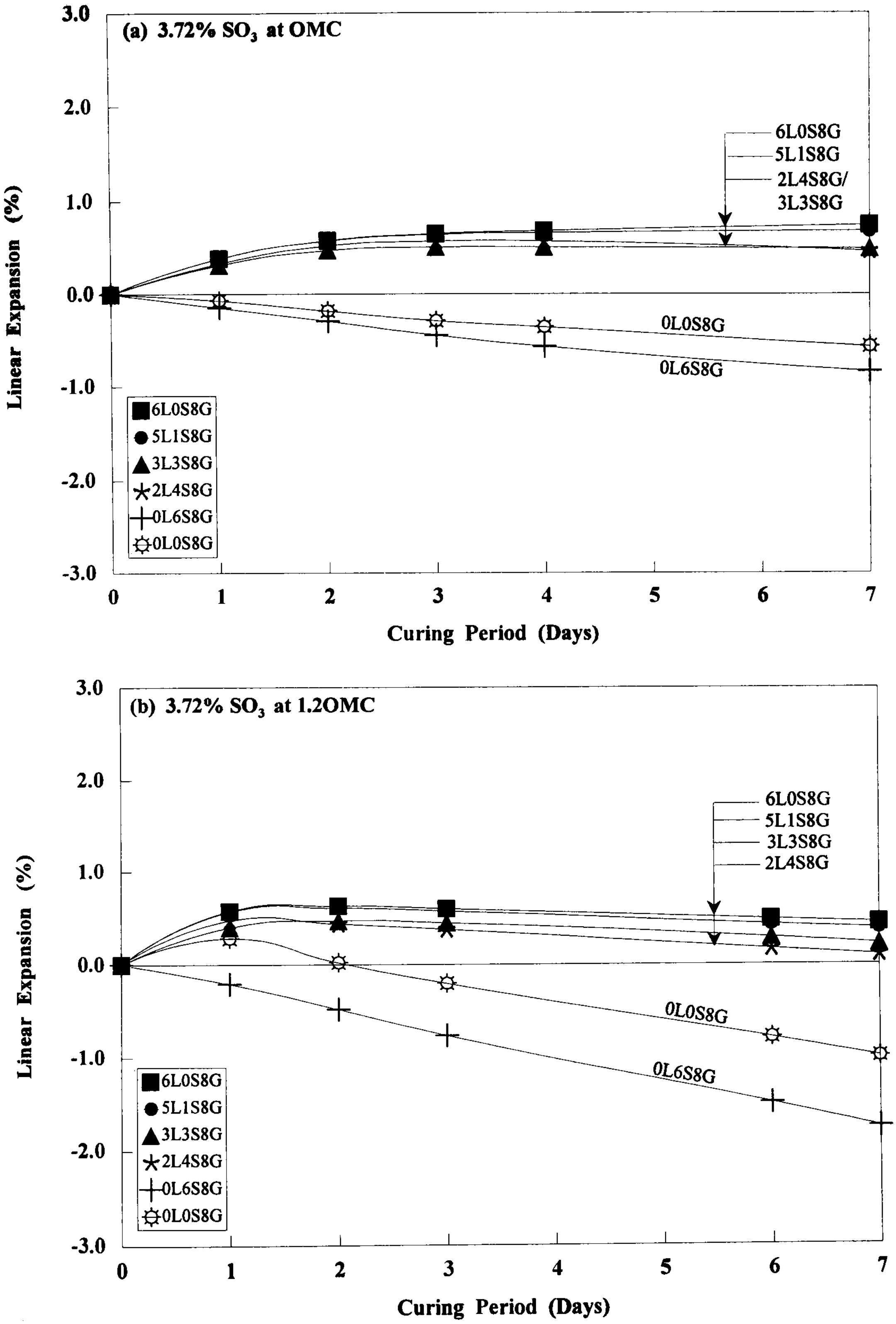
L - Lime
S - Slag
G - Gypsum
6 - 6Wt.%

Figure 8.1-7 Linear expansion during moist curing vs. Curing time for kaolinite-6wt.% lime cylinders containing (a) 1.86 and (b) 2.79% SO_3 additions of gypsum at 30°C and 100% relative humidity *(MDD=1.41 Mg/m^3; OMC=30.55%).*



L - Lime
S - Slag
G - Gypsum
6 - 6Wt.%

Figure 8.1-8 Linear expansion during moist curing vs. Curing time for kaolinite-lime-ggbs cylinders containing 3.72% SO_3 additions of gypsum at (a) 0.6 OMC *(18.33%)* **and (b) 0.8 OMC** *(24.44%)* **at 30°C and 100% relative humidity.**



L - Lime
S - Slag
G - Gypsum
6 - 6Wt.%

Figure 8.1-9 Linear expansion during moist curing vs. Curing time for kaolinite-lime-ggbs cylinders containing 3.72% SO_3 additions of gypsum at (a) OMC *(30.55%)* and (b) 1.2 OMC *(36.66%)* at 30°C and 100% relative humidity.

8.1.3 LINEAR EXPANSION DURING SOAKING

8.1.3.1 Effects of Gypsum

Figure 8.1-10 illustrates the effects on linear expansion during soaking of the addition of various amounts of gypsum to kaolinite - 6wt.% lime mixes. Throughout the soaking period, specimens with a sulphate concentration equivalent to 0.93% SO_3 (2wt.% gypsum) recorded expansions of equal magnitude to the control mix, higher SO_3 concentrations recording higher linear expansions. The ultimate linear expansion increased rapidly, by about 10 times, from 0.93 % to 1.86 % SO_3 concentration. The increase in expansion with increase in SO_3 concentration then reduced gradually and by 2.79 % SO_3, further increase in sulphate concentration resulted in only a minor increase in linear expansion. This indicated a turning point and a possible maximum SO_3 concentration of about 2.8% SO_3 beyond which on soaking, further increase in gypsum addition would not likely result in further expansion, for this level of lime content

8.1.3.2 Effects of Magnesium Sulphate

Linear expansion upon soaking increased with the addition of $MgSO_4$, all levels of SO_3 concentrations recording linear expansion magnitudes higher than those observed for the control mix (See Figure 8.1-11). As was the case for gypsum addition, the expansion increased rapidly from 0.93% to 1.86% SO_3. Thereafter, further increase in SO_3 concentration resulted in very little increase in expansion and beyond 2.79% SO_3, further sulphate concentration led to a reduction in linear expansion. A comparison of Figures

8.1-10 (b) and 8.1-11 (b) indicates very similar behaviour between the expansive effects of magnesium and calcium sulphates with calcium sulphate producing rather greater expansions at the highest sulphate levels and longest soaking times. In both cases expansion is very substantial. However, differences occurred when one compares strength results with expansion results. In the case of gypsum, specimens which achieve maximum strength during moist curing also tend to be the most expansive during soaking (compare Figures 7.3-1 (a) with 8.1-10 (a)) while in the case of magnesium sulphate this is not the case (compare Figures 7.3-2 (a) and 8.1-11 (a)). Thus high expansion on soaking does not necessarily imply weakness in respect of the unsoaked moist cured material.

8.1. 3.3 Effects of Sodium Sulphate

The expansive effects of sodium sulphate on the control mix are illustrated on Figure 8.1-12. Sodium sulphate recorded maximum expansion at 3.72 % SO_3 content. Expansions of specimens with 0.93 and 1.86 % SO_3 concentrations were lower than those of the control mix and those between 2.79 and 3.72 % SO_3 were higher. Also very little increase in expansion occurred between sulphate concentrations of 2.79 and 3.72% SO_3. Thus there appears to be a critical and limited SO_3 concentration range (for Na_2SO_4 additions) where expansion takes place. This is indicated in Figure 8.1-12 (b) to be between 1.5% and 3% SO_3.

8.1.3.4 Effects of Potassium Sulphate

Figure 8.1-13 illustrates the expansive behaviour of specimens when K_2SO_4 was added to the control mix. Expansions were lower than those of the control mix up to an SO_3 concentration of 1.86 %, showing a similar effect to that observed for Na_2SO_4. Also as for the case of Na_2SO_4 addition, maximum ultimate linear expansions were recorded at 3.72 % SO_3 although marginally lower than for Na_2SO_4.

8.1.3.5 Summary of the effects of sulphates on soaking

All specimens recorded rapid expansions immediately upon soaking (Figure 8.1-10 (a) - 8.1-13 (a)). Generally, most of the expansion was attained within 7 - 15 days of soaking for cylinders containing divalent cation sulphates and within 3 days of soaking for cylinders containing monovalent cation sulphates. The largest increases in expansion occurred between sulphate levels of 0.93 % SO_3 and 1.86% SO_3 for specimens containing calcium and magnesium sulphates and between 1.86 % SO_3 and 2.79 % SO_3 for specimens containing sodium and potassium sulphates (Figures 8.1-10 (b) and 8.1-13 (b)). There was a significant initial drop in expansion (from the control) upon the addition of the monovalent alkali metal sulphates at low SO_3 concentrations (below 1.86%). In fact relative to the control no significant additional expansion occurred in specimens containing Na_2SO_4 and K_2SO_4 until the sulphate concentration exceeded 1.86% SO_3, and no significant additional expansion of specimens containing $CaSO_4$ occurred until the sulphate concentration exceeded 0.93% SO_3 whereas with $MgSO_4$ additional expansion occurred at much lower SO_3 concentrations.

The summarised effects of the addition of the different sulphate types and progressive soaking are illustrated in Figure 8.1-14 (a) - (d). These illustrate very clearly the very similar behaviour produced by the two monovalent sulphates and the very similar behaviour produced by the two divalent sulphates and the contrasting behaviour between the effects of the monovalent and divalent sulphates. It would seem probable therefore that the genealogy of the behaviour of lime stabilised clays starts right from the cation exchange process, where behaviour of divalent cations was distinctly different from that of the monovalent cations. Figure 8.1-14 illustrates these effects at particular soaking periods of 1, 2, 4 and 6 weeks for specimens which have been initially moist cured for 1 week. In addition, the effects of prolonged initial moist curing before soaking are illustrated in Figures 8.1-15 (a) and (b) which show the maximum expansion on soaking for initial moist curing periods of 12 and 14 weeks at two sulphate levels, (a) 0.93% SO_3 and (b) 1.86% SO_3 respectively. From these figures, it can be seen that long initial moist curing periods of at least 10 weeks are required prior to soaking in order for the mixes containing high proportions of sulphates to fully stabilise and show negligible expansion during soaking. This suggests that it is the initial surface products formed during the very early stages of curing, which are implicated in absorption of water and excessive expansion. In brief,

1. for gypsum, linear expansion during soaking and strength development were both approximately directly proportional to the SO_3 content.
2. gypsum and magnesium sulphate displayed similar patterns in linear expansion during soaking although the two sulphates differed in the correlation between SO_3 concentration, linear expansion and strength development.

he sulphates containing monovalent cations displayed lower linear expansion (≈50%) han those containing divalent cations

in all cases of sulphate addition, the rate of increase in linear expansion showed a significant drop beyond of 2.79% SO_3 content

a higher SO_3 concentration (1.86- 2.79%) was required before the onset of expansion during soaking for the case of sulphates containing monovalent cations than for those containing divalent cations (0.93 - 1.86%).

the observed difference in expansion between divalent and monovalent cations would seem to suggest that the effects of the initial cation exchange and their influence on initial surface reaction products determine the long-term swelling material properties during soaking.

negligible expansion occurs during soaking if samples are moist cured for at least 10 weeks before soaking.

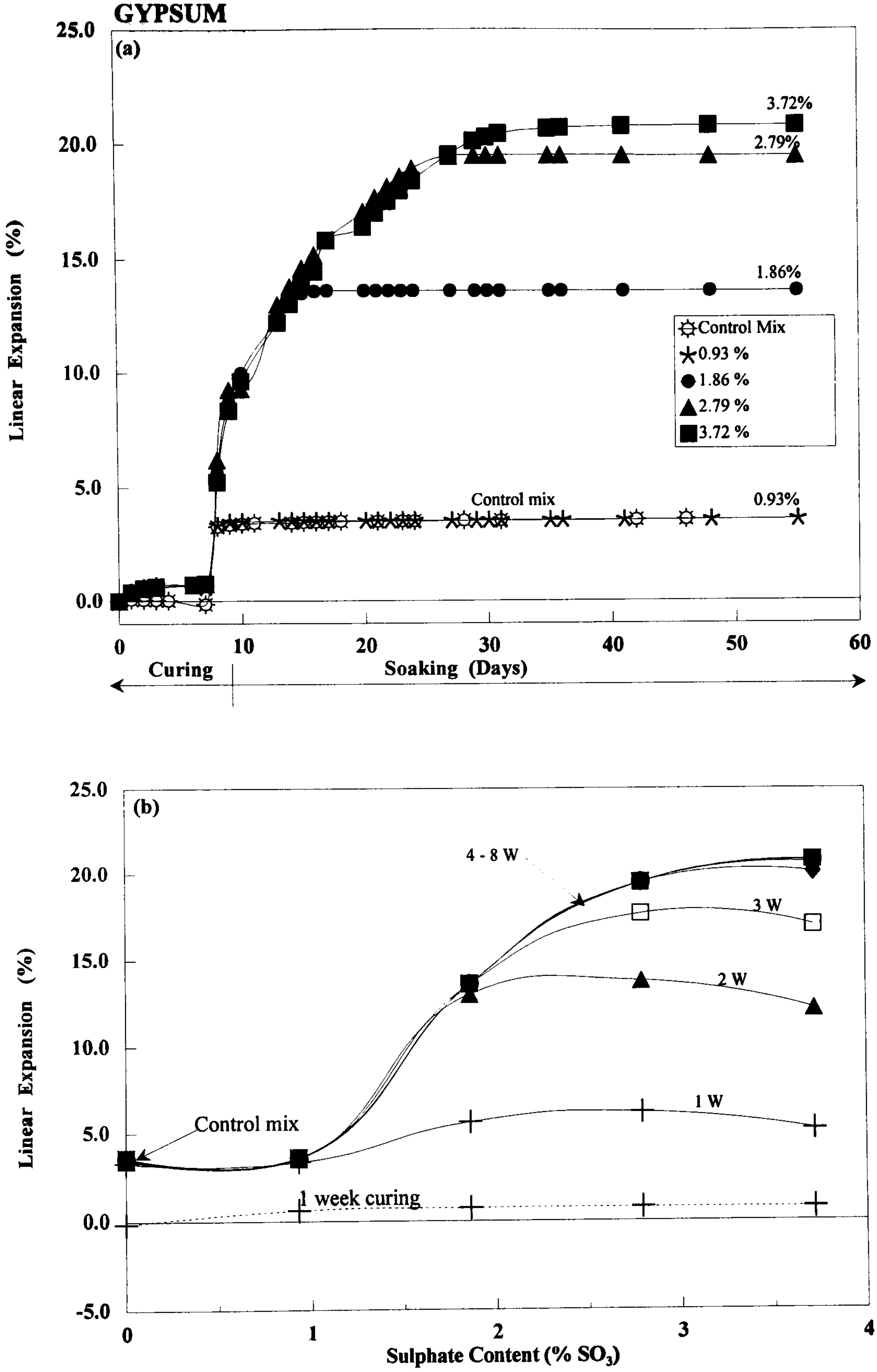


Figure 8.1-10 (a) Linear expansion during soaking vs. Curing time and subsequent soaking time and (b) Linear expansion during soaking vs. Sulphate content for kaolinite-6wt% lime cylinders with varying additions of gypsum at 30°C and 100% relative humidity. *(MDD=1.41Mg/m^3 ; OMC = 27.4 %)*.

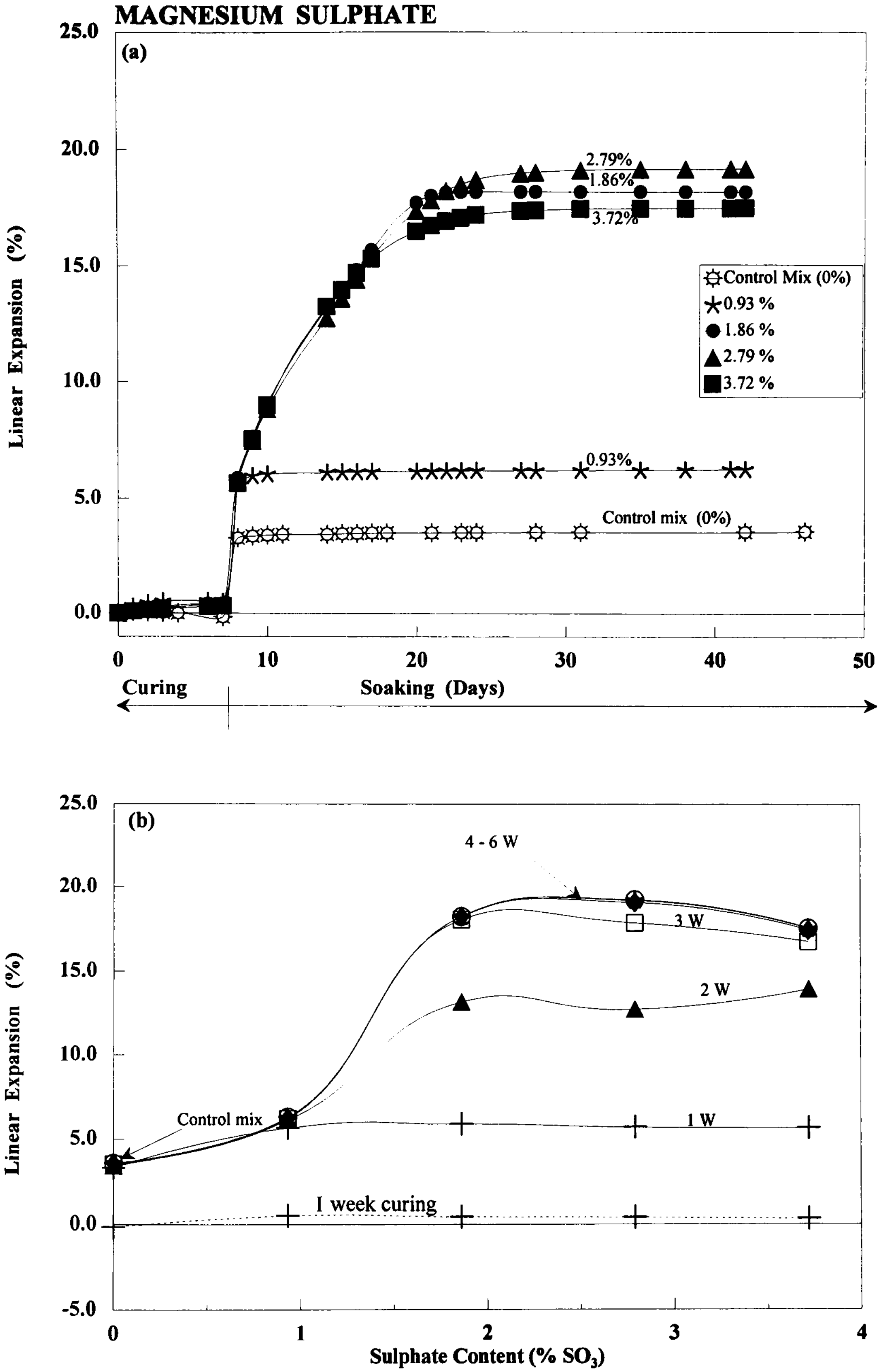


Figure 8.1-11 (a) Linear expansion during soaking vs. Curing time and subsequent soaking time and (b) Linear expansion during soaking vs. Sulphate content for kaolinite-6wt% lime cylinders with varying additions of magnesium sulphate at 30 °C and 100% relative humidity. *(MDD≈1.41Mg/m³ ; OMC = 27.4 %).*

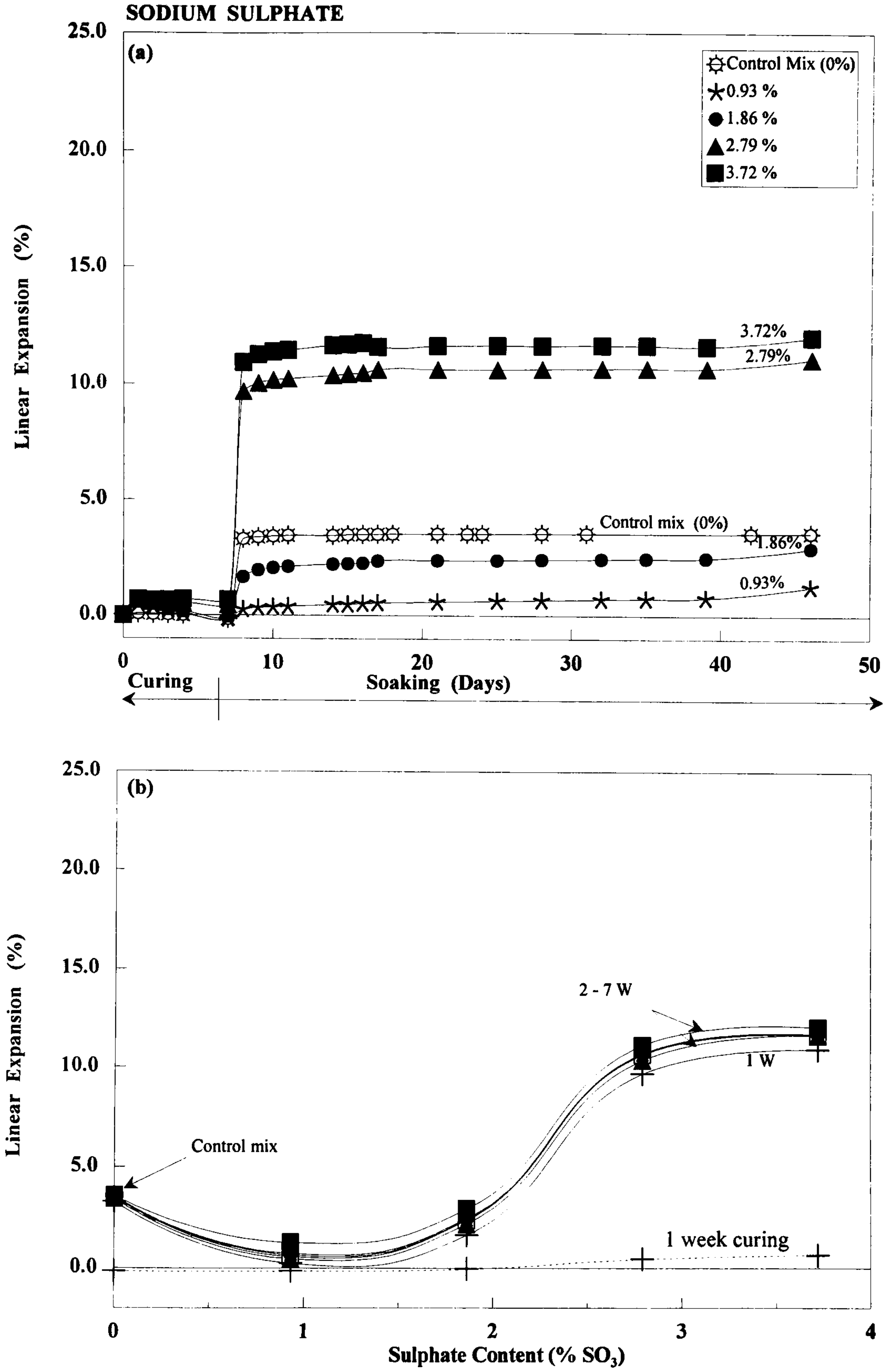


Figure 8.1-12 (a) Linear expansion during soaking vs. Curing time and subsequent soaking time and (b) Linear expansion during soaking vs. Sulphate content for kaolinite-6wt% lime cylinders with varying additions of sodium sulphate at 30 °C and 100% relative humidity. *($MDD \approx 1.41 Mg/m^3$; $OMC = 27.4$ %).*

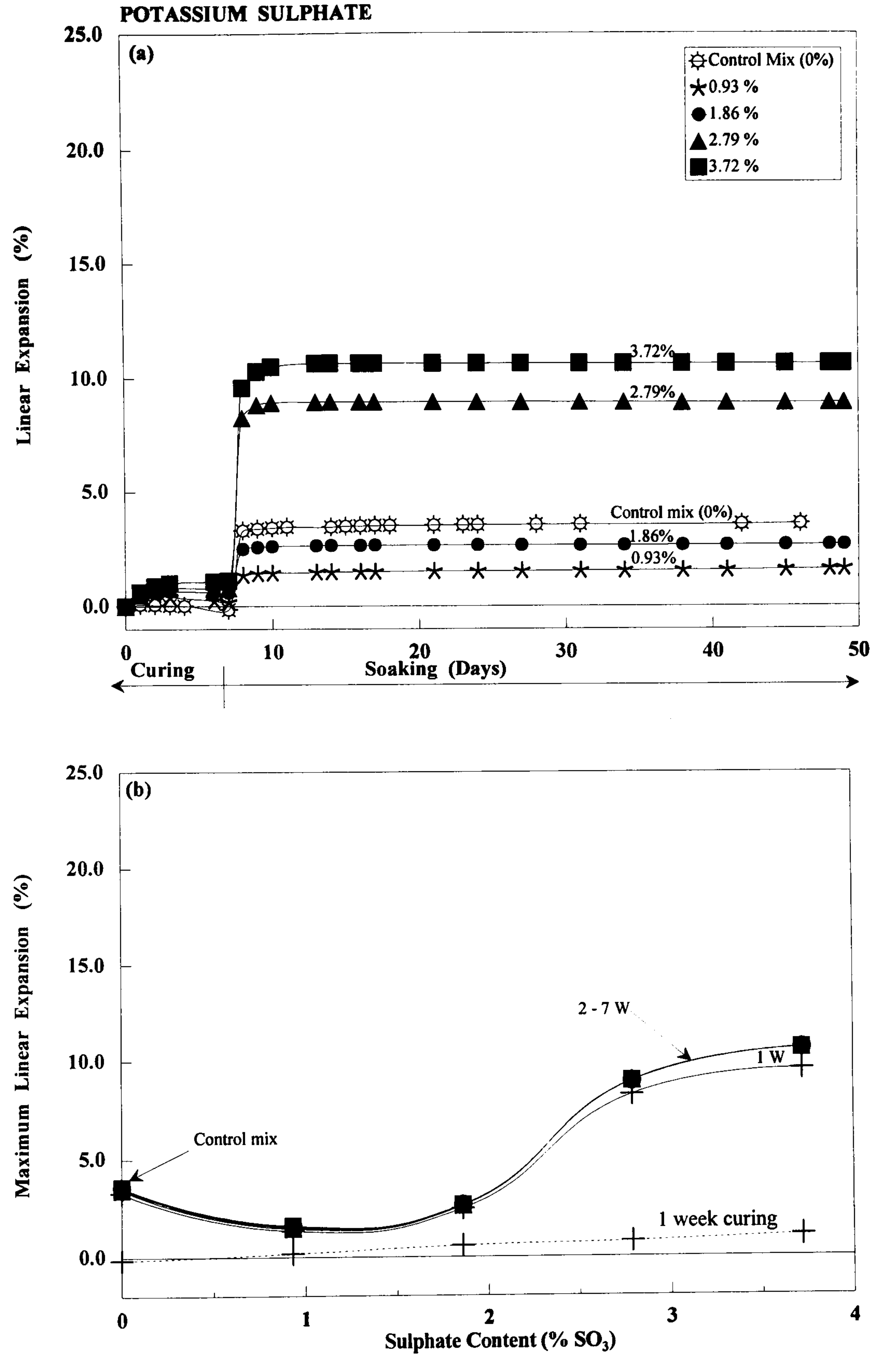


Figure 8.1-13 (a) Linear expansion during soaking vs. Curing time and subsequent soaking time and (b) Linear expansion during soaking vs. Sulphate content for kaolinite-6wt% lime cylinders with varying additions of potassium sulphate at 30 °C and 100% relative humidity. *(MDD$\approx$1.41Mg/m^3 ; OMC = 27.4 %).*

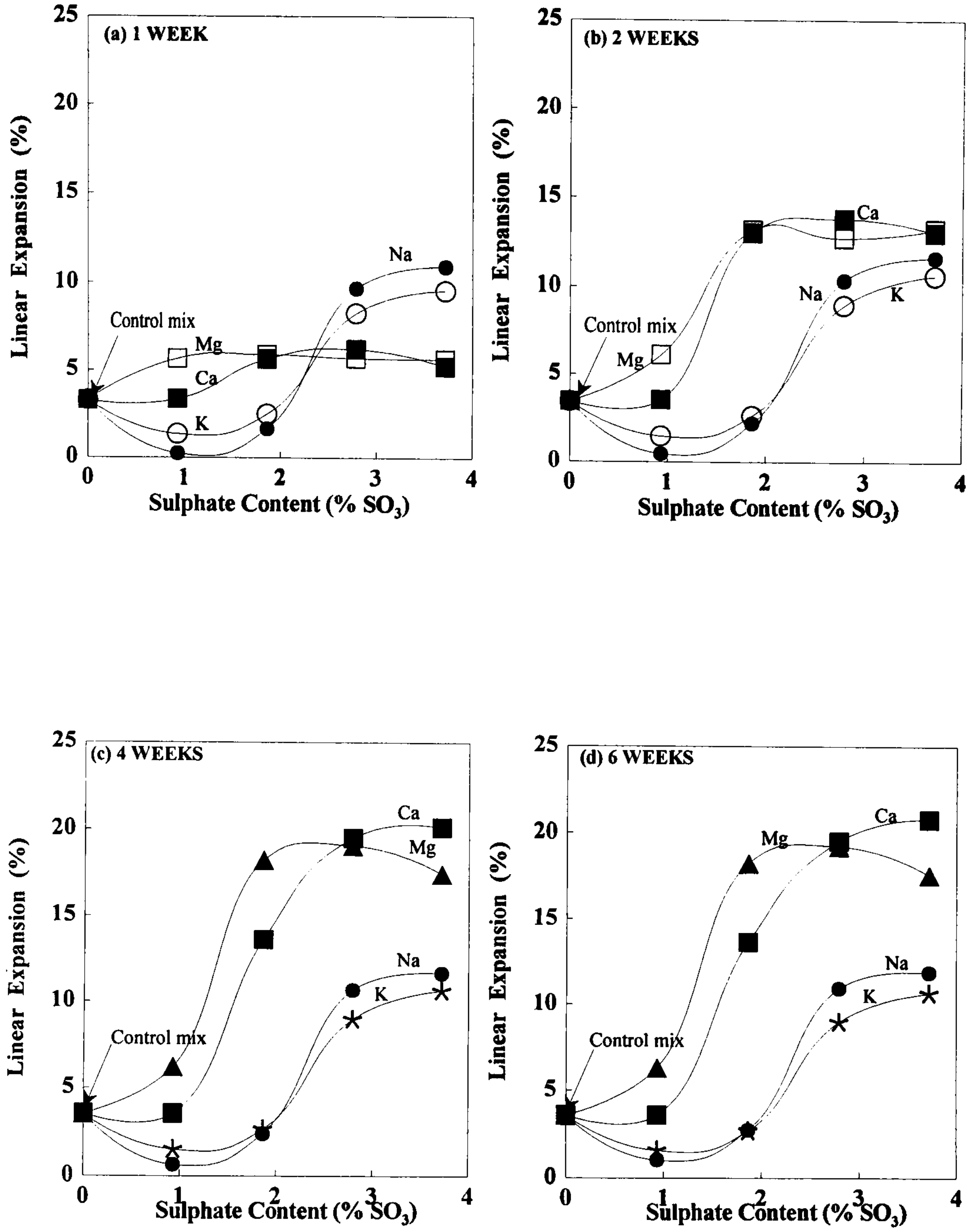


Figure 8.1-14 Linear expansion during soaking vs. Sulphate content for kaolinite-6wt% lime cylinders with varying additions of various metal sulphates, cured for 7 days at 30°C and 100% relative humidity and then soaked for (a) 1 (b) 2 (c) 4 and (d) 6 weeks. *(MDD$\approx$1.41Mg/m^3 ; OMC = 27.4 %).*

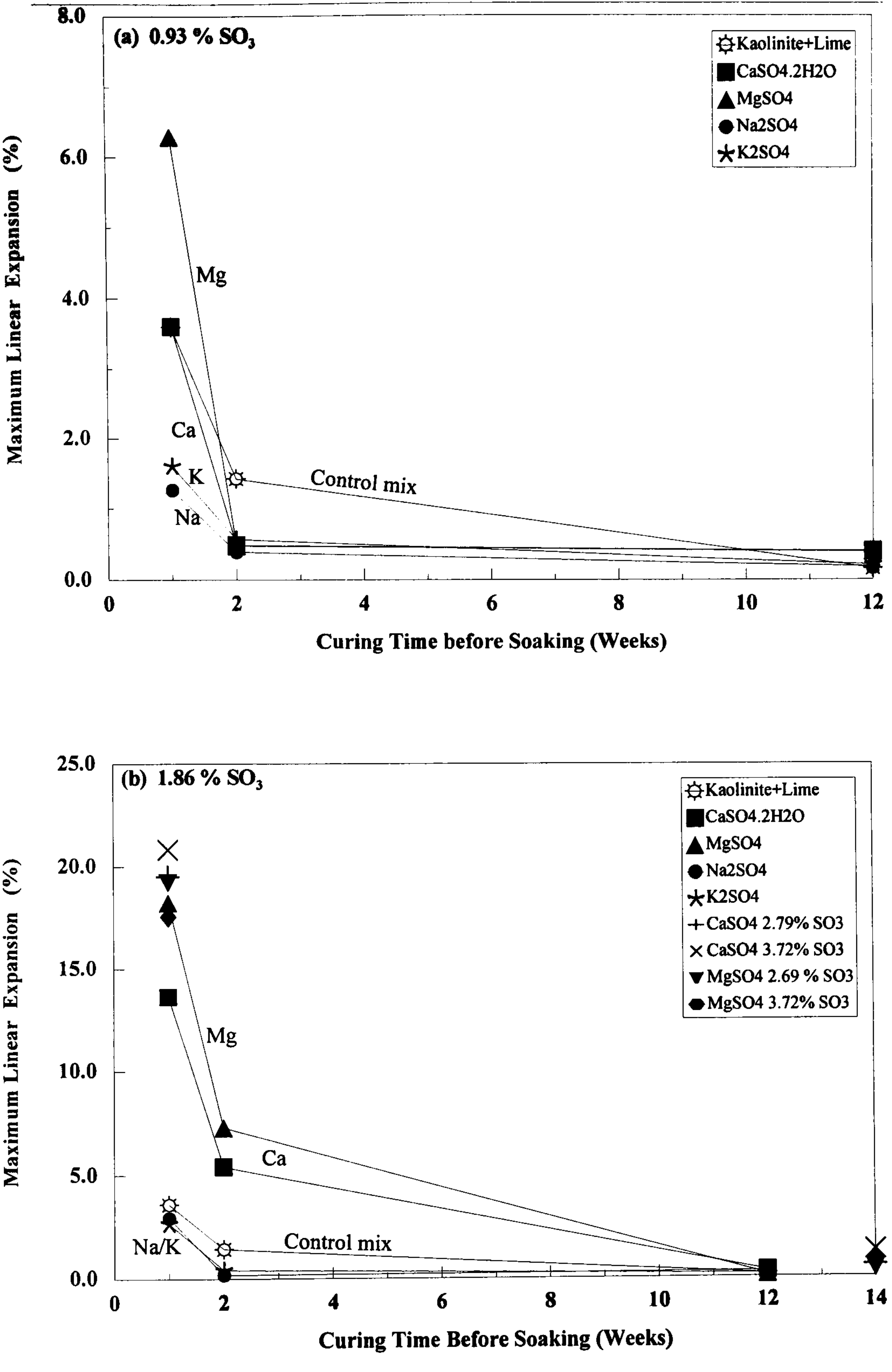


Figure 8.1-15 Maximum linear expansion during soaking vs. Curing time before soaking for kaolinite-6wt% lime cylinders containing (a) 0.93 and (b) 1.86 % SO_3 *(unless otherwise stated)*, **of various metal sulphates at 30°C and 100% relative humidity.** *(MDD$\approx$1.41Mg/m^3 ; OMC = 27.4 %).*

8.1.3.6 Effects of substitution of lime with GGBS on expansion during soaking, for stabilised kaolinite containing gypsum.

Figures 8.1-16 - 8.1-21 illustrate the influence of progressively replacing lime with GGBS in the kaolinite - lime - GGBS - gypsum system, at gypsum contents equivalent to 0%, 0.93%, 1.86% 2.79% and 3.72% SO_3. The majority of samples recorded rapid expansion on soaking. The time taken to attain maximum expansion mainly depended on the SO_3 content, with the most expansive samples taking longer periods, i.e. from 1 to 3 days of soaking for 0-1.86 % SO_3 levels and 3 to >30 days of soaking for SO_3 levels in the range 2.76-3.72%. For all compositions investigated the ultimate (maximum) expansion consistently decreased with increasing substitution of lime with GGBS. It should be noted that the vertical linear expansion scale is expanded with change in sulphate concentration (from 5% to 15% then to 30%) in order to separate the different curves. Comparison of these swelling trends with strength results in Figures 7.3-6 (a), (b) and (c) in Section 7.3 show very convincingly the advantages of using a high slag-low lime stabiliser in minimising sulphate expansion and maximising strength gain in kaolinite - lime - sulphate - GGBS systems.

Using the Department of Transportation (DTp.) allowable average swell limit of 5mm for a 127 mm high CBR mould (about 4% linear swell), all samples without any added gypsum or those containing 0.93 % SO_3 equivalent of gypsum addition, satisfied this requirement (see dotted lines in Figure 8.1-16). Most of those containing 1.86 % SO_3 also satisfied this requirement, with the exception of sample 3L3S4G which failed, and sample 6L0S4G which recorded exactly 4% linear expansion (Figure 8.1-17 (a)).

Interestingly, of the samples containing 2.79% SO_3, sample 3L3S6G, which had failed at 1.86% SO_3 content, this time satisfied the 4% average swell limit (Figure 8.1-17 (b)). Other samples with higher slag and lower lime contents and containing 2.79% SO_3 also satisfied the 4% expansion limit whereas samples 6L0S6G and 5L1S6G fail this requirement, as well as failing the 8% DTp. maximum swell limit of 8%. However sample 2L4S8G was very close to the limit and it might be anticipated that a sample of composition 1L5S8G would satisfy the limit. In addition, samples 6L0S8G, 5L1S8G and 3L3S8G, failed both limits.

For those samples without lime, the expansion of sample 0L0S8G stabilised at the 4% DTp. expansion limit. Meanwhile, sample 0L6S8G displayed a behaviour which was very uncharacteristic. For forty days, no expansion was observed. Indeed very minor shrinkage was recorded throughout and then suddenly, the expansion rose sharply and within 10 days both DTp. limits had been exceeded. The fact that there was no lime originally in the sample, and all other indications from this work suggest that lime along with sulphate is required to produce substantial swelling leads to two theories which could possibly explain what might have happened.

1) lime (Ca^{2+} + OH^-) might have migrated from nearby samples (as the samples were all soaked in one tank (See Figure 6.1-1 in Chapter 6), or

2) the kaolinite-6wt.%slag-8wt.%gypsum system became expansive with prolonged soaking because of very slow release of lime from very slowly hydrating slag

It is reported in the literature (Daimon, 1980; Caijun Shi *et al.,* 1993) that slag alone can indeed hydrate slowly in water, releasing Ca^{2+} ions into solution. It was not clear from the evidence of the current work which of these swelling initiators might have operated. However, the experiment has been subsequently repeated in an isolated container and identical results have been obtained. Thus, hypothesis number 2 above is now the most likely mechanism. The implications of this observation to the potential practical and commercial applications of the process are clearly evident and more work is required in this area.

Figures 8.1-19 (a) and (b) show the effect of increasing replacement of lime by slag on the "ultimate" expansion on soaking of kaolinite - slag/(lime) - gypsum cylinders. In general as the lime is replaced by slag the "ultimate" expansion falls. The effect is particularly marked at high sulphate concentration and Figure 8.1-19 indicates that the most favourable compositions are those where the lime content has been reduced to the minimum possible level, whilst still being sufficient to fully activate the slag.

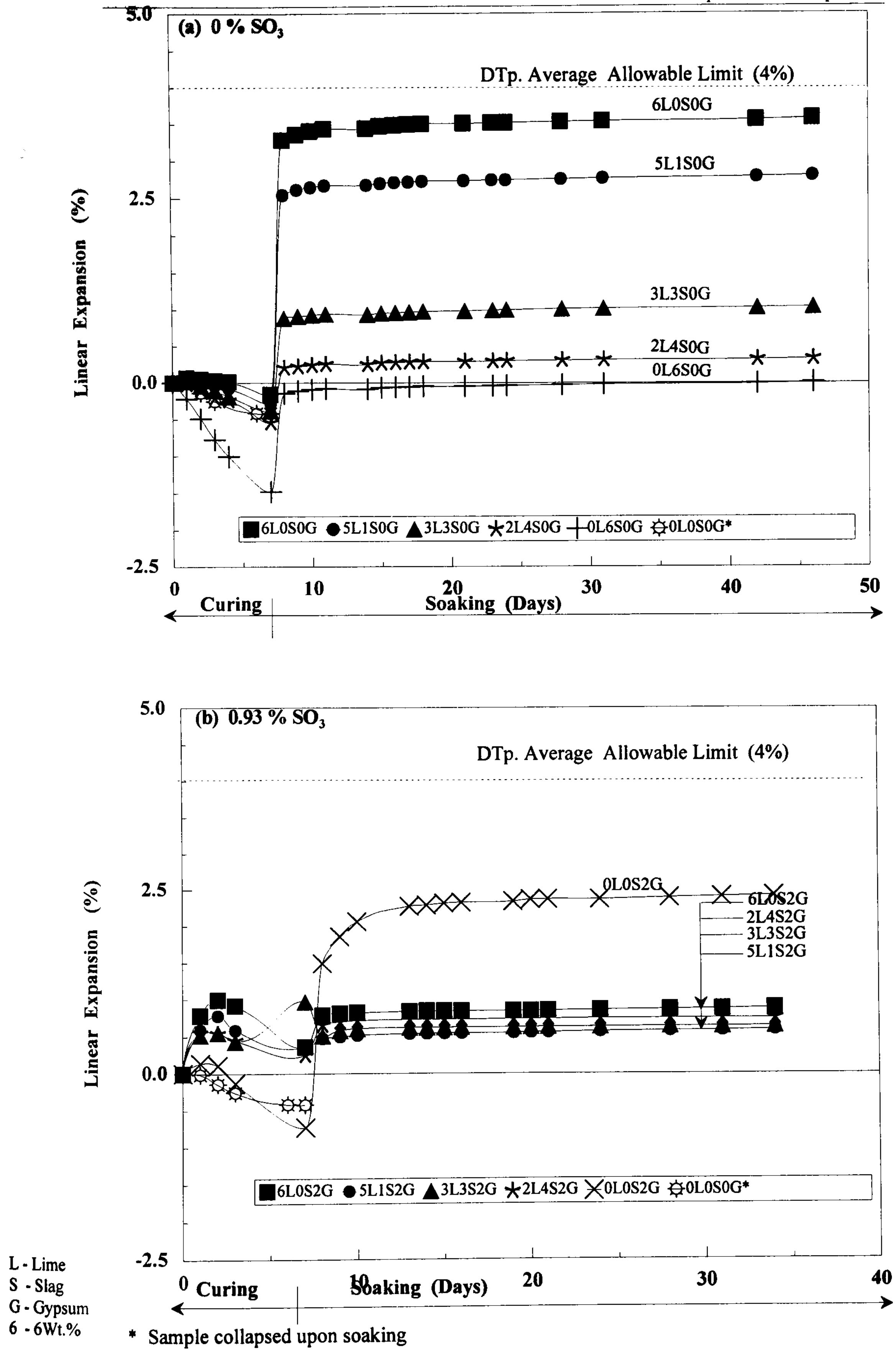
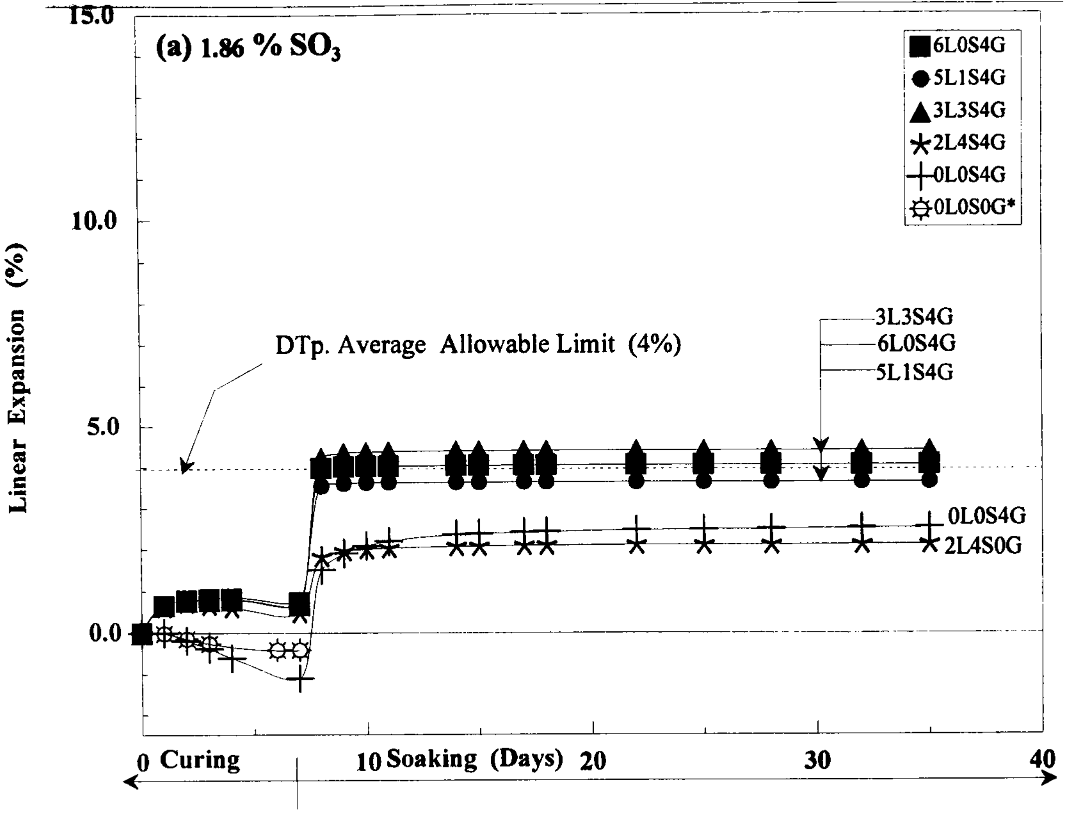
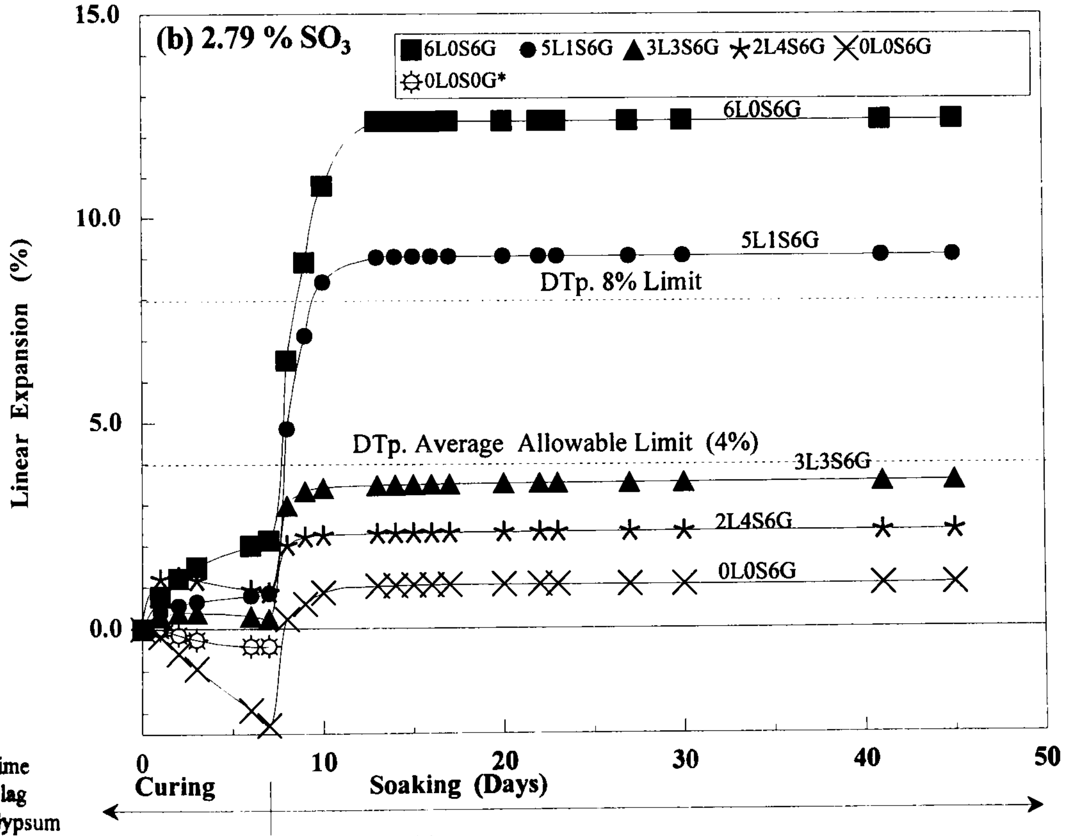


Figure 8.1-16 Linear expansion vs. curing time and subsequent soaking time for kaolinite-6wt.% lime cylinders containing (a) 0 and (b) 0.93% SO_3 additions of gypsum at 30°C and 100% relative humidity. *(MDD=1.41 Mg/m^3; OMC=30.55%).*



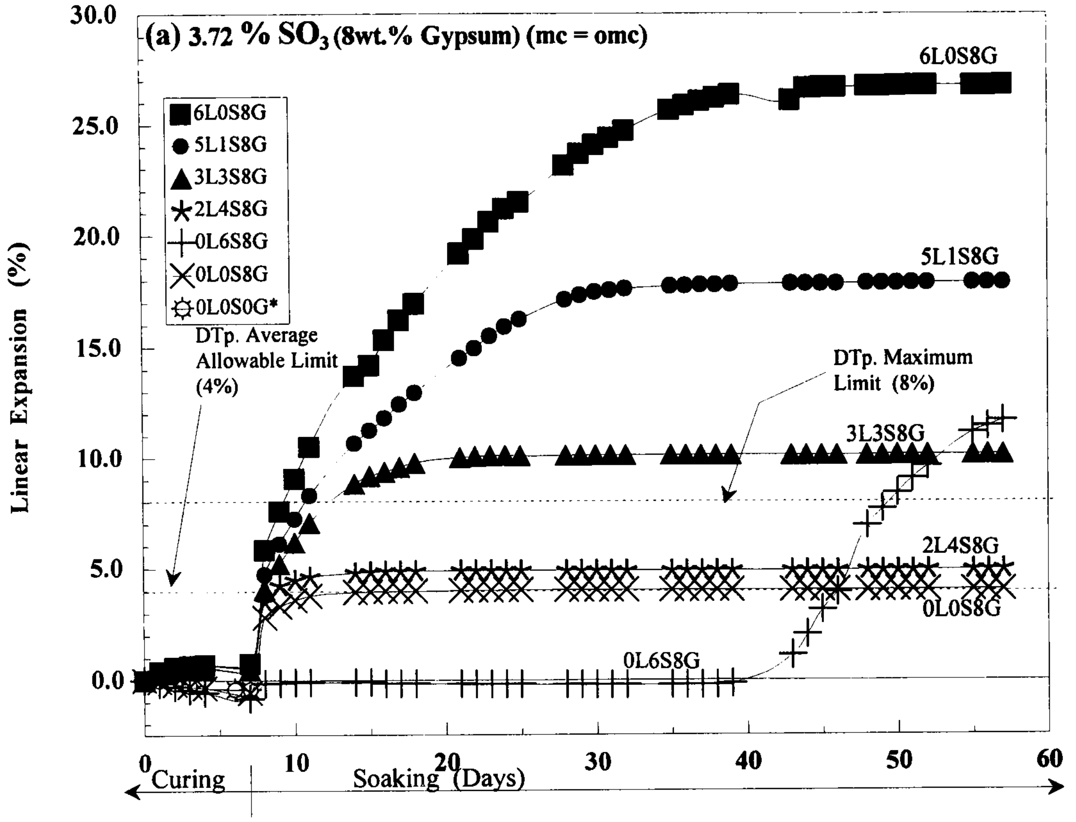
(b) 2.79 % SO3



L - Lime
S - Slag
G - Gypsum
6 - 6Wt.%

* Sample collapsed upon soaking

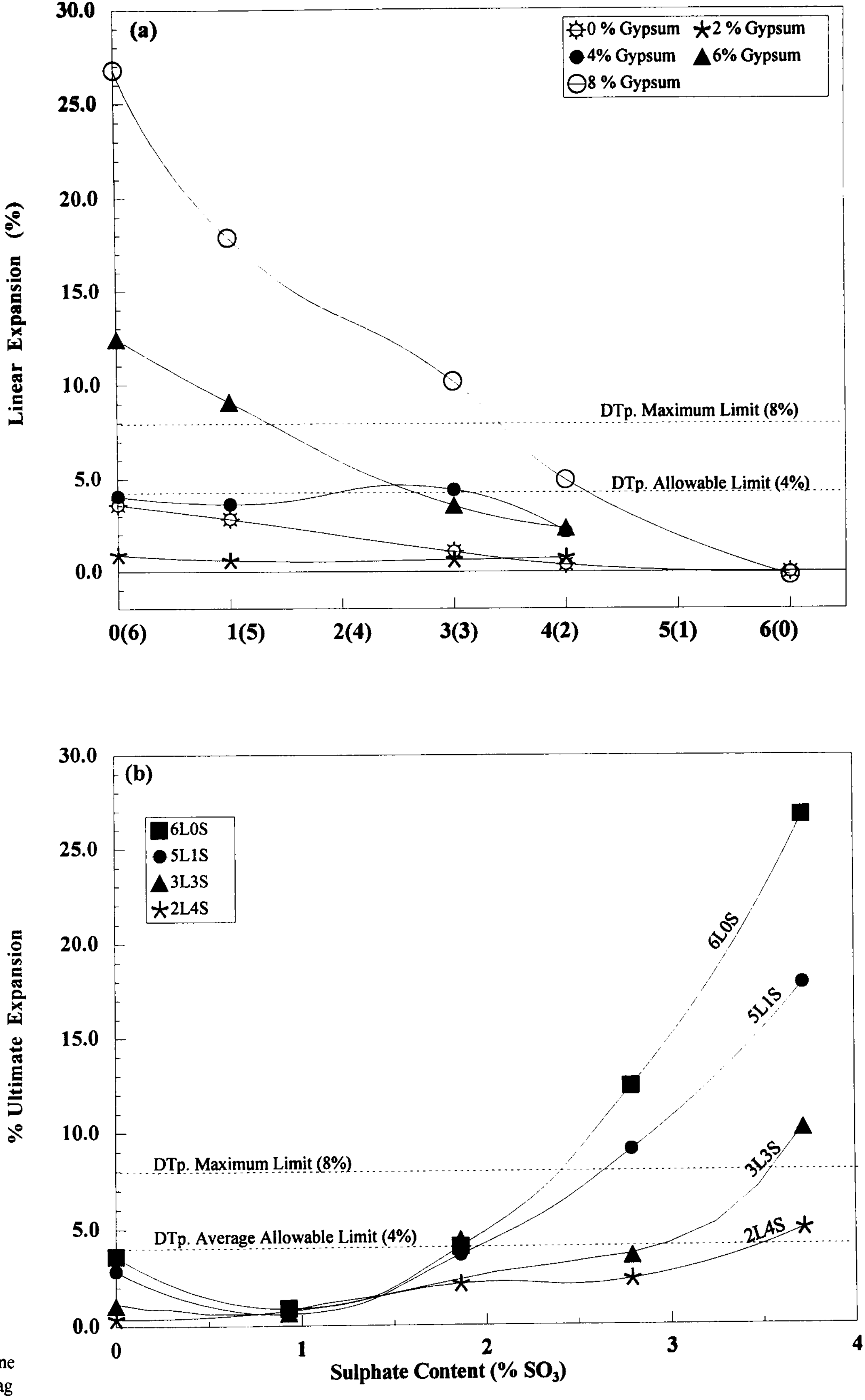
Figure 8.1-17 Linear expansion vs. curing time and subsequent soaking time for kaolinite-6wt.% lime cylinders containing (a) 1.86 and (b) 2.79% SO_3 additions of gypsum at 30°C and 100% relative humidity. *(MDD=1.41 Mg/m^3; OMC=30.55%).*



* Sample collapsed upon soaking

L - Lime
S - Slag
G - Gypsum
6 - 6Wt.%

Figure 8.1-18 Linear expansion vs. curing time and subsequent soaking time for kaolinite-6wt.% lime cylinders containing 3.72% SO_3 additions of gypsum at 30°C and 100% relative humidity. *(MDD=1.41 Mg/m³; MC=OMC=30.55%).*

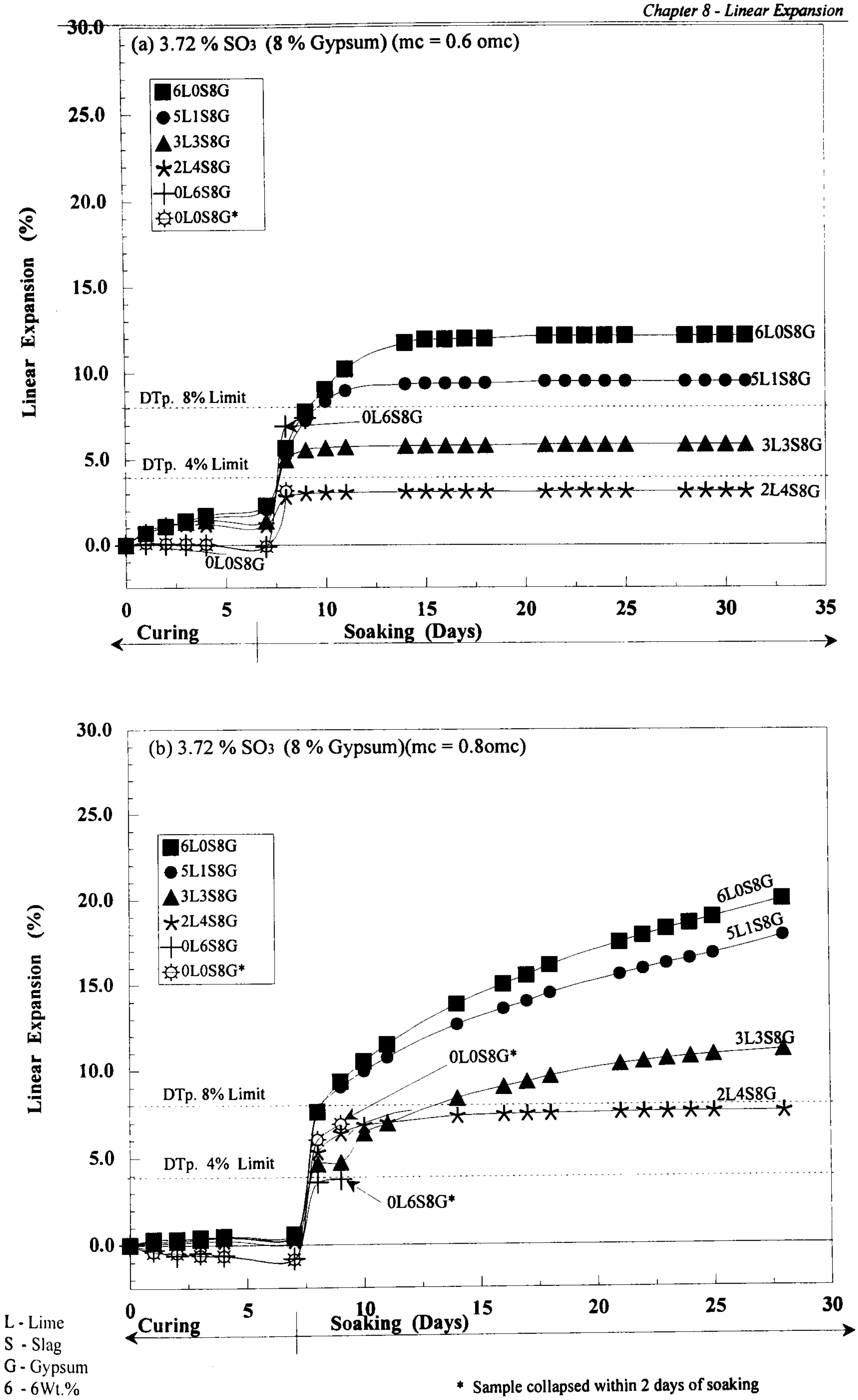


L - Lime
S - Slag
G - Gypsum
6 - 6Wt.%

Figure 8.1-19 (a) Maximum linear expansion during soaking vs. Slag/Lime ratio and (b) Maximum linear expansion during soaking vs. Gypsum content for kaolinite-lime-ggbs cylinders, at 30°C and 100% relative humidity. *(MDD=1.41 Mg/m^3; OMC=30.55%).*

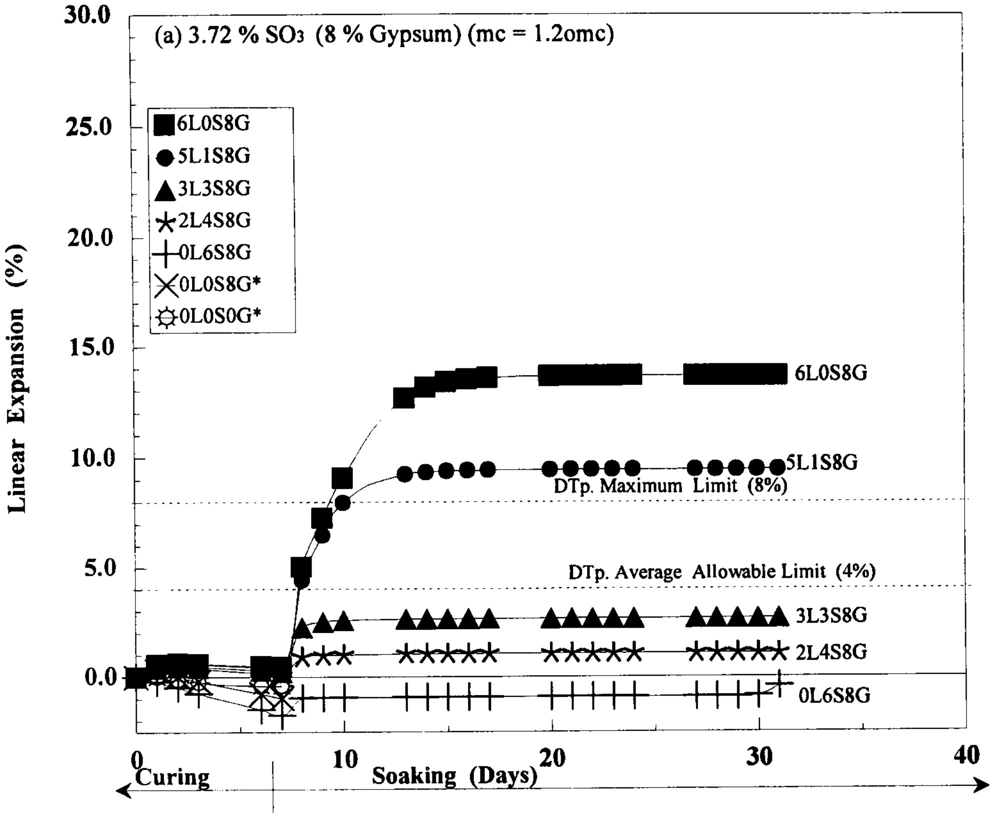
8.1.3.7 The influence of compaction moisture content on swelling

Figures 8.1-20 and 8.1-21 show the effect of varying the compaction moisture content of kaolinite - lime - GGBS mixes containing 8wt.% gypsum (3.72% SO_3) content. The samples compacted at 0.6OMC were in general poorly bonded and close to collapse due to low moisture content, and therefore recorded low expansion. Specimens compacted at 0.8 OMC continued to expand up to at least 28 days. Combined with Figure 8.1-18 (at OMC), the results show marked fall in expansion in going from OMC to 1.2 OMC (Figure 8.1-21). This effect was also observed during moist curing (Figures 8.1-8 and 8.1-9) and may also be a result of increased free volume which expanding material can occupy. With the exception of samples 6L0S8G and 5L1S8G both of which failed both of the DTp. limits, all the other samples passed both limits at this moisture content (1.2OMC). This shows the advantage of compacting at a moisture content slightly in excess of OMC, in reducing potential swelling. Further research work is however required in this area to establish the limiting deviations from OMC in sulphate bearing clay - lime - GGBS systems to maintain low expansions. In normal practice, compaction is done wet of OMC. This would not only lower the subsequent expansion but also (if the water is not very much in excess), enhance the strength development especially for stabilised soil. Thus, the importance of the cut off point for optimal operation for high strengths, accompanied by low expansions cannot be overemphasised.



* Sample collapsed within 2 days of soaking

Figure 8.1-20 Linear expansion vs. curing time and subsequent soaking time for kaolinite-6wt.% lime cylinders containing 3.72% SO_3 additions of gypsum at (a) 0.6OMC *(18.33%)* and (b) 0.8OMC *(24.44%)* at 30°C and 100% relative humidity.



L - Lime
S - Slag
G - Gypsum
6 - 6Wt.%

* Sample collapsed upon soaking

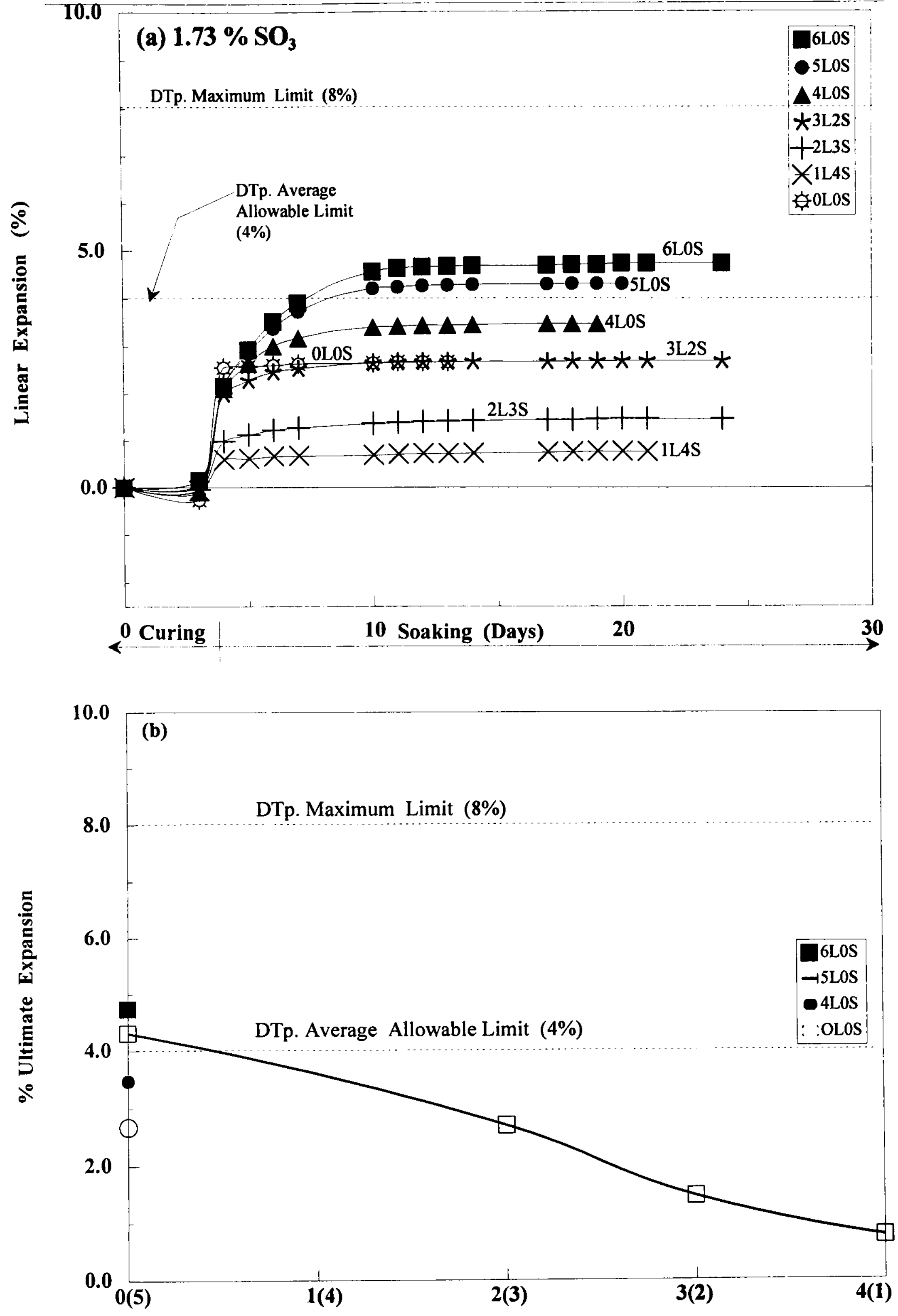
Figure 8.1-21 Linear expansion vs. curing time and subsequent soaking time for kaolinite-lime-ggbs cylinders containing 3.72% SO_3 additions of gypsum at 1.2OMC (36.66) and at 30°C and 100% relative humidity.

8.1.3.8 Effects of substitution of lime with GGBS on expansion during soaking, for stabilised Kimmeridge Clay.

The minimum lime requirement for Kimmeridge Clay was established as 5 wt.% (see section 7.1.1). Linear expansion work, using this clay was done on cylinders containing 4, 5 and 6wt.% lime contents and also on some cylinders containing slag-lime compositions of 5wt.% total stabiliser content (Figure 8.1-22). With the exception of samples containing 5 and 6 wt.% lime contents which marginally failed the DTp. 4% average swell limit, all the Kimmeridge Clay - lime - GGBS mixes satisfied this requirement. The expansion, as in the case of kaolinite, decreased with increasing slag content (and decreasing lime content). This decrease in expansion with increase in slag content occurred even though the unconfined compressive strength (See Figure 7.3-9 (a)) also showed a general decrease with increase in slag content (at total stabiliser content of 5wt.%). Low unconfined compressive strengths might be expected to correspond with high expansions because of the reduced resistance to swelling pressure. This therefore indicates that the effects that GGBS has on the expansive behaviour of lime stabilised soils is not only to resist swelling pressure but also to reduce the actual pressure generated. In fact the data in Figure 7.3-9 (a) indicated that a total stabiliser content of 5% was too low for this soil and that much more viable total stabiliser contents for this soil would be between 8 and 10% as illustrated from the UCS values in Figures 7.3-11. Here, as with kaolinite, there was a progressive increase in strength with increase in slag to lime ratio and these specimens would (particularly for the high slag contents) be expected to produce very small or negligible expansions. It was therefore considered unnecessary to continue with the expansion tests at the higher stabiliser contents of 6, 8 and 10wt.% as it would be unlikely that the swellings already obtained (using a total stabiliser of 5 wt.%) would be exceeded, other than at the high lime-low slag compositions.

In Summary,

1. The duration during which expansion took place depended on the SO_3 content, specimens containing high SO_3 contents taking longer to achieve ultimate expansion than those containing low contents.
2. Specimens containing high slag-low lime contents recorded the lowest linear expansion and highest strength.
3. Increase in SO_3 content reduced the expansion of low lime mixes while a similar addition to high lime cases led to expansion
4. At very high sulphate levels ($\approx$ 3.72) even specimens with high slag:lime ratios failed the DTp. 8% maximum swell limit.
5. The presence of unreacted slag may be potentially expansive
6. Partial replacement of lime by slag also reduces swelling of lime-stabilised Kimmeridge Clay, the reduction being proportional to the degree of replacement (as in the case of kaolinite).



L - Lime
S - Slag
G - Gypsum
6 - 6Wt.%

Figure 8.1-22 (a) Linear expansion vs. curing time (3 days) and subsequent soaking time for and (b) Maximum linear expansion during soaking vs. Lime/Slag content for Kimmeridge clay-lime-ggbs cylinders at 30°C and 100% relative humidity. *(MDD=1.41 Mg/m^3; OMC=24.22%).*

8.2 SWELLING PRESSURE MEASUREMENTS

8.2.1 INTRODUCTION

The swelling potential of a soil mass (as discussed in Chapter 2) may be expressed either in terms of volumetric (or dimensional) change and/or in terms of the swelling pressure generated by the soil mass (when these volumetric changes are not allowed take place).

In the current work, linear expansion (and hence volumetric) changes of all the experimented clay-lime-sulphate-slag combinations were determined both during moist curing for 3-7 days and also during subsequent soaking at 30°C and approximately 100% relative humidity. Since the level of the unconfined volume expansion is not necessarily an indicator of the level of the swelling pressure generated on confinement, the swelling pressure generated was also determined. However, it was decided (purely due to time considerations) to only monitor the swelling pressure generated by a selection of the systems under study. Thus, pressure measurements were taken on the kaolinite-lime-sulphate system only. The work was done using the sulphates of calcium (gypsum), magnesium, sodium and potassium at concentrations giving sulphate ion concentrations equivalent to 0.93, 1.86, 2.79 and 3.72 % SO_3.

Swelling pressure measurements were performed on compressed cylinders during moist curing for 7 days and then during subsequent soaking until no further significant swelling pressure changes occurred. As was the case for linear expansion, the moist curing and soaking operations were performed in one continuous operation. The trends observed (shown in Figures 8.2-1 to 8.2-5) show distinct similarities to those observed for linear expansion during soaking. During the 7 days of moist curing, the swelling pressure increased gradually during the first 1-4 days after which it started to decrease (implying shrinkage) until the end of the moist curing period. Upon soaking, the pressure increased rapidly during the first day of soaking and then the rate of increase declined. At 0.93% SO_3 content, no further significant increases in pressure were observed after the first day of soaking (see Figure 8.2-1 and 8.2-4). At other sulphate concentrations, the swelling pressure continued to increase at a decreasing rate, with the sulphates containing monovalent cations tending to attain ultimate swelling pressure within 2 to 10 days of soaking (Figures 8.2-3 and 8.2-4). Those containing divalent cations tended to achieve higher swelling pressures and to take longer periods to achieve them and at high sulphate concentrations pressure continued to increase up to the recorded monitoring period of 20 to 30 days. At this point measurements were terminated due to a number of factors :-

(i) no further increase in pressure was anticipated, (sodium + potassium sulphate)

(ii) the transducer limit was approached (calcium + magnesium sulphate at 3.72% SO_3)

(iii) the environmental chamber malfunctioned and could not maintain constant conditions (last two days for calcium sulphate at 3.72% SO_3)

Swelling pressure was very sensitive to variations in temperature, and it increased sharply on the occasion that the temperature rose from the set operating temperature of 30°C when the environmental chamber malfunctioned in (iii) above. Since the observed pressures reduced (within minutes) after restoration of the set temperature, it would seem likely that the pressure increase related directly to reversible thermal changes and osmotic changes rather than formation of expansive products. Any thermal expansion within the sample holding perspex and/or the restraining metal framework would not increase the pressure because the coefficients of expansion for all these materials are higher than that of the soil.

8.2.2 EFFECTS OF DIFFERENT SULPHATES

8.2.2.1 Gypsum

Figure 8.2-1 (a) illustrates the swelling pressure generated in kaolinite - 6wt.% lime - gypsum cylinders during 7 days of moist curing and during subsequent soaking. During the 7-day moist curing period, cylinders containing low sulphate concentrations (0.93 - 1.86 % SO_3) recorded higher swelling pressures than those containing higher (2.79 - 3.72% SO_3) concentrations. During soaking, the situation was reversed and cylinders with the higher sulphate concentrations eventually recorded higher swelling pressures although the development of this ultimate pressure took longer (at least 10 days) than was the case for those cylinders with lower SO_3 concentration (1 - 7 days). The swelling pressure generated after 20 days was in the sulphate concentration order:-

3.72 > 2.79 > 1.86 >> 0 (Control) ≥ 0.93 % SO_3 (see Figure 8.2-1 (b)).

It should be noted that this sequence is exactly similar to that observed during the linear expansion measurements (see Figure 8.1-10 (a)). In both cases (swelling pressure and linear expansion), magnitudes at 0.93 % SO_3 were close to those of the control mix, while the major increase in both parameters occurred between 0.93% SO_3 and 1.86% SO_3. Also, the high sulphate bearing specimens (2.79-3.72 % SO_3) recorded the highest linear swelling and the highest strengths as well as the highest pressures.

8.2.2.2 Magnesium Sulphate

Cylinders containing $MgSO_4$ did not record significant swelling pressure increases during the first 7 days of moist curing as compared with those occurring during subsequent soaking (see Figure 8.2-1 (a) and (b)). Upon soaking, cylinders with intermediate sulphate concentration (1.86 and 2.79 % SO_3) recorded high swelling pressure increases while those with low (0.93 %) or high (3.72 %) SO_3 concentrations, ultimately recorded swelling pressures close to the those of the control mix. The ultimate order of swelling pressure increase was in the sulphate concentration order:-

1.86 > 2.79 >> 3.72 > 0 (Control) > 0.93 % **SO_3** (see Figure 8.2-2).

In both the cases of pressure and linear expansion changes, cylinders containing high (3.72 %) and low (0.93 %) SO_3 concentrations recorded lower measurements than those containing intermediate (1.86 - 2.79 %) SO_3 concentrations. Also as for the case of gypsum addition, the major increase in both parameters occurred between 0.93% SO_3 and 1.86% SO_3. However, cylinders containing high (3.72%) SO_3 developed very small pressures during the period of observation. This is an indication of a turning point (or optimum SO_3 concentration) where linear expansion and swelling pressure generation occurs.

8.2.2.3 Sodium Sulphate

All the cylinders containing different concentrations of sodium sulphate recorded little swelling pressure during the initial 7 days of moist curing (see Figure 8.2-3 (a)). This small initial rise in swelling pressure took place during the first two days of moist curing. Upon soaking, all the cylinders recorded their maximum swelling pressure within 2 days of soaking. Of the sulphate types tested, the cylinders containing sodium sulphate displayed the most rapid initial swelling pressure on soaking, although the maximum pressure achieved was much less than for cylinders containing calcium and magnesium sulphates.

There was no significant variation in swelling pressure generation with variation in SO_3 concentration (see Figure 8.2-3 (b)). Unlike in the previous case of gypsum, the SO_3 order at ultimate swelling pressure (1.86 > 2.79 > 3.72 > 0.93 > 0 % (Control)) had no similarity with the one obtained for linear expansion (i.e. 3.72 > 2.79 >> 0 (Control) > 1.86 > 0.93 % SO_3). This behaviour suggests lack of (or a significantly different) relationship between swelling pressure and linear expansion for the case of sodium sulphate addition. The behaviour perhaps also suggests a slight difference between the swelling pressure generation mechanism for the case of sodium sulphate addition compared with the two divalent sulphates already discussed.

8.2.2.4 Potassium Sulphate

On addition of potassium sulphate to kaolinite - lime cylinders, the swelling pressure generation during moist curing was generally low as in the cases of $MgSO_4$ and Na_2SO_4 addition. During soaking, the swelling pressure generation increased rapidly, stabilising after 1-10 days of soaking depending on the sulphate content. For cylinders containing 0.93% SO_3 the pressure generated was significantly below that of the control (Figure 8.2-4 (a) and (b)). With further increase in the sulphate concentration, the swelling pressure increased and at 2.79% SO_3 concentration, further concentration did not result in further swelling pressure increase.

8.2.2.5 Summary

At low sulphate concentrations, cylinders containing sodium sulphate displayed the highest ultimate swelling pressure although values were similar to those for the control and only slightly above those for cylinders containing calcium and magnesium sulphates. Cylinders containing potassium sulphate gave swelling pressures significantly below those of the control (see Figure 8.2-5 (a))..

At intermediate sulphate concentrations (1.86 - 2.79% SO_3), the divalent metal sulphates displayed the highest swelling pressures (Figure 8.2-5). However at 3.72% SO_3 , cylinders containing magnesium sulphate recorded the least swelling pressure whereas for cylinders containing calcium sulphate the pressure continued to increase. Gypsum is the only sulphate which shows this trend. It is also the only sulphate which is sparingly soluble. The more soluble sulphates (such as Na_2SO_4, $MgSO_4$ and to some extent

K_2SO_4) are likely to over-saturate the soaking water with cations, lowering the sample swell and swelling pressure. Thus, apart from gypsum which maintained a high pressure, all the other sulphates recorded lower swelling pressures at higher SO_3 concentrations (2.79. - 3.72% SO_3). Similar observations were made by Warketin and Schofield (1962) while studying the swelling pressure exerted against a confined restraint of Na-montmorillonite in NaCl. They found that swelling pressure decreased with increase in NaCl concentration outside the soil sample. This was further confirmed in the current work by introducing a concentrated sulphate solution in the water reservoir during swelling pressure measurements. The swelling pressure was observed to drop significantly within a few hours, confirming the osmotic swelling pressure generation mechanism.

The results of pressure measurements would suggest that in practice the most dangerous sulphate is calcium sulphate. Figure 8.2-1 (a) and (b) suggests that not only does pressure continue to increase with increasing sulphate concentration but also with time for time periods in excess of those that were able to be monitored in the current work. Magnesium sulphate also produces substantial pressure rises at certain concentrations and could also present a serious problem. Sodium and potassium sulphates are unlikely to present a serious problem as pressure stabilises within a relatively short period and does not continue to increase with increase in SO_3 content. In brief,

1. specimens containing low gypsum concentrations recorded, in general, higher swelling pressures during moist curing than those containing higher concentrations. This trend was reversed during soaking.
2. in the case of gypsum, swelling pressure is directly proportional to SO_3 content

3. there is little variation in the swelling pressure generated with variations in sulphate content for the case of sodium sulphate addition.
4. the sulphates of magnesium sodium and potassium recorded maximum swelling pressures at relatively low sulphate concentrations (1.86-2.79% SO_3) compared with gypsum which recorded maximum swelling at higher sulphate levels (3.72% SO_3). The loss in cementation due to the presence of the former sulphates is thought to be the likely cause of this behaviour.

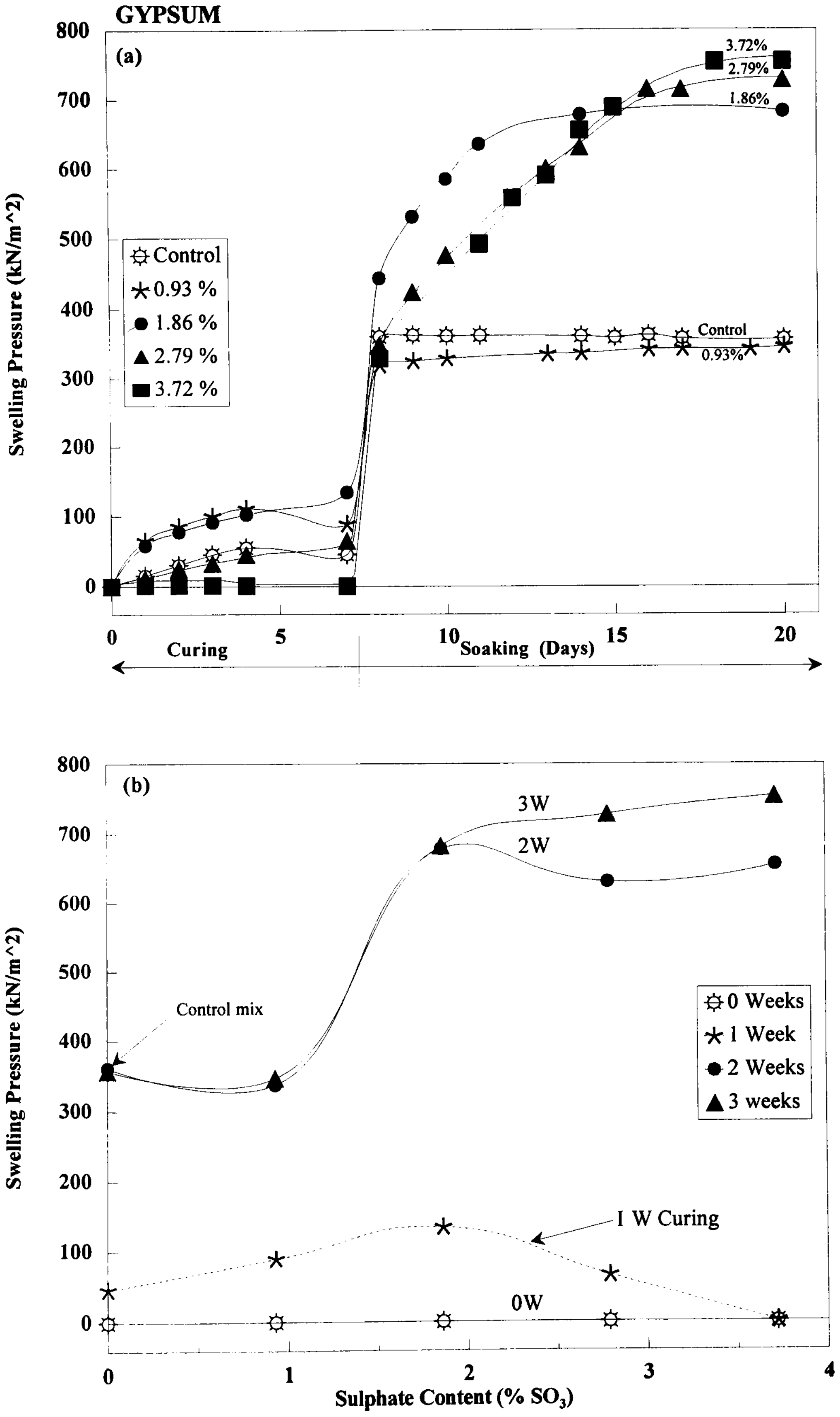


Figure 8.2-1 (a) Swelling pressure vs. Moist curing or soaking and (b) Swelling pressure vs. sulphate content for kaolinite-6wt.% lime cylinders with varying additions of gypsum at 30°C and 100% relative humidity.

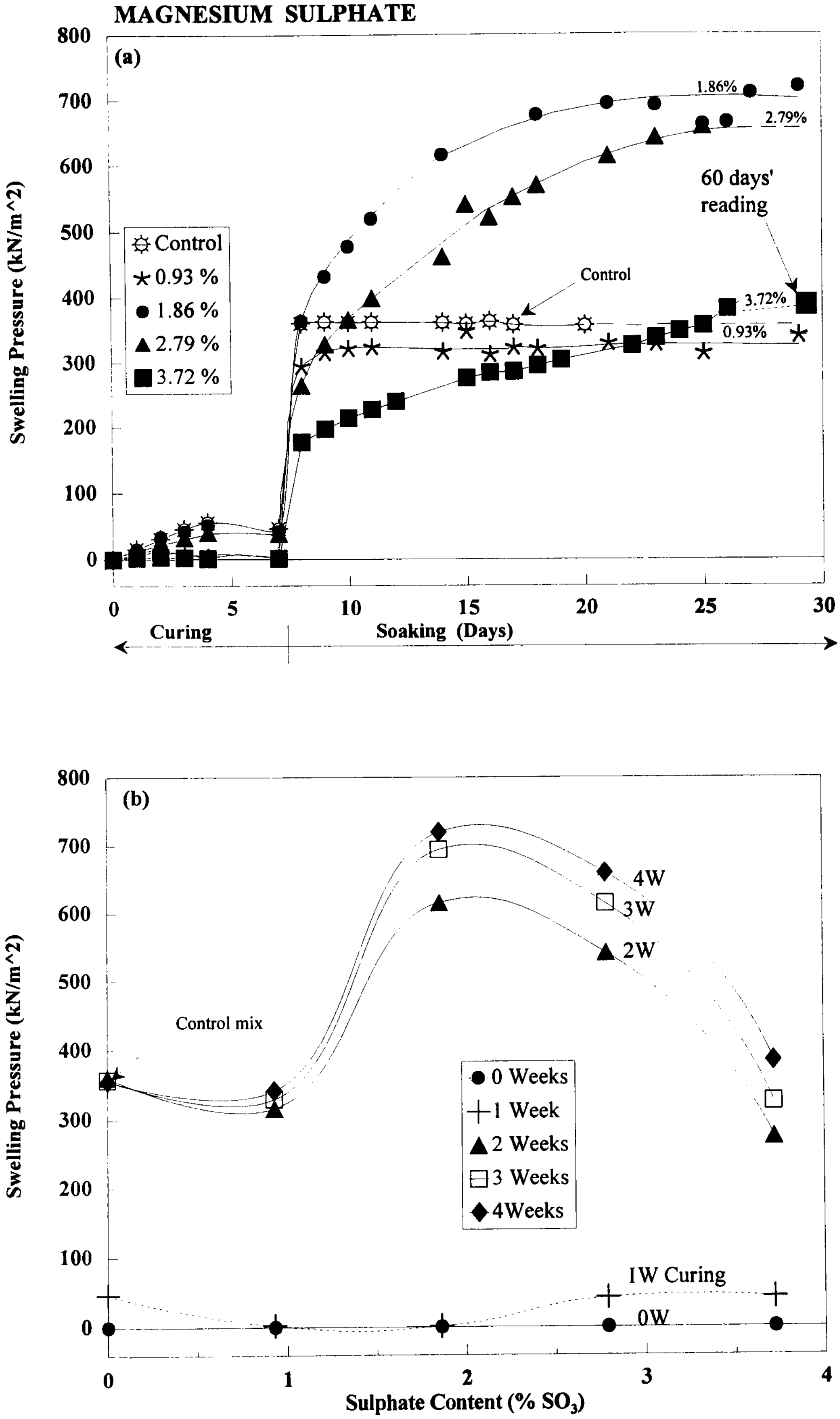


Figure 8.2-2 (a) Swelling pressure vs. Moist curing or soaking and (b) Swelling pressure vs. sulphate content for kaolinite-6wt.% lime cylinders with varying additions of magnessium sulphate at 30°C and 100% relative humidity.

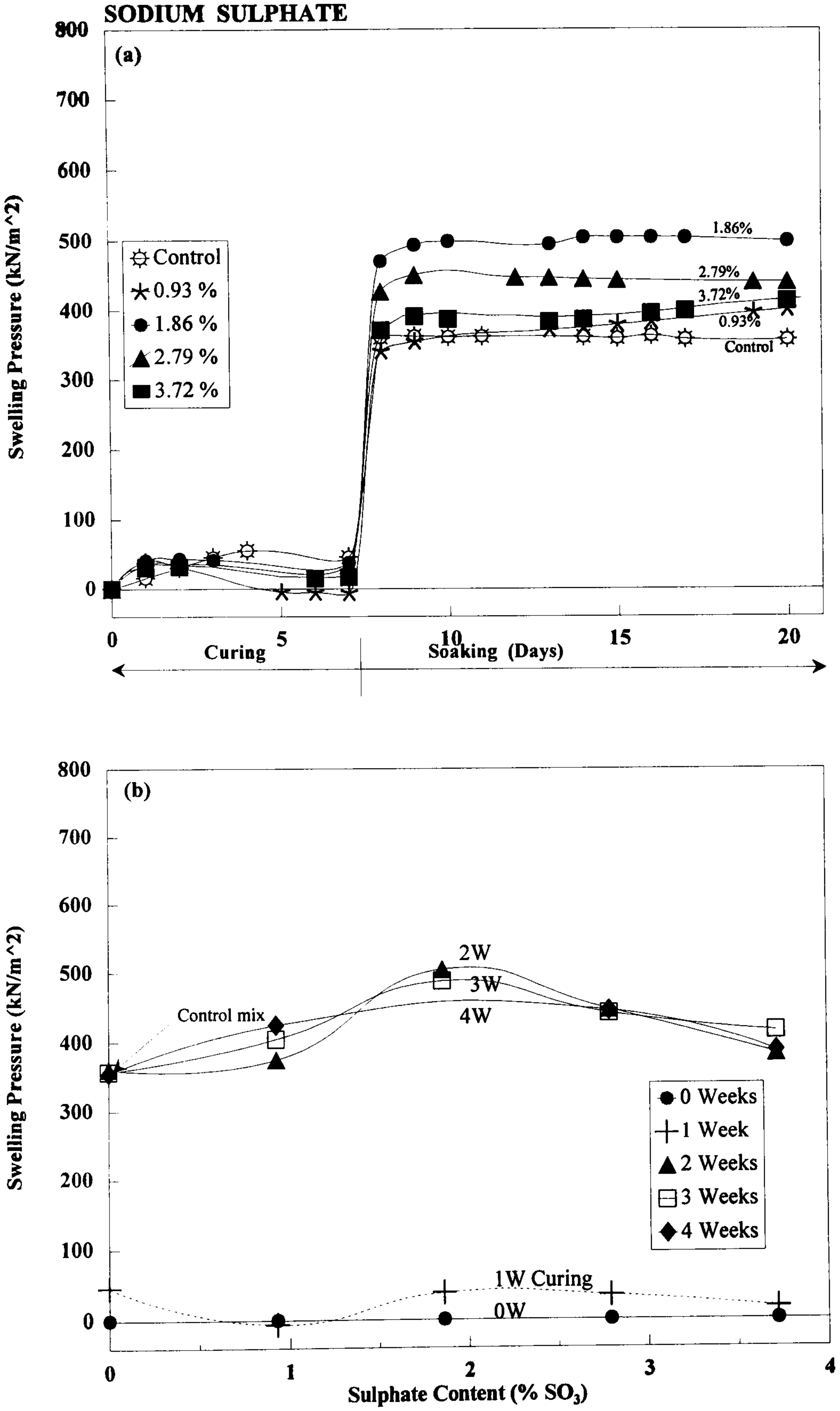


Figure 8.2-3 (a) Swelling pressure vs. Moist curing or soaking and (b) Swelling pressure vs. sulphate content for kaolinite-6wt.% lime cylinders with varying additions of sodium sulphate at 30°C and 100% relative humidity.

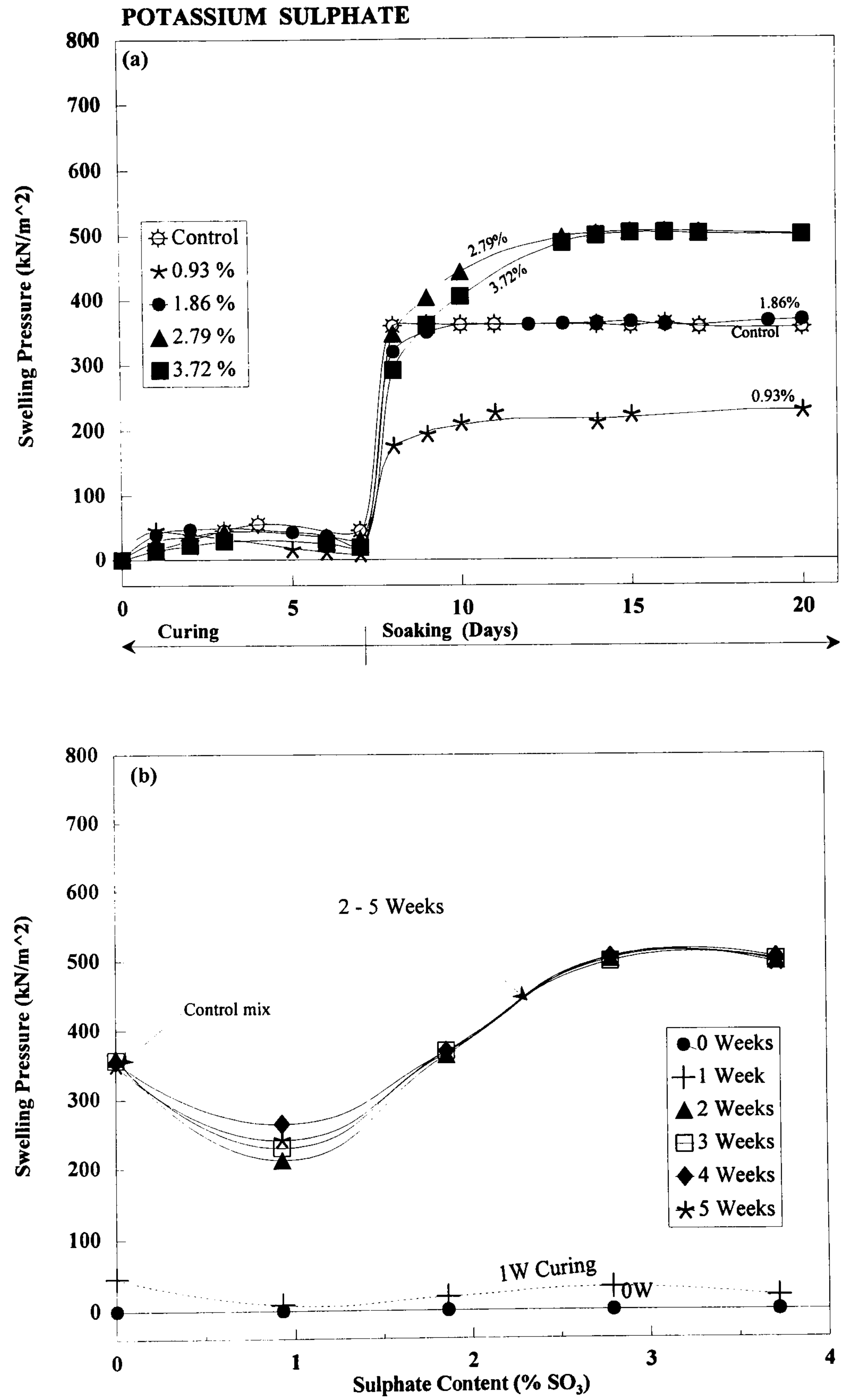


Figure 8.2-4 (a) Swelling pressure vs. Moist curing or soaking and (b) Swelling pressure vs. sulphate content for kaolinite-6wt.% lime cylinders with varying additions of potassium sulphate at 30°C and 100% relative humidity.

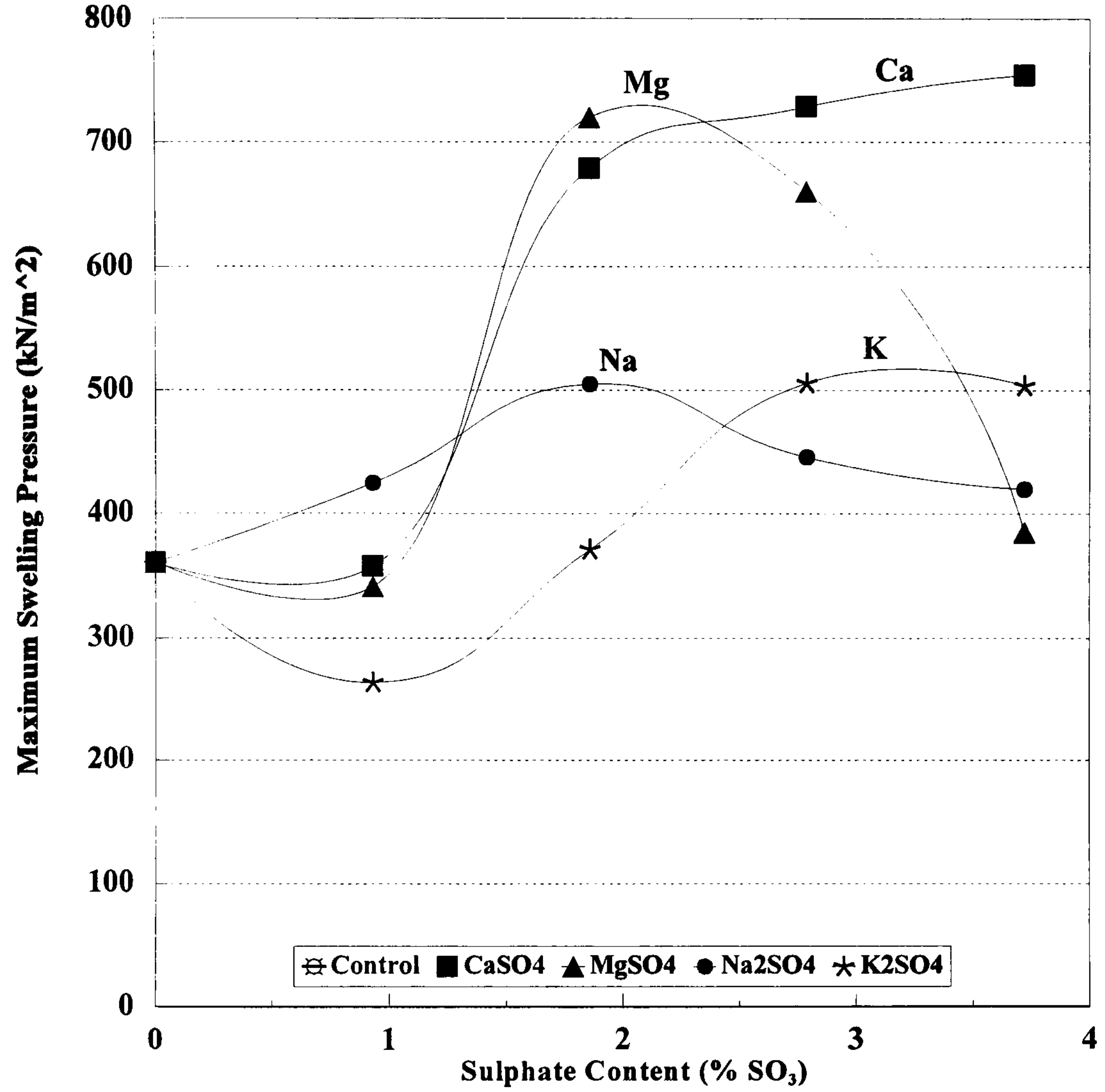


Figure 8.2-5 Maximum swelling pressure during soaking vs. sulphate content for kaolinite-6wt.% lime cylinders containing varying additions of various metal sulphates cured at 30°C and 100% relative humidity.

8.3 PHASE ANALYSIS AND MICROSTRUCTURE

8.3.1 INTRODUCTION

The primary objective of the current research work is to establish the engineering material property changes of lime and (lime/slag) stabilised kaolinite in the presence of various metal sulphates. Therefore, the identification of the products of hydration causing these changes (although essential to a fundamental understanding of the process), is intended only to provide a guide to possible mechanisms. The analytical work was therefore limited to a few carefully selected specimens aimed at giving key indications as to the nature (and possibly the sites) of the reaction and reaction products. The selection of specimens for microstructural analysis was done to represent two of the major material systems under study – the kaolinite - lime - metal sulphate system and the kaolinite - lime - GGBS - gypsum system. No microstructural analytical work was done on for example the Kimmeridge Clay - lime or the Kimmeridge Clay - lime - GGBS systems. For the two systems concerned, the analytical techniques used were (a) X-ray diffraction (XRD) and (b) Scanning electron microscopy (SEM).

XRD analysis was conducted on both the kaolinite - 6wt.% lime - metal sulphate systems using the four sulphates – calcium sulphate, magnesium sulphate, sodium sulphate and potassium sulphate, as well as on the kaolinite - lime - GGBS - gypsum system, while SEM was only done on the kaolinite - lime - GGBS - gypsum system with the lime progressively substituted with GGBS from 6wt.% to 0wt.%. XRD analysis on the kaolinite - lime - sulphate system was conducted on 26 samples at the R and D Centre of English China Clays (ECC) International, St Austell, Cornwall, England, using a Philips PW 1825 X-ray generator and CuKα radiation. 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. From the XRD analysis the relative amounts (%) of gypsum and ettringite present (if any) after 1 or 5 weeks of moist curing of samples containing the sulphates of $CaSO_4$, $MgSO_4$, Na_2SO_4 and K_2SO_4 were obtained (Table 8.3-1). The analysis also obtained the relative proportions of kaolinite, mica, quartz, feldspar, and other parent constituents remaining in the various samples at these curing periods. The XRD on the kaolinite - lime - metal sulphate systems did not, however, give any indications of other reactants and the extent to which these occurred cannot be ascertained from this analysis. However, an indication of those reactions occurring when gypsum was the added sulphate were obtained from a second programme of XRD analysis on the kaolinite - lime - GGBS - gypsum system (See Figures 8.3-1 - 8.3-4 (and Tables A8-1 to A8-5 in Appendix 8)).

The second programme of XRD work was on the kaolinite - lime - GGBS - gypsum system and was mainly performed in order to establish the influence of ground granulated blastfurnace slag (GGBS) either as additional to, or as a substitute for the lime present in the system. The underlying purpose of this work was to establish the reasons behind the observed lowering (and sometimes total elimination) of swelling by the presence of GGBS in the clay - lime - gypsum system with no adverse effects on strength. In order to achieve this, it was found necessary to monitor the occurrence of lime, gypsum and ettringite phases, when the GGBS progressively replaced the 6wt.% lime originally present in mixes with and without 6wt.% gypsum. Samples were cured up to a maximum of 4 weeks only. The X-ray equipment used was a PW1965 Phillips diffractometer, a PW1730 generator and a graphite monochromator and CuKα radiation of wavelength (λ) of 1.54179Å in the Department of Mechanical, Materials and Manufacturing Engineering, University of Newcastle. The 1 and 4 weeks of moist curing adopted for the work were selected to coincide with the curing periods used for the determination of the unconfined compression strength. Figures 8.3-1 to 8.3-4 (and Tables A8-1 to A8-5 in Appendix 8) show the XRD results from this analysis featuring progressively reducing lime (and increasing slag) both in the absence and in the presence of 6 wt.% gypsum. They show the 2θ angle, the calculated d-spacings and the compounds they represent.

The SEM work was carried out at the University of Glamorgan mainly for microstructural examination of the reacted kaolinite - lime - GGBS - gypsum mixtures. A Cambridge Instruments Stereoscan (Model S240) operating at a voltage of 25 kV was used. The examination was performed on specimens obtained from samples which were moist cured for 1 week and then vacuum dried before being given a coating of evaporated gold ≈ 10-20 mm thick. The key observations from SEM results are shown in Plate 1.

8.3.2 THE KAOLINITE-LIME-SLAG-GYPSUM SYSTEM

Figures 8.3-1 and 8.3-2 show the X-ray powder diffraction traces from compacted kaolinite-lime-slag cylinders moist cured at respectively 1 week and 4 weeks. The total stabiliser content is 6 wt.% and the relative amounts of slag and lime vary from 6% lime - 0% GGBS to 0% lime - 6% GGBS. There is no evidence of formation of any new crystalline phases at either one week or four weeks. All the peaks present can be attributed to kaolinite, lime and mica. Only the major kaolinite peaks or those not overlapping with other compounds are marked. The only phase which systematically changes in relative amount with change in mix composition is lime which as expected systematically decreases with increase in slag content and decrease in lime content when lime is progressively substituted with slag (i.e. in going from a) to e) in Figures 8.3-1 to 8.3-4). It is difficult to positively identify the presence of lime beyond 3L3S0G after 1 week and beyond 6L0S0G after 4 weeks. However the limit of resolution of the technique means that lime at concentrations below about 2% would not be detected on the diffraction traces. The results therefore indicate that after one week there has been very little reaction with the lime but at four weeks significant reaction has taken place although it was not possible to identify the products of this reaction.

Figures 8.3-3 and 8.3-4 show the X-ray powder diffraction traces from the compacted kaolinite - lime - GGBS - gypsum cylinders at respectively the same two curing times. After 1 week of moist curing both lime and gypsum are clearly visible. There is little evidence of any lime for compositions with initial lime contents below that of the composition 5L1S6G but gypsum is clearly visible for all compositions. The relative amount of gypsum does not appear to vary significantly with change in composition although the composition 0L6S6G does appear to contain slightly more gypsum than the other compositions. After 4 weeks of moist curing there is a very marked change, in that for the high lime low slag compositions gypsum disappears and diffraction peaks of ettringite appear. Ettringite is primarily indicated by a new and isolated sharp peak at 4 weeks of moist curing, identified at 5.644Å (Red peak in Figure 8.3-4 (a) at angle $2\theta=15.4^{o}$). For compositions 6L0S6G and 5L1S6G no gypsum is apparent and it then appears in increasing amounts as the lime continues to be replaced by slag (i.e. at mixes of composition 2L4S6G and 0L6S6G).

The SEM observations although unfortunately limited to only one week cured material do generally support and confirm the X-ray observations. The technique is also more sensitive than the X-ray technique and even after one week ettringite 'rods' are clearly visible both on the surface of, and protruding from, the kaolinite plates. The effect is identical to that previously reported by Wild et al (1993) in which EDAX analysis was employed to positively identify the rods as having a composition compatible with ettringite. The 'rods' are clearly visible on the kaolinite plates at compositions 6L0S6G and 5L1S6G (Plate 1 (a) and (b)) but became more difficult to observe at increased replacements of lime by slag (i.e. 2L4S6G and 1L5S6G; Plate 1 (c) and (d)). Also the SEM micrographs of 1 week moist cured specimens of composition 6L0S6G show the small ettringite crystals with bloated ends perhaps indicating the crystal growth being in process (See Plate 1 (a)). In addition for specimens with low lime high slag (Plate 1 (d)), there are apparent isolated pockets containing relatively large lath-like clustered crystals.

Although EDAX analysis was not available the X-ray observations would suggest that these are gypsum crystals rather than ettringite. The electron microscopy atlas showing techniques for small particle identification (by Walter C. Mcrone and John Gustav) describe gypsum crystals as similar in appearance to quartz and as sometimes elongated, adhering, rhomb-shaped monoclinic crystals, with clear cleavages which are due to numerous smaller adhering crystals. This description fits perfectly with the appearance of the crystals in Plate 1 (d). Coupled with the sharp XRD peaks of gypsum for closely identical mixes (XRD gypsum peaks in Figure 8.3-3 (d) and (e) for mixes 2L4S6G and 0L6S6G respectively), the evidence of the existence of gypsum is clear. These observations support the view that as slag replaces lime in moist cured gypsum containing kaolinite - lime - GGBS samples the quantity of ettringite forming on the surfaces of the kaolinite plates is considerably reduced and may be totally eliminated at high slag low lime compositions.

8.3.3 KAOLINITE - LIME - SULPHATE SYSTEM

Table 8.3-1 shows the residual products of hydration in the kaolinite - 6wt.% lime - sulphate system for various additions of the sulphates of calcium, magnesium sodium and potassium. Residual primary gypsum was detected at 1 and 5 weeks of moist curing when gypsum was added. When $MgSO_4$ was added secondary gypsum was produced by reaction with $Ca(OH)_2$ which was also detected at 1 and 5 weeks. In both cases the amount of gypsum detected tended to increase with increase in sulphate content and at lower sulphate levels no gypsum was detected at all. However ettringite was detected at all compositions and the level remained approximately constant. Thus gypsum is only detected when it is in excess and has not been fully consumed in ettringite formation. The level of gypsum detected was, surprisingly, not much greater for calcium sulphate additions where the gypsum is a major reaction component (i.e. primary gypsum) whereas for magnesium sulphate additions gypsum had been produced by reaction with lime (i.e. secondary gypsum) and the amount formed depends on the kinetics of that reaction and the availability of lime.

The fact that the level of ettringite detected did not increase with sulphate level suggests that for the levels of sulphate chosen the amount of ettringite formed is determined by other factors which include the reaction kinetics and the availability of aluminium rather than availability of sulphate. The levels of ettringite observed were in the range from 1 - 2 and (See Table 8.3-1). Surprisingly, gypsum and magnesium sulphate recorded similar levels of ettringite formation (Table 8.3-1). In addition, the highest recorded ettringite level (2%) was from $MgSO_4$.

After 5 weeks of moist curing the amount of ettringite detected does not show any systematic increase when magnesium sulphate is present and the same level of gypsum (2%) is detected at the highest (3.72%) SO_3 content. This suggests that ettringite formation is near to completion after 1 week. Unfortunately data were not obtained for $CaSO_4$ containing samples using this system. However comparison of Figures 8.3-3 (a) and 8.3-4 (a) using the less sensitive conventional X-ray diffraction system does confirm that between 1 and 4 weeks gypsum continues to be consumed and the amount of ettringite formed increases significantly.

For both sodium sulphate and potassium sulphate additions in general, the amount of ettringite detected is just within the detection level of the system and is not quantifiable (in the range < 0.1 - 1 %). Thus very little ettringite is formed in these two systems at either curing period. Thus in these two systems most of the sulphate added is neither "fixed" as ettringite or as gypsum and must remain in the pore solution or be taken up in other reaction products. However, for both 1 and 5 weeks of moist curing, Na_2SO_4 recorded (< 0.1 - 1%) marginally higher levels of ettringite than K_2SO_4 (< 0.5 % in all cases). On comparing the one week data, the relative levels of ettringite detected reflect the relative magnitudes of expansion of soaked specimens containing these sulphates i.e.

$$\mathbf{CaSO_4 \approx MgSO_4 >> Na_2SO_4 > K_2SO_4}$$

8.3.4 SUMMARY

1. High levels of $MgSO_4$ resulted in high amounts of secondary gypsum
2. At short curing periods (1 week) gypsum and magnesium sulphate produced similar amounts of residual gypsum.
3. In the kaolinite - lime - metal sulphate system, sodium and potassium sulphates produced no gypsum and only traces of ettringite at 1 and 5 weeks.
4. The amounts of residual kaolinite detected ranged from 83 - 93% for 1 and 5 weeks of moist curing. As the pure kaolinite was specified as containing ≈84% kaolinite suggesting that only a tiny fraction of the clay is consumed even after 5 weeks of moist curing.
5. Lime was consumed faster in the presence of both GGBS and gypsum than in the absence of either of them.

6. Results suggest increased lime consumption by the inclusion of gypsum with close to simultaneous disappearance of lime and gypsum at 4 weeks of moist curing (compare Figures 8.3-3 (a) with Figure 8.3-4 (a)). This would seem to suggest that for the kaolinite - 6wt.% lime - 6wt.% gypsum system, neither lime nor gypsum is in excess. From Table 8.3-1 gypsum is however likely to be in excess at 1 week of moist curing, when it is added to this system in levels in excess of 1.86 % SO_3.
7. The persistence of gypsum peaks as lime is progressively substituted with GGBS suggest that it is likely that lime deficiency (and hence reduced pH) is the likely cause for lack of ettringite formation and not deficiency in gypsum. This would explain, at least partly, the massive reduction in linear expansion by the addition of GGBS in the kaolinite - lime - gypsum system. It is known that under conditions of reduced pH (which will probably develop at low lime concentrations) ettringite crystals are larger than at high concentrations (Mehta (1983), and other researchers) and that these large crystals do not cause expansion.
8. The SEM analysis at 1L5S6G show crystallisation of residual gypsum in large lath-like crystals when there is little or no lime (i.e. when high or only GGBS is present).

This chapter and the previous one have reported in detail all the results obtained in the investigations. The next two chapters will respectively discuss these results, and then draw conclusions and recommendations.

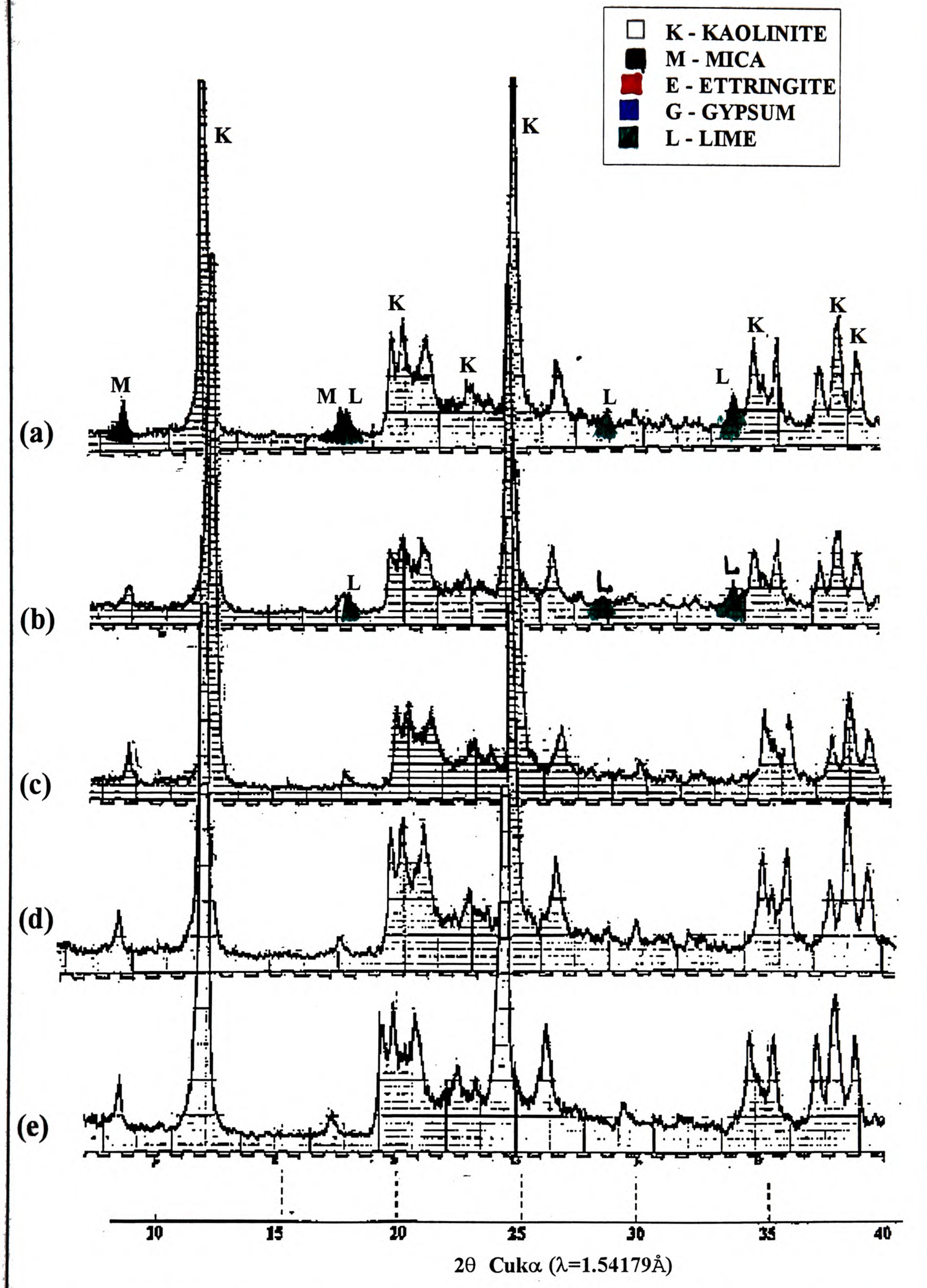


Figure 8.3-1 XRD traces of 1 week moist cured kaolinite-lime-ggbs specimens with lime progressively substituted with slag i.e. (a) 6L0S0G (b) 5L1S0G (c) 3L3S0G (d) 2L4S0G & (e) 0L6S0G.

Note: *1. Only peaks due to individual compounds are marked in Figure 8.3-1(a).*

2. Only peaks due to ettringite, lime and gypsum are marked beyond Figure 8.3-1(a).

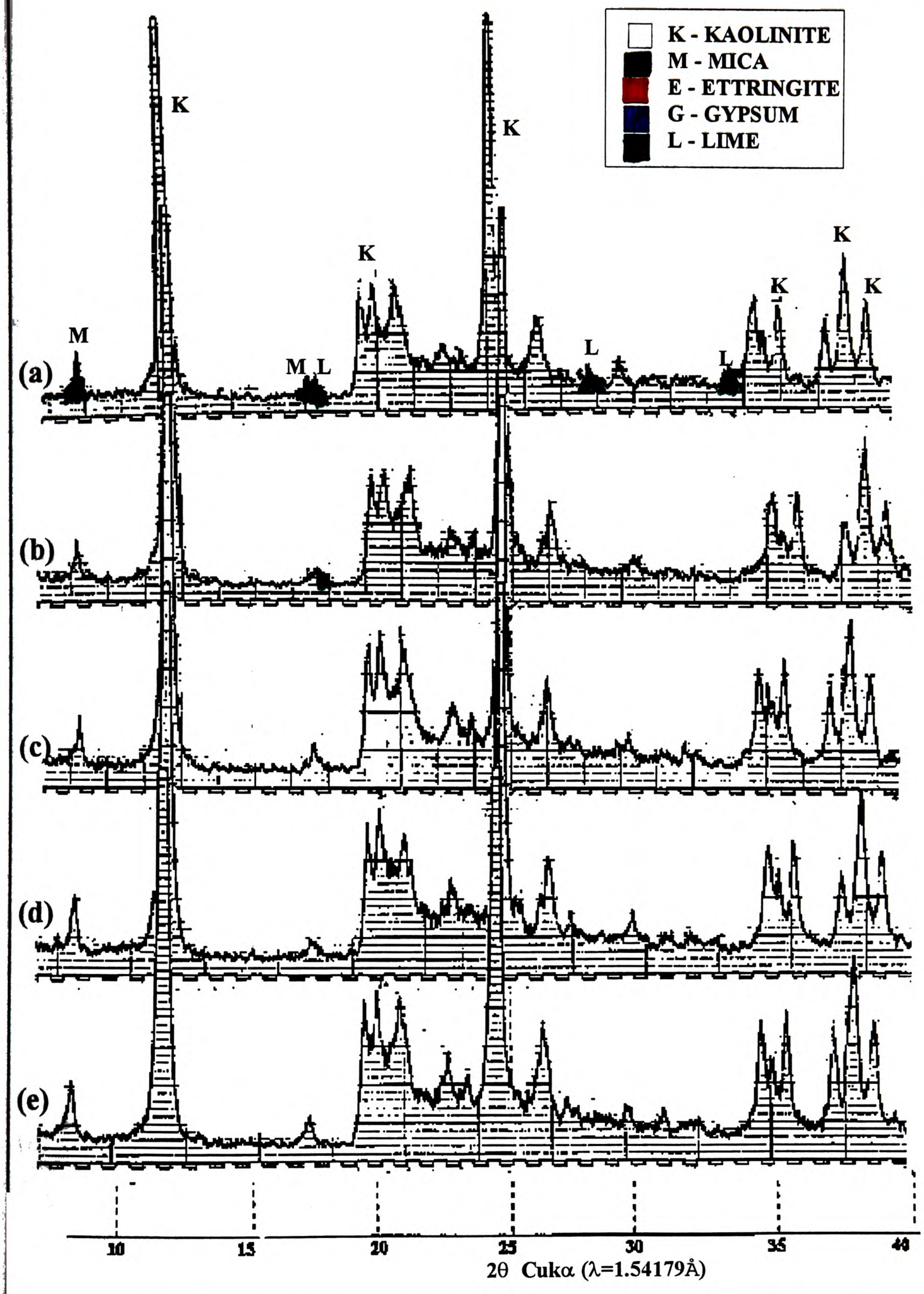


Figure 8.3-2 XRD traces of 4 weeks moist cured kaolinite-lime-ggbs specimens with lime progressively substituted with slag i.e. (a) 6L0S0G (b) 5L1S0G (c) 3L3S0G (d) 2L4S0G & (e) 0L6S0G.

Note: *1. Only peaks due to individual compounds are marked in Figure 8.3-2(a).*

2. Only peaks due to ettringite, lime and gypsum are marked beyond Figure 8.3-2(a).

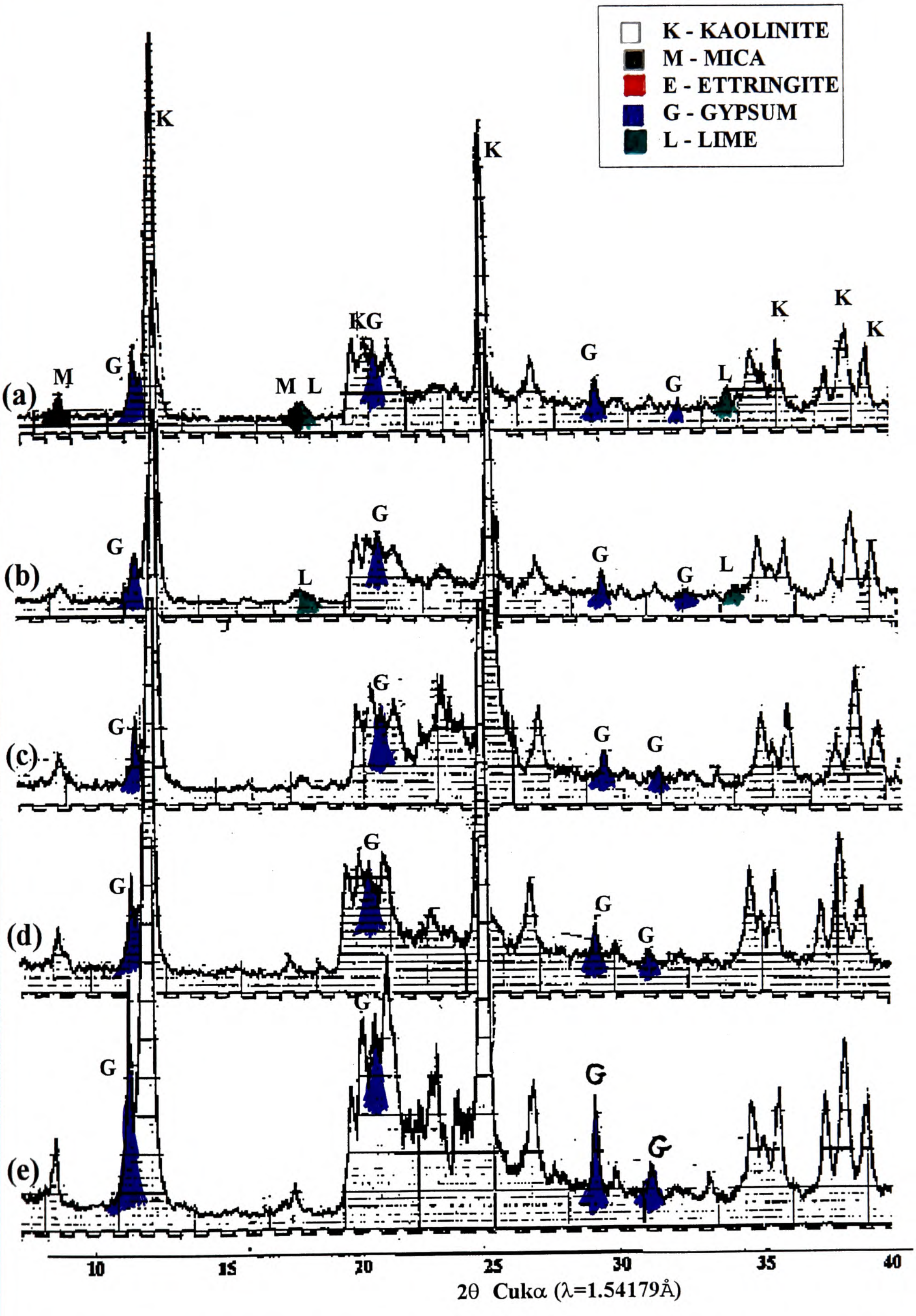


Figure 8.3-3 XRD traces of 1 week moist cured kaolinite-lime-ggbs specimens with lime progressively substituted with slag i.e. (a) 6L0S6G (b) 5L1S6G (c) 3L3S6G (d) 2L4S6G & (e) 0L6S6G.

Note: *1. Only peaks due to individual compounds are marked in Figure 8.3-3(a).*

2. Only peaks due to ettringite, lime and gypsum are marked beyond Figure 8.3-3(a).

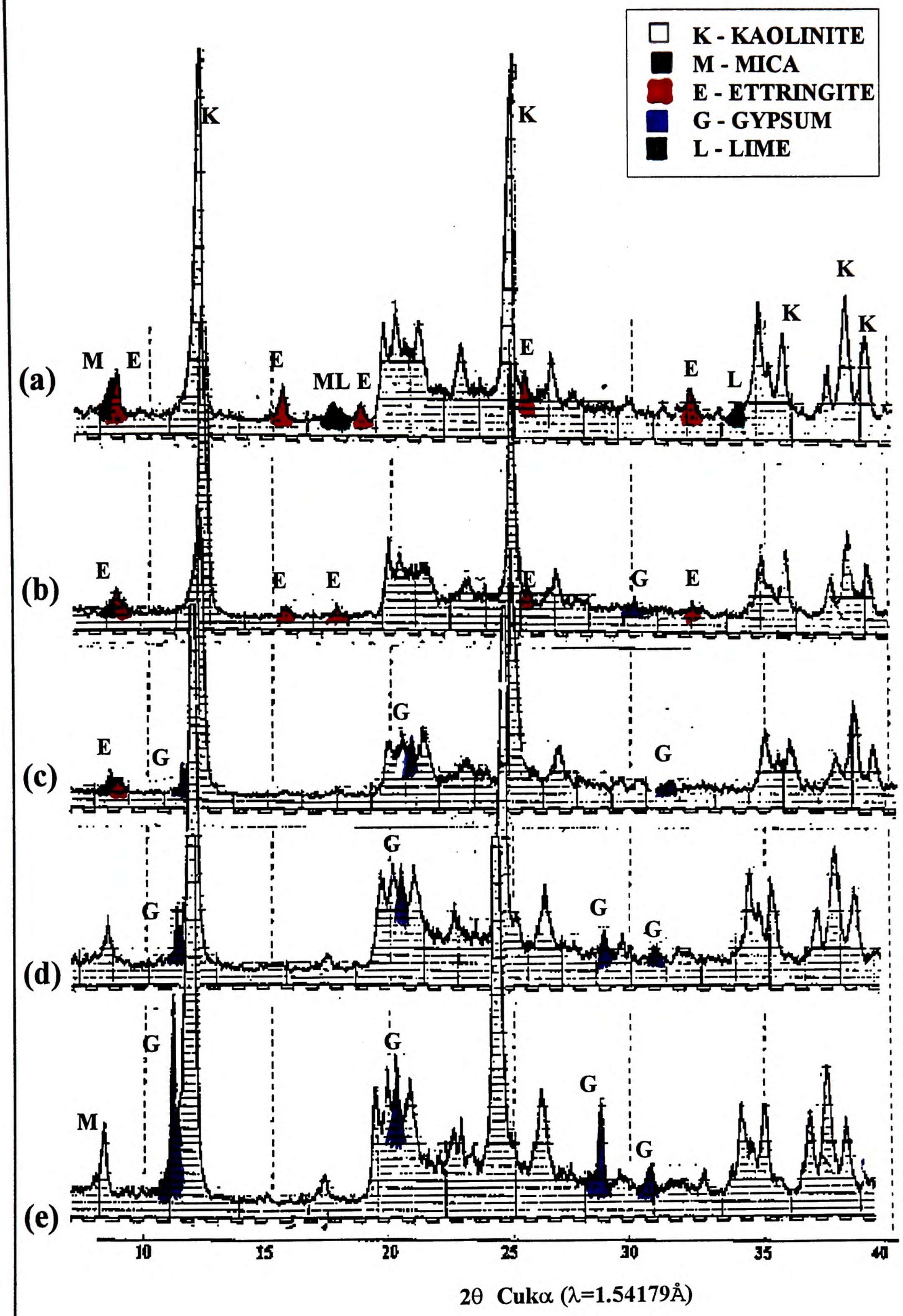


Figure 8.3-4 XRD traces of 4 weeks moist cured kaolinite-lime-ggbs specimens with lime progressively substituted with slag i.e. (a) 6L0S6G (b) 5L1S6G (c) 3L3S6G (d) 2L4S6G & (e) 0L6S6G.

Note: *1. Only peaks due to individual compounds are marked in Figure 8.3-4(a).*

2. Only peaks due to ettringite, lime and gypsum are marked beyond Figure 8.3-4(a).

Sulphate Type	SO_3 Content	Curing Period (Weeks)	Ettringite (%)	Gypsum (%)	Kaolinite (%)	Mica (%)	Quartz (%)	Feldspar (%)	Tourmaline (%)	Albite (%)
Control (Kaolinite + 6wt% Lime)	0	1	-	-	91.0	8.0	< 0.5	1.0	0.0	0.0
	0	5	-	-	90.0	8.0	< 0.5	2.0	0.0	0.0
$CaSO_4$	0.93	1	1	< 0.5	89.0	7.0	< 0.5	2.0	0.0	0.0
	1.86		1	-	90.0	7.0	< 05	2.0	0.0	0.0
	2.79		1	4	87.0	6.0	< 05	2.0	0.0	0.0
	3.72		1	9	83.0	5.0	< 0.5	2.0	0.0	0.0
$MgSO_4$	0.93	1	1	-	90.0	5.0	1.0	3.0	0.0	0.0
	1.86		1	-	92.0	6.0	< 0.5	< 0.5	0.0	0.0
	2.79		1	1	93.0	4.0	< 0.5	1.0	0.0	0.0
	3.72		1	2	89.0	6.0	1.0	1.0	0.0	0.0
	0.93	5	< 0.5	-	91.0	6.0	< 0.5	2.0	0.0	0.0
	1.86		2	-	90.0	6.0	< 0.5	2.0	0.0	0.0
	2.79		1	-	89.0	7.0	1.0	2.0	0.0	0.0
	3.72		1	2	91.0	5.0	1.0	< 0.5	0.0	0.0
Na_2SO_4	0.93	1	1	-	91.0	6.0	1.0	1.0	0.0	0.0
	1.86		-	-	87.0	11.0	1.0	1.0	0.0	0.0
	2.79		< 0.1	-	91.0	8.0	< 0.5	1.0	0.0	0.0
	3.72		< 0.5	-	89.0	8.0	< 0.5	2.0	0.0	0.0
	1.86	5	< 0.5	-	87.0	11.0	< 0.5	1.0	0.0	0.0
	2.79		1	-	92.0	6.0	< 0.5	1.0	0.0	0.0
K_2SO_4	0.93	1	< 0.1	-	92.0	6.0	< 0.5	2.0	0.0	0.0
	1.86		< 0.1	-	92.0	6.0	< 05	2.0	0.0	0.0
	2.79		< 0.1	-	89.0	9.0	< 05	2.0	0.0	0.0
	3.72		< 0.5	-	89.0	8.0	< 0.5	2.0	0.0	0.0
	0.93	5	-	-	91.0	7.0	< 0.5	2.0	0.0	0.0
	1.86		< 0.5	-	91.0	7.0	< 0.5	1.0	0.0	0.0

Table 8.3-1 XRD analysis results for the kaolinite-6wt.%lime-sulphate system using specimens containing varying amounts of various sulphates moist cured for 1 week and 5 weeks at 30°C and 100% relative humidity.

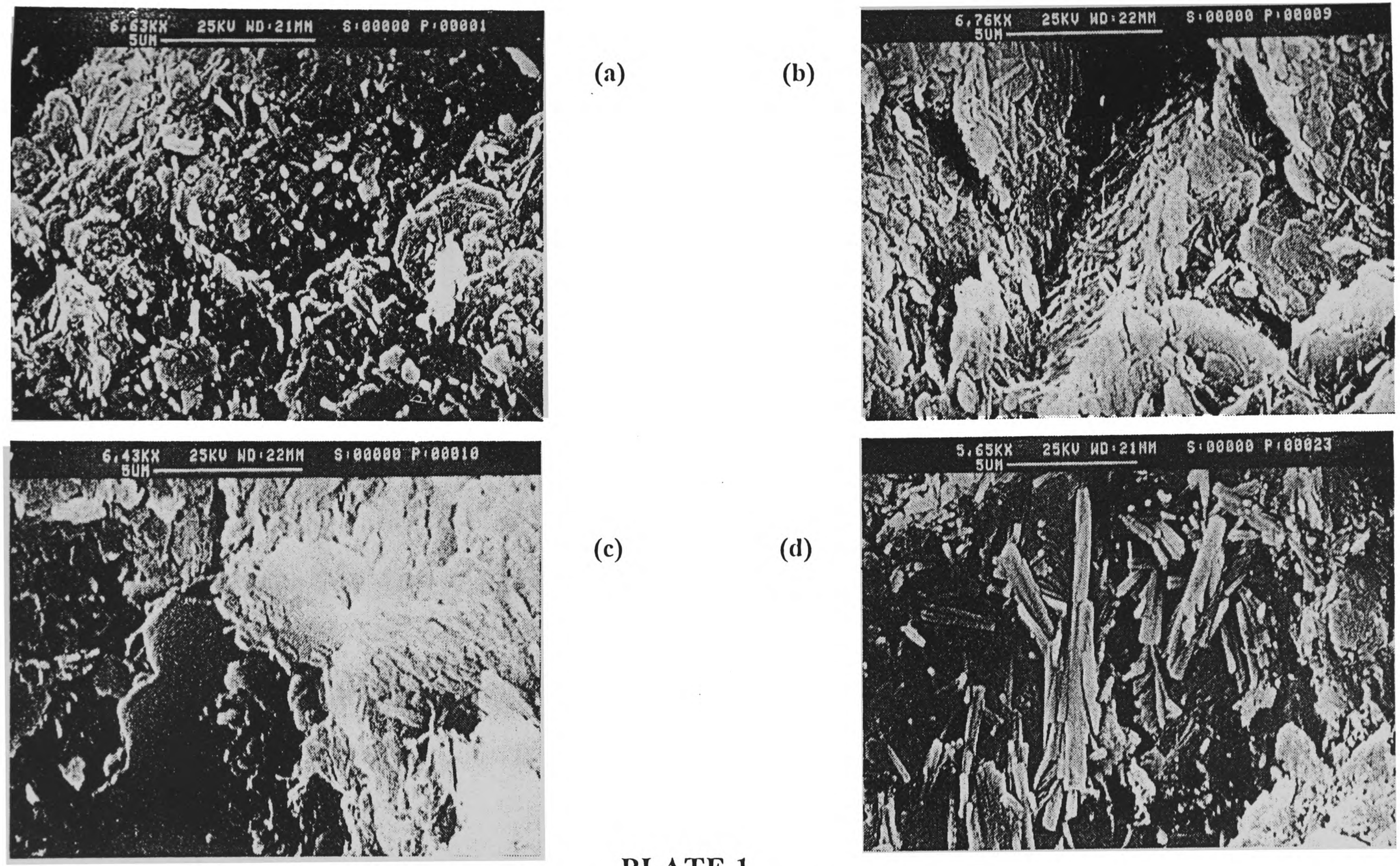


PLATE 1

SEM Micrographs of kaolinite-lime-ggbs-gypsum specimens moist cured for 1 week at 30°C and 100% relative humidity. ((a) 6L0S6G; (b) 5L1S6G; (c) 2L4S6G & (d) 1L5S6G)

CHAPTER 9 - DISCUSSION

9.1 INTRODUCTION

The properties of lime stabilised soil may be viewed in terms of short-term properties that emanate from the immediate material changes that occur (within a few hours) during the stabilisation process, and in terms of long-term material properties that take a relatively longer period to occur ranging from a few hours to several years. In both cases, it would appear from the preceding investigations that, 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. Other factors include the type and amount of lime, compaction moisture content, time of mellowing before compaction and the curing period in general.

For an effective discussion of these properties, the short-term and long-term material properties will be discussed separately. The short-term properties will very much be determined by, and will be discussed under, the cationic exchange process. This process has been discussed in much more detail in Chapters 2 and 3. In this chapter, only its effects on material properties for the specific materials under study - kaolinite and Kimmeridge Clay need be discussed. The short-term effects will mainly consist of effects on the Atterberg limits and on the British Standard (BS) Proctor compaction. The long-term effects, which will in general be discussed under pozzolanic activity, will include effects on the pozzolanic reactions that influence strength and dimensional stability as a result of the swelling pressure generated both during moist curing and during soaking.

9.2 EFFECTS OF BASE (CATION) EXCHANGE ON THE ATTERBERG LIMITS AND COMPACTION PROPERTIES OF LIME STABILISED CLAY SOILS

Due to the positive charges that cations possess, cation concentrations in the pore solution lead to neutralisation of the clay particle negative charges, and compression of the electric diffuse double layer surrounding them. For kaolinite, 3-6wt.% of lime was found to be the optimum lime content for this neutralisation to take place (see Figures 7.1-1 and 7.1-2). Similar observations by other researchers using kaolinite are in agreement (Abdi, 1992; Silvapullaiah, 1987). This is the lime content at which the cation exchange process produces maximum flocculation beyond which further addition of lime has no major consequences. The clay particles are therefore said to be "fixed" by this lime content.

The neutralisation of the clay particle negative charges allows closer approach of the clay particles leading to flocculation and agglomeration of the flocculated particles. In this agglomerated state there is increased pore volume which lowers the maximum dry density (MDD). It also accommodates more water during compaction, raising the optimum moisture content (OMC). The liquid limit (LL) and the plasticity limit (PL) on the other hand are also affected during the cationic exchange process. At the LL, (by definition) the shear stress of the material is reduced to zero. Since the material at LL is fully saturated, the flocculated structure has already collapsed and has no effect on the LL. Thus, it is proposed that the difference between the effects of cationic exchange on Proctor compaction and on the Atterberg limits is, that particularly for LL, the effects are not due to the macro effects (flocculation and agglomeration) but rather due to micro effects. In the latter, molecular water layers are attracted on to the clay particle surfaces reducing the particle-particle friction to zero. In contrast, the changes in PL occur at the plastic-solid phase shear stress region where the material is at a considerably lower moisture content (than for LL) and the changes are as a result of combined macro and micro effects.

With high cation concentrations (as at high lime contents), the positive charge on or near the clay particle surfaces may be in excess and may lead to renewed repulsive forces. This change in inter-particle forces, from a decrease to an increase in net repulsion, imparts a corresponding change in the rate and magnitude of flocculation and agglomeration and partly explains the turning points or changes observed in the trends of the LL, PL, MDD and OMC [at ≈6wt.% lime content for kaolinite - lime (Figures 7.1-2, 7.1-3 and 7.2-1(a) and (b)), and at ≈ 4wt.% for Kimmeridge Clay - lime (Figures 7.1-3 and 7.2-2 (a) and (b))]. However, the renewed charges on the electric double layer are of minor consequences compared to the overall increase in OMC and decrease in MDD and overall changes in the Atterberg limits. Research on kaolinite in general indicates that the addition of small amounts of lime to kaolinite produces a marked increase in the plastic limit. The liquid limit may increase or decrease but in such a way that there is a general decrease in the plasticity index with increasing lime content. The current work is in agreement. For the case of Kimmeridge Clay, less research work has been conducted. However, findings from the current work are in agreement with previous unpublished work on Kimmeridge Clay, conducted for Buxton Lime industries by Littleton and Willavise (1992).

9.2.1 EFFECTS OF SULPHATES

Most of the effects of the different sulphates on the Atterberg limits and on the compaction properties of lime-stabilised clay may be explained by the cation exchange theory. In general from the lyotropic (or Hofmeister) series ($Li^+ < Na^+ < K^+ < Mg^{2+} < Ca^{2+} < B^{2+} < Al^{3+} < H^+$), sodium and potassium ions are less readily absorbed on to the clay particle surfaces than calcium and magnesium ions unless they are present in very high concentrations. However when monovalent sulphates are added to lime - kaolinite mixes there will be a tendency for calcium to be removed from the kaolinite - lime mix to form the sparingly soluble gypsum.

$$\mathbf{(Clay\text{--}OH)_2{}^{-}\text{-----}Ca^{2+} + Na_2SO_4 \longrightarrow 2((Clay\ OH^-)\text{--}Na^+) + CaSO_4 \downarrow}$$

The monovalent cations such as potassium and sodium are large and highly hydrolysed and many more of those cations can then be attracted to the clay surface. Thus the hydro-sphere of the clay particles, with sodium or potassium as the counter ions, becomes very large (see Figure 3.2-1 in Chapter 3). The consequent repulsion between particles (though slightly reduced by the cations) and the large hydro-sphere give maximum particle separation and deflocculation. In their study on the rheology of sodium and potassium illite suspensions in relation to colloidal stability, Hesterberg and Page (1993) observed greater inter-particle bonding in K-illite than Na-illite for the same pH level. From these results, one can hypothesise that K^+ ions are more effective than Na^+ ones in preventing deflocculation, with K^+ ions resulting in stronger and bigger floccs than Na^+ ions. This is confirmed by observations in the current work where potassium sulphate lowered the

MDD and raised the OMC by a bigger magnitude as compared to sodium sulphate (Figure 7.2-3 (a) and (b)). The divalent cations have a higher positive charge and a smaller hydro-sphere. Therefore, they tend to reduce particle separation by flocculation and agglomeration, further lowering the MDD and further raising the OMC of lime-stabilised clay soil.

Due to their large hydro-sphere, the monovalent cations lower the LL more than the divalent ones. The changes in PL, being as a result of both macro and micro effects, depend on the dominating factor among;

1) the degree of particle-particle lubrication by the hydro-sphere and
2) whether flocculation and agglomeration or defflocculation dominates.

If a flocculated and agglomerated structure prevails, the PL is increased due to the increase in pore volume while a high degree of particle-particle lubrication and a deflocculated structure in general leads to decreased PL (see Figure 7.1-5 (b)).

In the current work, where the liquid limit decreased with increasing sulphate content for all sulphate types, the reduction in liquid limit became greater in the cation order:

$$\mathbf{Ca^{2+} < Mg^{2+} < K^{+} < Na^{+}.}$$

Thus, the sulphate containing the cation to the right, which has a larger hydro-sphere than the one to its left and which is likely to result in a less flocculated structure and in lesser moisture intake, depressed the liquid limit by a bigger magnitude (see Figure 7.1-5 (a)). However, as in the case of lime addition, continuing to increase the concentration of the cations leads to a compression of the double layer, leading to increased flocculation. This explains the smaller reduction in liquid limit and plastic limit with increase in SO_3 content, especially by the monovalent cations (Na^+ and K^+) which are comparatively more hydrated than Ca^{2+} and Mg^{2+} cations. Thus with increasing SO_3 content, the increase in thickness of the double layer is enough to first cause dispersion and deflocculation, leading to massive reduction in floccs and hence to a reduction in voids, but subsequently leading to compression of the double layer and a lower degree of dispersion and deflocculation. This explains the reduction in the rate of decrease in liquid and plastic limits at SO_3 contents above 0.93wt.% especially for the sulphates of Na and K (see Figure 7.1-5(a) and (b)). These effects are further increased by the fact that the number of cations which can be attracted to the adsorbing surface is higher for Na^+ and K^+ cations (because of their lower charge) as compared to Ca^{2+} and Mg^{2+} cations. These differences in cations, also explain the reported changes in MDD and OMC, the more hydrated monovalent cations resulting in deflocculation, increased MDD and decreased OMC. Thus, the lowering in MDD from the control mix was least for the monovalent cations and highest for the divalent cations, viz: $Mg^{2+} > Ca^{2+} > K^+ > Na^+$, where the cation to the left lowered the MDD more than 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 (Figure 7.2-3 (a) and (b)).

Further short-term material changes occur when sulphates are present in clay-lime systems due to the formation of ettringite. Wild *et al.*, (1993) have shown from thermogravimetric work that ettringite ($C_3A.3C\overline{S}.H_{32}$) forms very rapidly in hydrated kaolinite-lime-gypsum mixes and is even present immediately after mixing. The ettringite forms and nucleates on the surfaces of the kaolinite particles, and this surface layer of reaction products imbibes water and swells. Ettringite like gypsum is a fairly insoluble product. Its formation leads to a further increase in porosity, by forcing the clay particles apart, and to a decrease in moisture content due to the chemical consumption of water during its precipitation and subsequent growth. These effects further affect the Atterberg limits, the MDD and the OMC. The effects of sulphates on the LL are similar to those of excess lime (beyond the lime fixation limit) whereby the LL and PI are further reduced (see Figures 7.1-3 to 7.1-5). The PL may increase or decrease depending on the type of sulphate, the sulphates containing divalent cations raising it while those containing monovalent ones lowering it.

The role of ettringite in the changes in both Atterberg limits and compaction parameters of MDD and OMC is undoubted. A minimum in MDD for Kimmeridge Clay - lime mixes, corresponding to a maximum in OMC, occurs at about 4wt.% lime content (See Figure 7.2-2). For this level of lime (4 wt.% $Ca(OH)_2$) to fully react to form ettringite, the ettringite composition would require 4.33% of sulphate as SO_3 (see Appendix 1). However around 2% of the lime will be involved in immediate cation exchange and modification, leaving the remainder (2%) which theoretically would require 2.16% SO_3 to combine with the aluminium (which is released) and the sulphate in the Kimmeridge Clay (1.73% SO_3). There is no doubt from previous observations by Wild *et al.*, (1993) that ettringite formation will begin to occur shortly after the Kimmeridge Clay is mixed with the other components and that formation will be most rapid at the ideal composition indicated above. It is therefore proposed that the compaction behaviour of the Kimmeridge Clay with increase in lime content derives from the sulphate content of the clay and is a result of maximum ettringite formation at a critical lime content.

9.2.2 EFFECTS OF SUBSTITUTION OF LIME WITH GGBS

The introduction of GGBS produces an additional complicating factor to the material's short-term (Atterberg limits and compaction) properties in that in the presence of lime the GGBS will begin to hydrate and take up water (and also some lime). The hydration of GGBS however takes a long time (relative to other short-term effects) and although it consumes water and lime, it is unlikely have a profound effect on the short-term material behaviour especially for unmellowed material. Only minor quantities of lime are essential for the flocculation process to take place, which explains why lime substitution by GGBS can reach high slag/lime ratios while still maintaining high flocculation. Flocculation is therefore only gradually reduced leading to a similarly gradual decrease in liquid limit and plastic limit, and a gradual increase in plasticity index (see Figures 7.1-6). If sulphates are present, the slag will also be involved in reaction with sulphates and will influence ettringite formation. By substituting lime with GGBS, less ettringite is formed (see Figure 8.3-4(a) - (e)) not only due to the physical reduction in lime but also by the chemical consumption of lime during GGBS hydration (Daimon, 1980; Regould, 1980).

Without mellowing, the level of ettringite crystallisation is not adequate to cause significant changes either on the micro or on the macro properties of the material. Thus, the effects of substitution of lime with GGBS in the presence of gypsum are not much different from those in the absence of gypsum (Figure 7.1-6 and 7.1-7). On mellowing, the presence of significant amount of ettringite, albeit gradually reducing as lime is substituted with GGBS, results in increased water demand thus lowering the water film on the clay particles. Slag hydration also consumes water and lack of water on the clay particle surfaces increases the shear strength of the soil. To reduce this shear strength to zero (i.e. at liquid limit), more water is therefore needed. Thus, in the current work where gypsum was used, there is a small rise in the LL of lime-stabilised kaolinite and the gradual substitution of lime with GGBS, despite gradually reducing the amount of ettringite formed also leads to a gradual increase in LL. Formation of ettringite also results in increased porosity of the uncompacted material as ettringite crystals keep the clay particles apart resulting in a more open structure. The formation of ettringite, coupled with increased water consumption due to slag hydration, not only increases the rate at which the LL increases but also reverses the decline in PL to a significant increase. Thus, mellowing is probably of significant effect only in the presence of sulphates, when the formation of ettringite is likely to influence the short-term property changes of the lime-stabilised material. The initial maintenance of flocculation with and without the presence of gypsum, as lime is substituted with GGBS, results in a situation where substitution of lime by GGBS does not have a significant effect on the compaction properties (see Figure 7.2-4 (a) and (b)). Only when the replacement of lime approaches a slag : lime ratio of approximately 5:1 for kaolinite and approximately 1:1 for Kimmeridge Clay are significant changes experienced. Since effectively the overall lime content is decreasing, one might therefore expect the MDD to increase and the OMC to decrease. There is in fact some decrease in OMC for Kimmeridge Clay but no equivalent increase in MDD (see Figures 7.2-5 (a) and (b)). This suggests that as lime is substituted with GGBS the effects of added gypsum on the OMC and hence on the cationic exchange of clay-lime-GGBS mixes are different from those of naturally occurring (and bound) gypsum. Added gypsum apparently raises the OMC while in the naturally occurring case (for Kimmeridge Clay), it is decreased. The behaviour in the case of Kimmeridge Clay as lime is progressively substituted with GGBS is therefore more characteristic than for kaolinite with added gypsum.

Other factors, apart from cationic exchange and ettringite formation, are also involved. For example, the effects of lime, GGBS and sulphates addition on the MDD may, in addition, be explained by a material replacement theory. Replacement of clay with lime may cause a reduction in maximum dry density despite the increased workability. This may be due to the fact that clay has a higher density than lime (See Table 3.3-1 in Chapter 3). Similar views have been made by Abdi (1992), in his work on the effects of gypsum on lime stabilised kaolinite. GGBS has a higher relative density than either lime, kaolinite or Kimmeridge Clay. Therefore, replacement of lime by GGBS would not, in theory, lower the MDD of either lime stabilised kaolinite or lime stabilised Kimmeridge Clay. If anything, the replacement should raise it. This would be in line with the generally sustained MDD observed as lime is replaced by GGBS. However the quantities of materials involved (lime, GGBS and gypsum) are very small compared to the bulk material (clay + additives) and the physical replacement of lime with GGBS will not in itself result in any significant variation in density either in the presence or in the absence of gypsum. Therefore, the reduced cation exchange due to either physical reduction of lime or its consumption by GGBS is bound to be of more significance. It is therefore not possible without very much more detailed analytical work to explain the manner in which lime replacement by GGBS influences the MDD and OMC in a fundamental way. It is however reassuring from a practical point of view that the current observations suggest that partial replacement of lime by GGBS should not result in major changes in compaction characteristics.

9.3 POZZOLANIC ACTIVITY

9.3.1 PHASE DEVELOPMENT, MICROSTRUCTURE AND STRENGTH

From the overall research work done on pozzolanic activity, the type and form of the reaction products determine the physical, chemical and mechanical properties of the bulk material. Thus, the nature of the long-term cementation in lime-stabilised clay soil will, depending on the curing time, determine among other things the strength of the mix. This will in turn depend initially on the nature of the immediate cation exchange reaction which occurs, while the much slower pozzolanic reactions will affect the long-term maximum strength. On prolonged curing, the pozzolanic reactions eventually slow down or even cease altogether depending on the curing environment. Besides soil type, lime type and content and temperature, other variables in the curing conditions include the pH value of the soil which changes during curing (Ingles and Metcalf, 1972; Bell and Coutharld, 1990; Waswa *et al.*, 1993). Figures 7.3-1 (a) suggests that these pozzolanic reactions can (for the case of gypsum addition), take considerable time even beyond the 20 weeks tested in the current work. Figures 7.3-2(a) - 7.3-4(a) indicate that most samples containing sulphates of magnesium or any of the monovalent cations, ceased to show further significant strength increase after 2 - 6 weeks of curing, showing that the strength enhancing reactions can also cease and deterioration may even occur.

In clay - lime systems in general, the cementing agent is calcium silicate hydrate (C-S-H) gel. The pore solution of these systems contain silicate and aluminate ion species which are produced by the dissolution of clay particles in the highly alkaline environment provided by the dissolved lime ($Ca(OH)_2$). Microstructural evidence of identical gels in Portland cement - GGBS blends suggests that the gel forms on the surface of the solid particles (Richardson *et al.*, 1994). Since kaolinite is high in alumina, the gel also contains alumina. In addition, crystalline calcium-aluminate hydrate (C-A-H) phases (such as C_3AH_6 and C_4AH_{13}) and calcium-aluminate silicate hydrates (C-A-S-H) (such as C_2ASH_8) are formed, and less of C-S-H, as observed by Croft (1964) in kaolinite - lime systems. In the absence of excess alumina, only C-S-H phases would normally form, as in the case of PFA-lime (Wild *et al.*, 1990).

When, in addition to Al^{3+} and Ca^{2+} cations, other cations such as Mg^{2+}, Na^+ or K^+ are introduced, the nature of the ensuing reactions is determined by the cation exchange process that is in turn determined by the lyotropic (or Hofmeister) series ($Li^+ < Na^+ < K^+ < Mg^{2+} < Ca^{2+} < B^{2+} < Al^{3+} < H^+$). Thus, the gel is likely to either :-

1. absorb some of these cations forming (especially at high cation concentrations) either substituent intermediate hydrates of the form C-X-S-H and/or admixed intermediate hydrates of the form C-'X'-S-H where X is the 'new' substituent (i.e. well or structurally bound) cation and 'X' its loosely bound (or admixed) version (Lees *et al.*, 1983; Taylor; 1993; Li *et al.*, 1996) and/or
2. decalcify either through direct replacement of Ca^{2+} in the C-S-H gel by X or through further reactions of the intermediate (C-X-S-H and/or C-'X'-S-H) hydrates to form silicates of the new cations (X-S-H). The decalcification is usually accompanied by the precipitation of a calcium salt, usually gypsum ($CaSO_4.2H_2O$) or calcite ($CaCO_3$) (Heller and Ben Yair, 1964; Taylor, 1993).

In the current work after 1 week of moist curing of kaolinite - lime mixes, only XRD peaks due to kaolinite and lime are apparent, which indicates that either little reaction has occurred, the XRD equipment was not sensitive enough to identify them and/or the products of reaction are amorphous. The latter is undoubtedly the case because cementation does occur and the C-A-S-H gel formed due to reaction of lime with kaolinite is not crystalline (Croft, 1964; Sloane, 1965; Wild *et al.,* 1993 and 1996). The crystalline products of the reaction which have been reported develop, if at all, at a very slow rate (Croft, 1964; McCallister and Petry, 1992).

For each of the soil types studied (kaolinite and Kimmeridge Clay), the factors that determine the strength of lime stabilised mixtures (see Chapter 3) were kept constant for all the samples tested. Therefore, the observed changes in strength, were attributable only to the nature and speed of the cation exchange process, the subsequent flocculation-agglomeration/deflocculation processes and to the long term pozzolanic reactions that take place during curing. Thus the reactions involved and subsequent material changes would very much depend on sulphate type and concentrations involved. The effects on strength due to the presence of the various sulphates of Ca, Mg, Na and K will be discussed for each sulphate type in turn. The discussion also includes the effects of substitution of lime with GGBS.

9.3.1.1 Effects of gypsum on strength

Early strength development in clay-lime mixtures in the presence of gypsum has been confirmed by many researchers. In the current work and especially at early curing periods of 1 - 3 weeks, it was noted that the rate of strength development was generally faster when gypsum was present (Figures 7.3-1 (a)). At high sulphate concentrations (2.79 and 3.72 % SO_3), the strength development in the first six weeks displayed a pattern of varying (alternately accelerated and retarded) rates of strength development (see dotted lines in Figure 7.3-1 (a)). Similar observations have been made by other researchers such as Wild *et al.*, (1990B), while working on the influence of gypsum content on microstructural development, strength and expansion of cured PFA+ 20wt.%lime mixtures with various additions of gypsum, and Lambe *et al.*, (1960), working on the improvement of soil with alkali metal compounds. In the case of Wild (1990), higher curing temperatures were employed (90°C instead of 30°C in the current work) and activation and retardation of the pozzolanic reactions took place at much closer intervals, of the order of hours, and over much shorter curing periods i.e. from 0 - 12 hours. The alternating acceleration and retardation in the rate of strength development is thought to be due to the alternate activation and retardation of the pozzolanic reactions during early curing, especially when high SO_3 contents are used. In the PFA-lime system, Wild *et al.*, (1990) attributed the alternate acceleration and retardation in the rate of strength development to the development and subsequent rupture of colloidal coatings around the PFA particles. In the current work, it is also likely that similar coatings are developed on the clay particle surfaces. From Figure 7.3-1 (b), the optimal SO_3 concentration for maximum strength development appears to depend on the curing period (see dotted line in Figure 7.3-1 (b)). Obviously at prolonged curing more sulphate will be consumed resulting in increase in optimum SO_3 concentration and strength. However there will clearly be a limit to the amount of sulphate which can be consumed which will depend on the original lime content. This limit, for lime content employed (6wt.%) in the current work, would appear to be about 2.79% SO_3.

9.3.1.2 Effects of magnesium sulphate on strength

The results of the current work on lime-stabilised kaolinite in which $MgSO_4$ is included, confirm previous, observations (see section 3.4.3.4 on sulphates and strength) that magnesium sulphate is among the most damaging of sulphates in its influence on the pozzolanic reactions. There are two major theories that may explain the mechanisms of the damaging effects due to the addition of magnesium sulphate in the $CaO\text{-}Al_2O_3\text{-}SiO_2$ system:-

- firstly, it attacks and decalcifies the C-S-H and C-A-H gels, to form brucite and gypsum (Heller and Ben-Yair, 1964) as shown by reactions represented by equation X in section 3.4.3.4. The magnesium hydroxide reacts further with SiO_2 gel to form hydrated magnesium silicate (M-S-H). Magnesium silicates are known to be of extremely low strength (Grim, 1968). According to Grim, the magnesium silicates are formed by considerable replacement of aluminium by magnesium in aluminium silicates. Sepiolite of composition $4H_2O.2MgO.3SiO_2$ (formed by substitution of aluminium by magnesium in aluminium silicates of S:A ratio of 1.5), is a very weak material often compared with "sea froth" or "cuttlefish" which has light and porous bones. Attapulgite with composition $(OH)_4(OH)_2Mg_5Si_8O_{20}.4H_2O$, and which has fibrous characteristics, is yet another example.
- Secondly, it has been established that ettringite, a major strength contributor, is unstable in the presence of magnesium sulphate and the presence of magnesium sulphate ultimately causes ettringite to decompose to gypsum and hydrated alumina (Gollop and Taylor, 1996). This is perhaps achieved by the lowering of the pH of the system, since the pH of saturated brucite is only 10.5. This also would not facilitate the formation of the strength enhancing silicates. Normally, a pH of at least 12.4 is

required for alumina and silica to go into solution, and from research work done in concrete, it is not until a pH of at least 11.5 is attained that traces of crystalline ettringite are found. The detrimental reactions discussed above explain the consistently low strength values obtained in the current work on the addition of magnesium sulphate compared to gypsum at most curing stages and SO_3 contents (compare Figures 7.3-1 (a) and (b) with 7.3-2 (a) and (b)). The formation of the weak magnesium silicates and/or decomposition of ettringite would seem to dictate the low strength development. At intermediate sulphate concentration (0.93-1.86% SO_3), significant strength development is however achieved between 0 - 10 weeks, although the long term strength is significantly below that of the control mix in all cases at curing periods beyond 12 weeks.

9.3.1.3 Effects of sodium sulphate on strength

Dissolution of Na_2SO_4 creates the alkaline activator NaOH which increases the pH of the system and the amount of $Ca(OH)_2$ (Lime) reacted at a particular time by increasing the solubility of the latter (Lambe *et al.,* 1960). Activation is also as a result of the sodium ions' ability to "disturb" the aluminium bonding (Van Lier *et al.,* 1960; Lees *et al.,* 1982), creating a situation whereby early dissolution of alumina and silica takes place. In such conditions, calcium ions more easily unite with alumina and silica to form early cementitious products. The formation of intermediate sodium silicate and sodium aluminate hydrates precede the cementitious formations caused by Ca^{2+} ions as discussed in section 3.4.2 (Clay - Lime - Sulphate Reactions). However high concentrations of sodium hydroxide may lower the solubilities of both lime and gypsum thus inhibiting the formation of ettringite by shifting the equilibrium of (i.e. reversing) the reactions involved in ettringite formation represented by equation V in section 3.4.2.2 in Chapter 3. i.e.

$$\mathbf{Ca_6[Al(OH)_6]_2(SO_4)_3 26H_2O + 8OH^- \longrightarrow 6Ca(OH)_2 + 2Al(OH)^-_4 + 3[SO_4]^{2-} + 26H_2O} \quad \ldots\ldots\ldots \mathbf{I}$$

Subsequently, gypsum may be formed.

$$\mathbf{Ca^{2+} + OH^- + [SO_4]^{2-} \longrightarrow CaSO_4 + OH^-} \quad \ldots\ldots\ldots \mathbf{II}$$

This decomposition of ettringite must be accompanied by loss of strength. This was observed by De Silva and Glasser (1992), who established the exacerbated delay in ettringite formation due to the low solubility of $CaSO_4$ in the presence NaOH. Thus there are two opposing phenomena that lead to restrained long term strength development (beyond 3 - 10 weeks depending on SO_3 content) as indicated by Figure 7.3-3 (a);

1) the increased pH and solubility of Al_2O_3 and SiO_2 by addition of Na_2SO_4 leading to increased lime consumption and early strength development on the one hand, and
2) incorporation of Na^+ ions as well as decalcification of the C-S-H gel and the reduced dissolution of (secondary) gypsum on the other, leading to inhibited ettringite formation and loss in strength.

XRD analysis of the kaolinite - lime - Na_2SO_4 system in the current work shows evidence of very little ettringite and no gypsum. Therefore, while the second phenomenon is partly confirmed in so far as the inhibition of ettringite formation is concerned, there is no evidence of precipitation of gypsum. It is proposed that both Ca^{2+} and SO_4^{2-} ions, together with Na^+ ions, are bound in an unidentified phase that is neither highly expansive nor imparts any structural strength. The formation of such a compound (i.e. an AFt-type phase) has been proposed by numerous researchers in systems containing Ca^{2+}, SO_4^{2-} and Na^+ ions, together with alumina (Van Lier *et al.,* 1960; Lees *et al.,* 1982; De Silva and Glasser, 1992; Li *et al.,* 1996; Shayan and Ivanusek, 1996). The effects on strength and expansion properties of this proposed phase are deduced from results on UCS (Figure 7.3-3); linear expansion both during moist curing and during soaking (Figures 8.1-3 and 8.1-12); swelling pressure generation (Figure 8.2-3) and phase analysis of the kaolinite-lime-Na_2SO_4 system (Table 8.3-1). It is likely that at around 1.86% SO_3 concentration, this currently unidentified phase (with properties similar to but not quite those of crystalline ettringite), readily forms. Thus, it may be more than a coincidence that the maximum strength, maximum linear expansion during moist curing, minimal linear expansion during soaking and maximum swell pressure generation all occur at or around 1.86% SO_3. However much more detailed analytical work is required to confirm this proposal.

9.3.1.4 Effects of potassium sulphate on strength

Compared with the sulphates of calcium, magnesium and sodium, there is less coverage in the literature on pozzolanic reactions involving either potassium sulphate or K^+ ions in general. However, due to the generally accepted similarity in behaviour in the elements and compounds of sodium and potassium, the reactions involved in the strength development of clay-lime mixes in the presence of K_2SO_4 are likely to be closely related to those involved in the presence of Na_2SO_4. In addition, it is reported by Marcano-Martinez and McBride in 1989, in their study on calcium-induced sulphate adsorption by soils (Bolan *et al.,* 1993) that the adsorption of Ca^{2+} ions by soil is low in the presence of K^+ ions. This would retard the formation of the cementitious C-S-H gel.

Also, there is excessive increase in pH in systems containing monovalent alkali ions (Li *et al.,* 1996; Shayan and Ivanusek, 1996) as discussed in section 3.4.2 (Clay - Lime - Sulphate Reactions). The effects of high pH on the stability of ettringite (and hence strength) would be similar to those already discussed for Na_2SO_4 addition. These factors also lead to generally lower strength development in the presence of potassium sulphate. Thus, with the presence of K_2SO_4, there is no further strength increase at all SO_3 concentrations tested beyond a curing period of 6 weeks (Figure 7.3-4(a)). Beyond 14 weeks of curing, all SO_3 concentrations resulted in strengths lower than the control. Therefore, next to $MgSO_4$, K_2SO_4 is another example of a particularly deleterious sulphate. Also, since only gypsum showed sustained strength development and only at intermediate levels of Na_2SO_4 was significant long-term strength enhancement observed, it is apparent therefore that the pozzolanic reactions involved in the presence of Ca^{2+} cations are rather different from those of other cations (i.e. Mg^{2+}, Na^+ and K^+).

9.3.1.6 Effects of substitution of lime with GGBS on strength

Although the performance of compacted clay-lime-GGBS mixes both with and without gypsum is determined by the relative amounts of all the materials involved, the moisture content at compaction, the slag/lime ratio and, the gypsum content are of particular importance. A major factor determining the degree of formation of the cementitious hydration products is the hydration properties of slag. The activation of slag by lime (and also in some cases by components in the clay soil) promotes slag hydration and hence also the formation of the cementitious calcium silicate, aluminate and alumino-silicate hydrates. The presence of lime guarantees some degree of activation while the presence of gypsum can be an added advantage. Not only does gypsum enhance the strength properties of lime-clay mixtures (Sivapullaiah *et al.*, 1987; Abdi, 1992; Wild *et al.*, 1993), but it also promotes the hydration of slag through alkali-gypsum activation (Daimon, 1980; Taylor, 1990; Xuequan Wu, 1990). XRD analysis results show that the favourable conditions for crystalline ettringite formation prevailing in the kaolinite - lime - gypsum system are either absent or greatly interfered with by the introduction of slag. Thus, the most significant effect that replacement of lime with slag has on the final product is the reduction or complete elimination of crystalline ettringite and the strength enhancement in clay - lime - slag - gypsum mixes must result from hydration of the slag and the formation of more C-S-H gel and not from ettringite formation.

The increase in strength as lime is substituted with slag is two fold. On the one hand there is the increased formation of the cementitious silicate, aluminate and alumino-silicates (mainly of calcium) assited (on the other hand) by the increased nucleation sites (Wild *et al.*, 1996). The nucleation sites could be the slag grains or the clay particles, the bulk of the lime dissolving into Ca^{2+} and OH^- ions. This will then lead to reduced porosity of the hydrated system (Bijen, 1996) as the gel develops within the pore spaces and closes off the capillary pores. The strength increases with increasing slag level as long as some lime is present to enable alkali-slag activation, and the increase in strength is more pronounced after 28 days, when sufficient time has elapsed for the slag hydration to be effective (Figure 7.3-6 and 7.3-7).

In the presence of gypsum, the sulphate further promotes activation of the slag and accelerates and enhances slag hydration, such that strength is enhanced significantly by 7 days. Added gypsum activates slag only in the presence of lime (and/or any other alkali (See Chapter 4)). Inclusion of gypsum in the clay - lime - GGBS system also accelerates the strength development by a second mechanism - ettringite formation. The enhanced strength development particularly at 28-days of moist curing and at low slag to lime ratios and high SO_3 contents (Figure 7.3-8) suggests that gypsum also has an accelerating effect on the lime - kaolinite reaction but in this case at a rather later stage than it does for the slag hydration reaction. In the kaolinite - lime system, the acceleration is known to be due to rapid removal of aluminium from solution, by formation of ettringite (Wild *et al.*, 1993). The clay - lime - gypsum system is thus very expansive.

In PC - GGBS systems, the higher amounts of C-S-H gel that are produced readily absorb CaO and Al_2O_3 (Gollop and Taylor, 1996) in a such manner that these components are not readily available for further reaction. In the kaolinite - lime - slag - gypsum system at low lime - high slag ratios where larger amounts of C-S-H gel will be produced, it might be expected that less ettringite will be formed as more CaO and Al_2O_3 are bound in the C-S-H gel. Thus in this case the pozzolanic reactions produce predominantly non-crystalline products and the strength enhancement is principally via C-S-H gel formation. Another strength enhancing component results from the growth and development of crystalline ettringite, the ettringite decreasing with increasing slag/lime ratio. Therefore, beyond 7 days gypsum will have a more marked strength enhancing effect at low slag/high lime ratios (which have excess CaO and bind less alumina) than at high slag/low lime ratios which remove most of the available CaO and Al_2O_3 needed for ettringite formation.

The overall effect of the presence of GGBS is that those samples with particularly low lime and high slag contents (1L5S) lack adequate alkalinity and show slightly reduced

28-day strength with increasing gypsum content (Figure 7.3-7 (b)). Also at short curing times (7 days) the optimum sulphate content to give maximum strength is low (0.93% SO_3), but at longer curing times (28-days) this optimum sulphate content increases (1.86% SO_3). A similar effect was observed for the system without slag for which much longer curing times were used (Figure 7.3-1(b)). It is suggested that this is a kinetic effect resulting from the time taken to consume a particular level of gypsum in strength enhancement reactions e.g. growth and development of ettringite crystals.

Samples with intermediate slag - lime composition attained relatively high strengths together with sustained strength development at most gypsum levels (samples 3L3S and 2L4S). However irrespective of the curing period, there is no strength development in the kaolinite - lime - GGBS - gypsum system when the lime is fully replaced with slag suggesting that there is no slag activation (point B in Figures 7.3-6 (a) - (c)).

In Kimmeridge Clay, unknown proportions of different phases of minerals, among them the kaolinitic dickite, are present (see Table 5.1-4 in Chapter 5). The other phases include quartz, calcite, several micas, dolomite and ankerite. The overall extent and rates of the different reactions between lime, GGBS and these mineral phases would determine the peak UCS for given curing times and stabiliser contents. When the total stabiliser (lime + slag) does not provide enough lime for both cation exchange and for pozzolanic activity to take place in addition to activation of the slag, the strength increase of slag - lime - clay mixes is limited to short curing periods of say 7-days (Figures 7.3-9 (a) and 7.3-11 (a) and (b)). During this period, part of the calcium ions are used for the cation exchange while at the same time the short-lived alkalinity only manages to activate the slag to a low level. Over long periods for the low total stabiliser content, only those samples with unsubstituted lime (i.e. low slag : lime ratio) will develop highest strengths, the others being gradually denied hydration, in proportion with decreasing lime (and hence, increasing slag).

Unlike in the case of kaolinite, there is some fairly significant strength development at total lime replacement with slag (points B and B' in Figures 7.3-9 and 7.3-10). The 28 day strength at total lime replacement generally increases with increasing stabiliser content whereas at 7 days there is little change in strength. There is no doubt therefore that in this case the slag is slowly activated. The activation must be due to one or more of various mineral phases in Kimmeridge Clay. Two possible contenders would be dolomite and calcite both of which are sparingly soluble and generate an alkaline environment in solution (pH of Kimmeridge Clay in solution was observed as 7.4 compared to a pH of 4.9 for kaolinite (see Appendix 3). Other on-going research with a second batch of Kimmeridge Clay has indicated a much higher alkaline level (pH of 9.6) for Kimmeridge Clay). Thus, there is the possibility that some of the phases shown in Table 5.1-4 in Chapter 5 help in activating the slag. More research is definitely required here to establish the mechanism or the factors involved in this form of slag activation.

9.3.2 LINEAR EXPANSION

9.3.2.1 Causes of expansion

The dependence of both volume change and swelling pressure generation in unstabilised clay soil on the nature of the pore volume, pore solution and particle to particle forces implies that the volume changes and internal pressure changes are very closely related. Thus, determination of the swelling pressure may give an indication of the expected dimensional (volume) stability of the soil mass and vice versa.

When a soil mass is stabilised, say with lime ($Ca(OH)_2$), forces due to pozzolanic mechanisms come into play. The calcium silicate hydrates (C-S-H), calcium aluminate hydrates (C-A-H) and/or calcium alumino silicate hydrates (C-A-S-H) formed (Croft, 1964; Wild *et al.,* 1993B) interfere with the particle-particle forces through the cementitious effects that these hydrates impart. These hydrates reduce the pore fluid and hence the pore fluid pressure, thus reducing the swelling pressure and the swelling potential of the soil mass in general, producing long term volume stability. Thus, virtually no significant expansion takes place both during moist curing and during soaking of lime-stabilised clays (Silvapullaiah *et al.,* 1987; Bell, 1988; Arabi and Wild, 1989; Abdi, 1992). Also, formation of these hydrates in cementitious systems is normally associated with some degree of chemical shrinkage, in that the volume of reaction products is smaller than the volume of reactants (Tazawa *et al.,* 1995). During moist curing, there is initially, an excess of pore water. As different hydration reactions proceed, finely divided hydrates precipitate from solution. These precipitates form colloidal products which absorb water (probably by an osmotic mechanism) and swell. However as more hydrates precipitate, water becomes more restricted and the samples begin to shrink. Therefore in most cases, shrinkage occurs during moist curing as observed in the current work (see control mix in Figures 8.1-1(a) - 8.1-4(a) and 8.1-6(a)). Similar observations have been reported by Silvapullaiah *et al.*, (1987) on the effects of sulphates (gypsum) on volume change behaviour of lime treated kaolinitic soils. For such (lime-stabilised) soils, the volume changes are, at least approximately, also related to the swelling pressure generated upon soaking.

The addition of metal sulphates into the clay - lime mixes raises the cation concentration at the clay particle surfaces. The increased cation concentration enhances the osmotic potential leading to a much greater osmotic pressure and propensity for water (if available) to migrate from external sources into the clay particle interstices leading to expansion. Divalent cations are likely to be more effective in promoting this water migration because of their higher positive charge as compared to monovalent cations.

A complicating factor arises when sulphates are involved in clay - lime reactions, since ettringite nucleates either within the pore fluid or on the clay particle surfaces depending on the prevailing chemical environment, especially alkalinity (pH) of the pore solution (Deng Min and Tang Mingshu, 1994; Mehta, 1973 ; Taylor, 1993). At low pH, the few aluminate $Al(OH)_4^-$ ions that are produced in hydrated clay - lime mixes move from the clay particle surfaces into the pore solution and ettringite is predominantly formed in the voids, resulting in little or no expansion. With increase in pH, the main ettringite nucleation centres gradually shift to in situ (i.e. on the clay particle surfaces) where the

$Al(OH)_4^-$ ions are relatively more saturated. In either form of nucleation, the pore fluid pressure and/or the particle-particle reactions are increased leading to increased swelling potential. The swelling potential results in actual volume increase as observed in all cases where sulphates and lime are present. However, the lack of sufficient water during moist curing does not allow the full potential for the formation of cementitious hydrates, and/or that of ettringite and its subsequent growth to be realised and as outlined above internal self desiccation and shrinkage can occur. Thus for swelling to occur at any particular time, conditions conducive for a) formation of hydration products especially ettringite, and/or b) osmosis to take place must exist. Both of these requirements demand water. The magnitude of this expansion depends on,

1. the period of moist curing before water ingress,
2. the period of soaking
3. the concentration of sulphate
4. the type of cations deriving from the sulphate.

Therefore, a sample without lime and/or any sulphate will not show excessive expansion, even on soaking, unless it already has cations capable of absorbing water such as most montmorillonites and some illites. Thus, any significant expansion reported in the current work has been in the presence of gypsum and/or other metal sulphates. The significance of water in the expansion process warrants the mechanisms involved in the expansion process during moist curing and during soaking to be reviewed separately.

9.3.2.2 Effects of moist curing on linear expansion

During moist curing, the amount of water available in a soil sample is limited to the compaction moisture content. Soon after sample preparation, the partially saturated pores attain a pressure which is in balance with the atmosphere. Therefore any further water movement would be osmotic in nature and since there is no external source of water, any osmotic gradients formed in the environs of the clay or other particles (due to cation exchange) are small and will not cause significant expansion. The only other cause for expansion would be any that is due to the products of hydration which for lime stabilised clay include - silicate, aluminate and/or alumino-silicate hydrates of existing metals. These hydrates, although they are capable of absorbing significant amounts of water resulting in some degree of expansion, would not result in expansion in the absence of a water source. Thus, no swell was recorded for kaolinite - 6 wt.% lime samples during moist curing at 30°C and 100% relative humidity and the cation exchange and the formation of cementitious hydrates caused shrinkage (see control mix in Figures 8.1-1(a) - 8.1-5(a) as well as Figure 8.1-6(a)).. The reduction in swelling results from decreased affinity for water of the Ca-saturated clay upon addition of lime and the formation of a cementitious gel (Arabi and Wild, 1989). Thus, volume stability is enhanced by the binding together of the clay particles. Also, assuming a closed system in which water is neither allowed to leave or enter (as during moist curing), any shrinkage which occurs must be due to redistribution of material within the specimen. This would be due to chemical shrinkage. Chemical shrinkage is a result of internal chemical reactions whereby the volume of the reaction products is less than the volume of reactants (due to differences in their densities). Shrinkage could also be due to particle rearrangement whereby an initially flocculated structure breaks down due to changes in the charge distribution around particles (which are now coated with hydration products), the charge distribution being brought about by either progressive chemical reaction or cation exchange. The repulsive forces (between the negatively charged clay particles) are reduced due to the increase in cation (Ca^{2+}) concentration on addition of lime. With the reduction in repulsive forces, there is closer particle-particle packing leading to shrinkage.

The presence of about 1 % SO_3 equivalent of sulphates during moist curing significantly increases the swelling (Figures 8.1-1 - 8.1-5). With prolonged curing, those samples with low sulphate concentration cease to expand due to depletion of reactants, especially the SO_4^{2-} ions, while those with high concentration continue to expand. However, they soon cease to sustain the expansion due to the depletion of water (beyond 3 weeks in Figure 8.1-5). In all cases, a peak in expansion occurs at about 2% SO_3 concentration. It is interesting to note that in order to combine with all the 6wt.% lime in the mix, the formation of monosulphate ($C_3A.C\overline{S}.H_{12}$) would require a gypsum content equivalent to approximately 2.16% SO_3. The equivalent gypsum content for ettringite ($C_3A.3C\overline{S}.H_{32}$) formation is the equivalent of 6.48% SO_3 (see Appendix 1). The maximum in expansion at ≈2% SO_3 and the marked drop in expansion rate above this concentration suggests formation of a sulphate containing expansive phase, the maximum amount of this phase being formed at ≈2% SO_3. At sulphate concentrations above 2% SO_3, formation of this phase declines. When gypsum is the sulphate, this primary phase is replaced by a secondary expansive phase at even higher sulphate levels and thus expansion again increases to even higher values. An identical but less expansive secondary phase also occurs for the case of sodium sulphate.

The two obvious candidates for these primary and secondary phases are monosulphate and ettringite. Monosulphate would be the more likely one to be the cause for the earlier primary peak at ≈2% SO_3 while ettringite for the second and, for the case of gypsum addition, the higher of the two peaks. When the sulphate is not gypsum, then monosulphate and/or ettringite formation would normally require additional calcium. For $MgSO_4$ addition, the current work indicates that some significant ettringite formation does take place (see Table 8.3-1). It is also interesting to note that the maximum ettringite content (2%) at 5 weeks of moist curing is recorded at intermediate SO_3 concentration where maximum ultimate swelling potential was also recorded. It is likely that the additional Ca^{2+} ions required for ettringite formation are due to the decalcification of the C-S-H gel.

For the monovalent cations and in a highly alkaline environment, solid solutions of monosulphate and/or ettringite occur in which AFm/AFt can accommodate cations such as Na^+ as well as OH^- ions (in a similar manner to the C-'X'-S-H (intermediate) hydrates discussed in section 9.3.1). From the observed results, these intermediate hydrates are less expansive than monosulphate and/or ettringite (compare Figures 8.1-1(b) with 8.1-4(b)). In the presence of more deleterious sulphates such as $MgSO_4$, the expansion may be comparable to (or exceed) that due to ettringite formation (compare Figures 8.1-1(b) with 8.1-2(b)).

Although this explanation would account for the development of two peaks in expansion as sulphate concentration increases it is not supported by the limited analytical work which has been carried out in that no evidence of crystalline monosulphate has been obtained and the only new crystalline product observed is ettringite. Thus much more detailed analytical work is required in this area.

9.3.2.3 Effects of soaking on linear expansion of 1 week moist cured specimens

During soaking, the potential for both osmosis and ettringite formation and growth is increased. The degree of swelling during soaking will be determined by the nature of the surface products which have been developed on the clay particles during the initial moist curing period, and the manner in which those products are able to imbibe water by adsorption or by osmotic processes. This will in turn depend on the type and concentration of ions in the pore solution. In contrast to the ultimate shrinkage observed in the current work during moist curing for kaolinite - 6wt% lime (of the order of -0.130 %), an expansion of 3.6 % (about 30 times) was recorded upon soaking. This is believed to be as a result of osmotic hydration of the colloidal gel coating the clay particles (Wild *et al.,* 1993). The expansion increases with period of soaking because the reactions involved (osmosis and hydration) are time dependent.

Introduction of metal sulphates in low concentrations (0.93-1.86% SO_3) changes the nature of the surface product and also results in the pore solution being slightly more concentrated with ions. Water may then be drawn out of colloidal material into the pore solution and in most cases the specimens show less expansion on soaking than the sulphate free control (Figure 8.1-10(b) - 8.1-13(b)). In the case of highly soluble monovalent metal sulphates, it is not until the sulphate concentration exceeds 1.86% SO_3 that swelling exceeds that of the control mix. For the divalent cations, swelling starts before, or soon after, the lower concentration of 0.93% SO_3. Further increased cation charge beyond these sulphate concentrations lead to increased formation of sulphate bearing hydration products on the clay particle surfaces leading to rapid expansion.

Another argument that would explain the relative dimensional stability at low metal sulphate concentrations and subsequent increase in swelling with increase in concentration of ions would be that the damaging period (in terms of expansion) is **during the formation** of the initial sulphate containing product. If the product is forming when there is abundant supply of water there is excessive expansion. If sulphate levels are low the major part of the reaction involving sulphate is complete in a relatively short period and the system becomes stable. The loss in cementation due particularly to deleterious sulphates (i.e. $MgSO_4$) further enhances swelling, even at relatively low (0.93%) SO_3 levels (Figure 8.1-11(b)). From the literature (Gollop and Taylor, 1996; Shayan and Ivanusec, 1996) deleterious sulphates such as $MgSO_4$ are known to decalcify the C-S-H gel and release Ca^{2+} cations. The Ca^{2+} may then combine with $[SO_4]^{2-}$ and alumina available in the system to form ettringite as discussed above and the expansion after decalcification may be exacerbated by the loss in cementation.

If the sulphate level is high then 7 days is not sufficient to consume all the sulphate (see Figure 8.3-3) and thus the expansive reactions are still occurring and continue to do so as long as there is free lime there as well. Figure 8.1-15 (a) and (b) shows the underlying process very effectively. i.e. as the sulphate content is increased (moving from Figure 8.1-15 (a) to 8.1-15 (b): note the difference in the vertical scale), the moist curing period necessary to stabilise the system (i.e. consume the sulphate and lime) increases. There is of course a maximum SO_3 content above which all the lime (and hence calcium and/or aluminate ions necessary for the formation of expansive phases) has been consumed but sulphate is still in excess, thus any further addition of sulphate produces very little further effect on expansion during soaking (Figure 8.1-14).

When gypsum is the added sulphate, ettringite forms readily and the swelling pressure during soaking increases with increasing sulphate content, high sulphate concentration taking longer to realise the full potential for ettringite formation and growth. Silvapullaiah *et al.*, (1987) made identical observations on free swell measurements on the addition of gypsum to kaolinite - 6% lime mixtures where expansions took longer to achieve at high gypsum levels than at low levels. If as indicated previously ettringite formation leads to strength enhancement, then this would restrain inter-particle movement. The lack of particle rearrangements would enhance the maintenance of both osmotic pressure build up in the pores and possibly also pressure generation due to further ettringite crystal formation and growth. Thus for gypsum, there is a direct relationship between swelling pressure generated and linear expansion (compare Figures 8.1-10 (a) and (b) and 8.2-1 (a) and (b)). From Figure 8.1-10 (b), it appears that with further increase in SO_3 concentration beyond 3.72%, more expansion would only occur by the addition of more lime beyond the 6wt.% used in the current work.

When $MgSO_4$ is the added sulphate, 1% ettringite was observed at 1 week of moist curing at all SO_3 concentrations (see Table 8.3-1), suggesting that the observed increase in expansion with increasing SO_3 concentration for specimens cured for one week is not predominantly through ettringite formation and growth but possibly also osmotic in nature. This osmotic swelling would be further enhanced by the destruction (by brucite) of any strength enhancing gels and/or ettringite crystals formed on the clay particle surfaces as the SO_3 levels increase, as reported under sections 3.4.3.4 and 7.3.2.2. It is suggested these damaging reactions lead to the observed increase in the linear expansion with increasing SO_3 concentration and also to the swelling pressure generated up to intermediate SO_3 concentration (1.86 - 2.79%). Excessive addition of $MgSO_4$ beyond this intermediate SO_3 concentration resulted in total loss in cementation leading to a decline in the swelling potential.

It is possible that the breakdown in cementation (through C-S-H decalcification and formation of brucite ($Mg(OH)_2$) rendered the mix more expansive, the easier particle movement and rearrangement reduced the swelling pressure build up. Thus, unlike in the case of gypsum addition, the relationship between linear expansion and swelling pressure generated is only applicable up to the maximum swelling potential at intermediate SO_3 concentration. Beyond this sulphate level, there was massive swelling pressure dissipation due to material fabric deterioration. Therefore, the large linear expansion at 3.72% SO_3 did not necessarily imply high swelling pressure at this sulphate level (see Figures 8.1-11(a) and (b) and 8.2-21 (a) and (b)).

In the case of Na_2SO_4 addition, the pH is expected to rise from 12.4 (the pH likely to prevail in clay-lime mixes) to 12.8 or higher as reported for PC-alkali or PC-GGBS-alkali systems (Shayan and Ivanusec, 1996). Reports from several researchers (Heller and Ben Yair, 1964; Deng Min and Tang Mingshu, 1994; Li *et al.*, 1996; Shayan and Ivanusec, 1996) also suggest that some ettringite may be formed in CaO-Al_2O_3-SiO_2 systems in the presence of Na_2SO_4. This is confirmed by research in the current work for the clay-lime-Na_2SO_4 system (Table 8.3-1) although the observed amount of ettringite is rather small.

Very high Na^+ cation concentration lowers the solubility of gypsum (Van Lier *et al.*,1960). The reduced gypsum solubility would lead to reduced ettringite formation, explaining the relatively lower linear expansion results recorded in the current work in the presence of Na_2SO_4 as compared to those observed for gypsum addition. The precipitation of gypsum in the clay-lime-Na_2SO_4 system is however not confirmed by results in the current work (see Table 8.3-1).

Van Lier *et al.,* (1960) also established that the solubility of crystalline and amorphous silica was increased by the presence of very low normality solutions of NaCl, the solubility decreasing in solutions with concentrations greater than about 1M. Although these findings do not indicate which of the ions (Na^+ or Cl^-) are responsible for this increased silica dissolution, they however do suggest the likely existence of an optimal Na^+ cation concentration at which ettringite formation would be optimal and the formation of C-S-H and/or other intermediate gels (as discussed in section 9.3.1), also fully enhanced. If this were to happen, the swelling pressure potential would be greatest at this optimum SO_3 level due to increased cementation by the formation of C-S-H gel and/or ettringite. This is likely to be the case in the current work where a reduction in swelling potential was observed. From Figure 8.2-3 (a), the optimal Na^+ cation concentration is provided by the addition of Na_2SO_4 equivalent to 1.86% SO_3. This optimal sulphate concentration is equivalent to 0.9 M Na_2SO_4 which is in close agreement with Van Lier's estimate of 1M concentration for optimum silica dissolution.

Further Na_2SO_4 addition leads to a reduction in swelling pressure potential possibly due to either dissolution of ettringite and/or reduced formation of cementitious hydrates as less silica dissolves. Therefore, as in the case of $MgSO_4$ addition, expansion at the higher sulphate range (2.79-3.72% SO_3) is more likely to be due to material disintegration rather than to ettringite formation. At this SO_3 range, maximum swelling occurs accompanied by least strength development and relatively lower swelling pressure (see Figure 8.1-12(a) and 8.2-3(a)). Potassium sulphate addition is likely to result in similar effects to sodium sulphate addition (because of similarity in behaviour of Na^+ and K^+ cations in general), explaining the similarity in linear expansion patterns for the two sulphates (compare Figures 8.1-12(a) and (b) with 8.1-13(a) and (b)).

Clearly the way in which different metal sulphates influence the swelling pressure generation and the unrestrained expansion is highly complex and is different for different sulphates. The present observations have identified and quantified these different physical responses. However very detailed analytical work using micro-optical methods is necessary to determine the various physico-chemical processes which are producing these responses. This is outside the scope of the current work.

9.3.2.5 Effects of GGBS on linear expansion of moist cured clay - lime - gypsum mixes

From the strength results, the reduction in lime and increase in slag in clay-lime-GGBS mixes resulted in stronger material on moist curing, leading to low linear expansion during moist curing and during soaking. Also, GGBS generally lowered the expansion of lime-stabilised clay soil both during moist curing and during soaking, both in the absence and in the presence of gypsum. In the absence of gypsum, shrinkage was recorded during moist curing in all samples containing lime and slag, and shrinkage increased with decreasing lime content (and increasing slag) (see Figures 8.1-6(a)), which is attributed to internal self-desiccation due to the slag hydration. Upon the introduction of gypsum, all samples containing lime recorded increased linear expansion during moist curing suggesting increased formation of expansive phases and chemical shrinkage as discussed in section 9.2.2.2. Samples with gypsum contents of up to 1.86% SO_3 started to shrink after 1-3 days (see Figure 8.1-6(b) and 8.1-7(a)). Those at higher SO_3 contents recorded linear expansions throughout the one week of moist curing, the expansion generally increasing with lime content (and with decreasing slag). Those specimens without lime (i.e. containing slag and/or gypsum) recorded significant shrinkage (samples 0L0S2G, 0L0S4G, 0L0S6G, 0L0S8G, 0L6S0G and 0L6S8G).

The initial linear expansion during moist curing is likely to be due to ettringite formation and growth which, though at a reduced rate due to less water availability and lime reduction as lime is substituted with GGBS, sustains some level of expansion and prevents excessive shrinkage. Therefore, the shrinkage is not as severe as in the case of no gypsum addition (compare Figures 8.1-6(b), 8.1-7(a) and 8.1-7(b) with Figure 8.1-6(a)).

Ettringite formation in the kaolinite - lime - gypsum system has been observed to take place as soon as mixing the dry reactants (kaolinite, lime and gypsum) with water occurs (Wild *et al.*, 1993). Therefore, although the XRD equipment (at the University of Newcastle) used for the production of Figures 8.3-1 to 8.3-4 was not sufficiently sensitive to show ettringite formation within one week of moist curing even at 6wt.%

gypsum content, the one (at ECC International Ltd.) used for the production of Table 8.3-1 and the SEM equipment (at the University of Glamorgan) were more sensitive and ettringite was observed on 7 day moist cured specimens both in the kaolinite - lime - gypsum system (Table 8.3-1) and in mixes with high lime/slag ratios (samples 6L0S6G and 5L1S6G) in the kaolinite - lime - GGBS - gypsum system (Plate 1 (a) and (b)). Therefore at 6wt.% gypsum (2.79% SO_3), the rate of expansion is higher and is sustained throughout the 7 day moist curing period (Figure 8.1-7(b)).

The reduction in the rate of expansion after the 3rd day of moist curing in most specimens (except 6L0S6G) is most likely due to internal self-desiccation and depletion of the water film surrounding the clay or any slag particle surfaces as a result of slag hydration and significant ettringite formation. Specimens containing both lime and gypsum will either show continuous expansion during moist curing (especially if significant amounts of ettringite are formed) or expansion followed by shrinkage if the level of ettringite formed cannot sustain the resultant expansion.

The fact that kaolinite - gypsum, kaolinite - slag and kaolinite - slag - gypsum were observed to shrink during moist curing is more difficult to explain. The shrinkage in lime free slag/gypsum bearing kaolinite specimens may be explained in terms of the cation exchange and subsequent flocculation and deflocculation upon moist curing. It is proposed that initially upon mixing cation exchange (using Ca^{2+} ions from gypsum) takes place, significant flocculation occurs and the resultant agglomeration causes material volume increase. During curing, polar water molecules are attracted towards the clay particles surfaces and gradually, the positive charges are neutralised leading to collapse of the agglomerates and the flocculated structure, leading to the observed shrinkage after 1-3 days. The higher the sulphate concentration, the higher is the cation exchange and the more flocculated the structure, and hence, the higher the shrinkage once the flocculated structure has collapsed. At relatively high sulphate content (i.e. at 3.72% SO_3), the effects of cation exchange are not fully neutralised by the limited water supply during moist curing. Therefore, there is no significant collapse of the flocculated structure and the observed shrinkage is relatively less. Thus, there is an maximum shrinkage at 6wt.% gypsum (2.79% SO_3) (see samples 0L0S2G, 0L0S4G, 0L0S6G and 0L0S8G at OMC in Figures 8.1-6 (b), 8.1-7 (a) and (b) and 8.1-9(a)). The overall order of observed shrinkage is:

2G > 4G > 6G < 8G

In the presence of lime alone (sample 6L0S0G), the C-S-H gel formed strengthens the flocculated network and in this case, the shrinkage is predominantly chemical (see section 9.2.2.2) which is not (Figure 8.1-6 (a)) as significant as in the case of gypsum alone. With the introduction of gypsum in these lime-containing specimens, the formation of ettringite (see Plate 1(a) and (b)) further helps to resist shrinkage. Thus, the higher the lime and/or gypsum the lower the shrinkage and the higher the expansion.

Although slag does not dissolve readily, there is some degree of release of Ca^{2+} and Mg^{2+} from kaolinite specimens containing slag only, as observed in Chapter 4. For these samples, it is suggested that there is also some degree of cation exchange accompanied by small but significant flocculation and subsequent shrinkage on moist curing as recorded for sample 0L6S0G (Figure 8.1-6 (a)). Thus in the absence of lime, specimens containing both slag and gypsum will also record shrinkage as already reported. Those containing both lime and slag will also shrink during moist curing but in this case the shrinkage is more likely to be due to chemical shrinkage resulting from slag hydration. If the the lime is partially substituted by slag, the shrinkage is dependent on the slag/lime ratio, those specimens lower in lime content (i.e. higher slag) recording more shrinkage. Thus, the shrinkage decreases in the order:

2L > 3L > 5L > 6L

4S > 3S > 1S > 0S

9.3.2.6 Mechanisms involved in the effects of GGBS on linear expansion during soaking

Upon soaking, the ultimate linear expansion for the kaolinite-lime-GGBS-gypsum system was observed (particularly at high SO_3 content) to decrease substantially on reduction of lime content (Figure 8.1-19(b)) and to decrease substantially on substitution of lime with slag (Figure 8.1-1-(a)). Similar observations may be drawn for the Kimmeridge Clay - lime - GGBS specimens of closely identical lime, GGBS and gypsum contents (by comparing Figures 8.1-19 (a) and 8.1-22 (b)). From the work on kaolinite, it may be concluded that at a particular lime content the expansion is also directly related to gypsum content (Figure 8.1-19(b)).

The introduction of slag in slag - Portland cement blends results in dense pastes of reduced porosity, reduced permeability and of increased strength due to the formation of substantial amounts of C-S-H gel (Bijen, 1996; Gollop and Taylor, 1996). In the current work, since increased strength and reduced expansion with increasing slag content was observed, slag is likely to have imparted similar properties to clay-lime mixes. Slag uses lime for its inherent reaction (Daimon, 1980; Caijun Shi, 1993; Lange and Mortel, 1995). For example for slag - cement blends, if 70 % of the cement is replaced by slag, the lime content drops to 10 % of that of the neat cement although the cement content has only been reduced to 30 % of that of the neat cement (Lange and Mortel, 1995). Thus the hydration of the slag consumes more lime than it produces. Therefore if lime in lime stabilised clay is progressively replaced by slag, it is more than likely that not only is the free lime content decreased due to the replacement, but it is further decreased due to the lime-slag reaction.

In the current work, when gypsum was not present in clay - lime - GGBS systems, increasing the slag to lime ratio but keeping the total slag and lime constant resulted in a systematic increase in strength (see Figure 7.3-6 (a) - (c)). This indicates that the slag hydration reaction, which is activated by lime, is a more rapid reaction than the lime - kaolinite reaction. For these specimens (without gypsum), expansion was extremely small (both during moist curing (Figure 8.1-6 (a)), and during soaking (Figure 8.1-16 (a))) and tended to decrease as the strength (and slag to lime ratio) increased.

As was observed in section 7.3.4 (on UCS), including gypsum in clay - lime - GGBS mixes results in two major competing reactions; 1) the slag hydration activated by lime in the presence of calcium sulphate to give C-S-H gel, calcium aluminate or alumino silicate hydrates and ettringite (see section 4.3.2 in Chapter 4), and 2) the kaolinite-lime aqueous reaction in the presence of calcium sulphate to give a colloidal C-A-S-$\bar{S}$-H product and ettringite (see section 3.4.2 in Chapter 3). There are also competing nucleation sites, the kaolinite particle surfaces on the one hand and the slag particle surfaces on the other (see also Wild *et al.*, 1996). Having established that the lime activated slag hydration reaction is faster than the clay-lime reaction (see section 7.3.4.1), slag is the more likely initial source of alumina rather than kaolinite. Thus the slag hydration reaction becomes the dominant reaction and the rapid consumption of lime (note the disappearance of lime(L) peaks upon the introduction of GGBS in Figures 8.3-1(a) and (b) - 8.3-4(a) and (b)) allows nucleation and growth of ettringite crystals only in the clay - lime - GGBS - gypsum mixes of high lime/slag ratios (such as for mix 5L1S6G in Plate 1 (b)). The other mixes of lower lime/slag ratios are starved of Ca^{2+} ions, preventing significant ettringite nucleation on the clay particle surfaces (Plate 1 (c)). At very low lime/slag ratios, the gypsum present is practically unreacted at 1 week (Figure 8.3-3(d) and Plate 1 (d)) and significant residual amounts are still present at 4 weeks (Figure 8.3-4 (d)). The lack of any identifiable ettringite, both from X-ray analysis and SEM investigations (Plate 1 (c)) seems to suggest that at low lime-high slag compositions all the lime is consumed during the cation exchange process and/or in slag hydration. In the absence of available lime, no significant clay-lime-gypsum reaction takes place and virtually all the gypsum remains unreacted (Figure 8.3-3 (e) and 8.3-4 (e)). Thus in the presence of GGBS the nature of the reaction product which forms on the clay particles is modified and the clay no longer undergoes extreme expansion when saturated with water.

There is no evidence to indicate which of the two ettringite forming reactions discussed above will cause the most expansion for a given amount of ettringite formed. What is known however is that the slag will release its alumina first due to its more rapid hydration (see section 7.3.4.1). Whether this alumina will be used immediately for ettringite formation or whether it will be absorbed by the C-S-H gel (Gollop and Taylor, 1996) is not proven although the presence of excess residual gypsum and the absence of ettringite in high slag - low lime compositions suggests the latter process. Also, if lime is available to both slag and kaolinite, more Al_2O_3 will be released from the kaolinite than from the slag since the former contains more alumina. Thus, it is not surprising that the kaolinite-lime-gypsum system is more expansive than the kaolinite - lime - GGBS - gypsum system. Swelling will continue until any one of the reactive ingredients are depleted, these being water (especially during moist curing), CaO (from the lime), $CaSO_4$ (from the gypsum) and Al_2O_3 (from either kaolinite or slag). When slag hydrates a C-S-H gel with low C/S ratio forms which can take in Al_2O_3 (Gollop and Taylor, 1996) and possibly additional CaO. Thus, as slag replaces lime in the kaolinite - lime - GGBS - gypsum system, the amount of freely available CaO rapidly decreases and thus the amount of ettringite formed decreases and the amount of residual gypsum increases (Figure 8.3-4) and expansion falls to a very low level. As there is excess residual gypsum at high slag to lime ratios and no crystalline ettringite is formed, the drop in expansion is not due to lack of available sulphate. It must therefore be due either to a deficiency in CaO and/or Al_2O_3 in solution or a nucleation problem possibly due to poisoning of nucleation surfaces with excess sulphate. The obvious explanation is the deficiency of CaO at high slag/lime ratios which has been amply verified by observations in the current work (Figures 8.3-1 - 8.3-4) and which must be a critical factor. Thus the amount of lime should be kept to a minimum to minimise the influence of the ettringite forming reaction. That minimum must however be sufficient to activate the slag, which is essential for provision of cementation. An additional factor which complements this explanation for the reduction in expansion is that as slag replacement levels increase and lime levels reduce, there ultimately will be, as reaction proceeds, a reduction in pH. Thus not only will less ettringite form but ettringite will become less stable relative to gypsum, but in addition less alumina (and silica) will go into solution. It is therefore not surprising that swelling reduces substantially. A further point to note is that it has been reported (Mehta, 1983; Deng Min *et al.*, 1994) that at low pH, ettringite forms in the material interstices and when ettringite forms in this manner it causes little or no expansion.

When the reactive ingredients are depleted, the samples may thereafter;

1. shrink due to internal self desiccation or chemical shrinkage. Alternatively,
2. the samples may attain dimensional stability both during moist curing and during soaking.

The period during which the dimensional stability mentioned in (2) above is maintained depends on the period during which the reactive ingredients (CaO, $CaSO_4$ and Al_2O_3) remain depleted. In clay-lime-GGBS-gypsum reactions, there may be considerable retention of significant quantities of unreacted slag and gypsum depending on the amount of lime used. Thus if low lime - high slag specimens (e.g. 0L6S6G, 0L6S8G or even 1L5S6G and 1L5S8G) were subsequently "contaminated" with lime, then delayed or "secondary" ettringite would form, and if such specimens were also saturated with water substantial swelling would be likely to occur particularly if only limited cementation had taken place (as for samples without lime (see Section 8.1.3.6)). "Contamination" here means appearance of Ca^{2+} ions either migratory from other sources in or outside the hydrating system or emanating from the slow hydration process that slag is known to undergo (See Chapter 4).

From Figures 8.1-18 and 8.1-21, sudden expansion occurred for lime free samples containing high amounts of slag and gypsum (i.e. samples 0L6S6G and 0L6S8G) as reported in section 8.1.3.6. It is proposed that in the absence of lime, the outer C-S-H and/or AFm type outer product formed on the slag particles (see Figure 4.5-1 (c) in Chapter 4) is very thin indeed. This product would be formed using Ca^{2+} released from the very limited hydration of the non-activated slag (see section 4.3 in Chapter 4). The formation of the Al-rich inner product may then absorb water and the unreacted slag may release additional Ca^{2+} ions which are shielded from the SO_4^{2-} ions by the coating products. Pressure in the zone of unreacted slag then builds up and the coating products burst, releasing the Ca^{2+} ions which trigger expansion. The time at which this bursting takes place is currently hard to determine. It must however depend, among other things, on the amount of unreacted slag and water available. The amount of sulphate in the system will obviously determine the magnitude and rate of expansion. It may also be likely that the amount of sulphate may also determine the time of rupture of the coating(s). For the 0L6S8G system compacted at OMC and at 1.2 OMC, the time of observed increase in expansion occurred at 40 and 30 days respectively. The time between the rupture of the coating and observation of increased expansion will most likely depend on the reacting ingredients, together with the pore structure and rigidity of the test specimens. This proposed mechanism of delayed expansion is currently under further study. By monitoring the pH and the expansion (and possibly phase and microstructural analysis) of the system, it may be possible to further investigate the processes involved.

9.4 COMMERCIAL IMPLICATIONS OF THE EFFECTS OF GGBS ON LIME-STABILISED CLAY SOILS

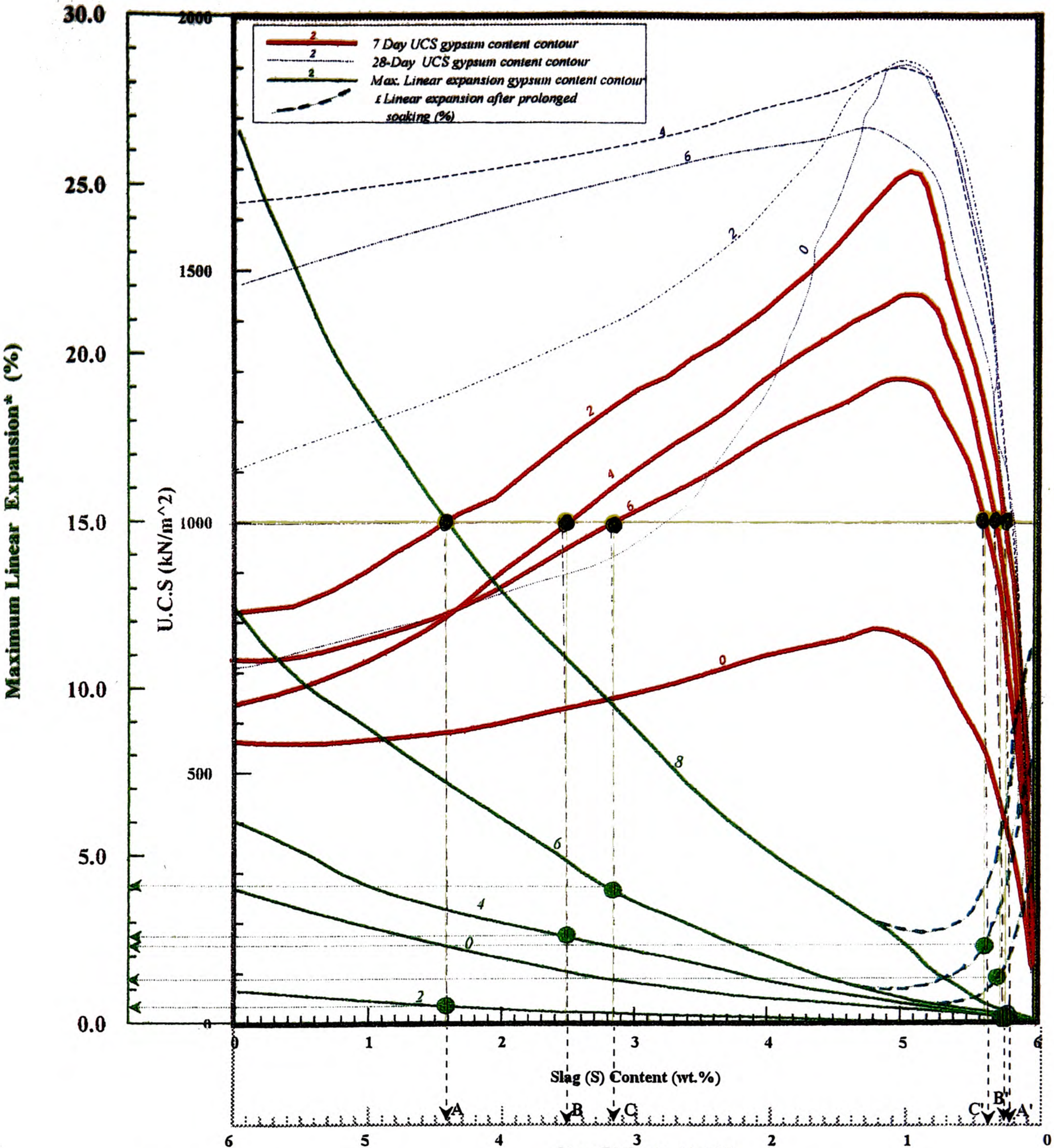
Results in the current work indicate that by incorporating ground granulated blastfurnace slag (GGBS) in the lime stabilisation process, the compaction properties (MDD and OMC) of clays are not significantly affected both in the absence and in the presence of gypsum. More importantly, higher (7 day and 28 day) strengths not previously achievable either with clay - lime or with clay - lime - gypsum compositions, coupled with reductions in initial (0 - ≈60 days) linear expansion have been achieved. Mellowing was found to be of significance only in the presence of gypsum. It improved material workability by increasing both the liquid limit and the plastic limit thus lowering the plasticity index. These observations result in very significant and viable commercial and industrial implications particularly for use in the lime stabilisation of sulphate bearing clay soils. At present, the Department of Transportation (DTP) offers no specific guidance on the use of these soils and the general and most common practice has been avoiding stabilisation of these soils, thus incurring heavy economic penalties in cutting, transporting and spoiling. Environmental factors such as increasing global awareness on pollution and taxes on waste disposal methods such as dumping encourage material upgrading by stabilisation of in-situ soil as an alternative to its export to land-fill and replacement by imported granular fill. Thus, the lime stabilisation of sulphate bearing soils will result in better control in environmental degradation by waste material dumping. Based on these findings, the Cementitious Slag Makers Association (CSMA), in collaboration with the DTP's Transport and Road Laboratory (TRL) and other relevant industries such as the Buxton Lime Industries (BLI) have recently (starting in June 1997) carried out a pioneering highway pavement pilot trial in the United Kingdom using GGBS on the A421 Tingewick Bypass, west of Buckingham. The trial involves the in situ soil stabilisation of sulphate bearing boulder clay using quicklime lime - Portland cement (PC) - GGBS optional compositions.

During preliminary mix design for the stabilisation of the boulder clay, the clay was mixed with 1.5wt.% quicklime (CaO) together with either 1.5, 2.5, 5.5 or 8.5wt.% PC or with 2, 3, 5.5 or 8.5 wt.% GGBS. The first two mixes in each case were subjected to soaked 7 day (3 days moist curing + 4 days soaking) and to 14 days (3 days moist curing + 11 days soaking) CBR and swelling tests. The remaining two mixes in each case were tested for cube crushing strength at 7 days, and at 14 days (both 14 days moist curing and also 7 days moist curing + 7 days soaking).

The clay-lime-GGBS option resulted in higher soaked and unsoaked strength results than the clay - lime - PC option of identical or closely identical total stabiliser (Lime + PC or Lime + GGBS) content. The swell magnitudes were also lower for the mixes containing GGBS (see Appendix 9). Although the results on equivalent clay - lime only and clay - PC only mixes are not available, they would almost certainly (based on the work reported in this study) be inferior to the observed results for mixes containing GGBS in this preliminary mix design.

For each of the five pilot trial sections of the Tingewick Bypass (Trial sections A, B, C, D and E), 1.5wt.% quicklime (CaO) was spread, rotorvated into the boulder clay as water was added, and the homogeneous mix compacted and allowed to mellow for 3 days. Slag (amounting to 6.5wt.% for trial sections A, B and C and to 8.5wt.% for either trial section D or E) was then spread, rotorvated and compacted into the boulder clay-lime mix. For the other trial section (D or E) without slag, 8.5wt.% PC was added to the lime stabilised boulder clay in a similar procedure to the slag. The moisture content during the second stage of slag or PC addition was adjusted as advised by the onsite supervisory soils laboratory staff. At relevant stages, samples were taken for the determination of onsite lime and GGBS spread rates, moisture content (MC) and moisture condition values (MCV) as well as cube strength, CBR and other mix material properties. The TRL team later determined the in situ density and stiffness of the stabilised layer at various curing and in service periods. At the time of writing this thesis, the monitoring of these trial sections is still in progress.

In order to enhance and facilitate the industrial response, nomographs have been designed with the intention of giving a feel for the values, as well as guidance on sulphate, UCS and swelling levels for the design of mix compositions. Figure 9.5-1 shows a nomograph for the 7-day and 28-day UCS, as well as for linear expansion of kaolinite - lime - GGBS - gypsum mixes of a fixed total stabiliser content (lime + GGBS) of 6wt.%, for cases where water ingress is anticipated after the frequently recommended 7 day moist curing period. Figure 9.5-2 on the other hand shows a nomograph for 7-day and 28-day UCS of Kimmeridge Clay - lime - GGBS mixes, where the total stabiliser content has been varied from 5-10wt.% and where soaking tests were conducted only on the most vulnerable mixes (i.e. those with a total stabiliser content of 5wt.%). Tables 9.5-1 and 9.5-2 show the relative material cost savings for the achievement of UCS values of 500, 1000, 1500 and 2000 kN/m^2 for kaolinite - lime - GGBS - gypsum and Kimmeridge Clay - lime - GGBS systems. The cost savings upon inclusion of GGBS are obvious. In the next chapter, an overview of the implications of the investigations reported in this and previous chapters is given, together with summarised conclusions and recommendations that may be drawn from the discussion of the results in this chapter.



Example: For a 7-day UCS of approximately 1000 kN/m^2, the table below shows the possible mixes.

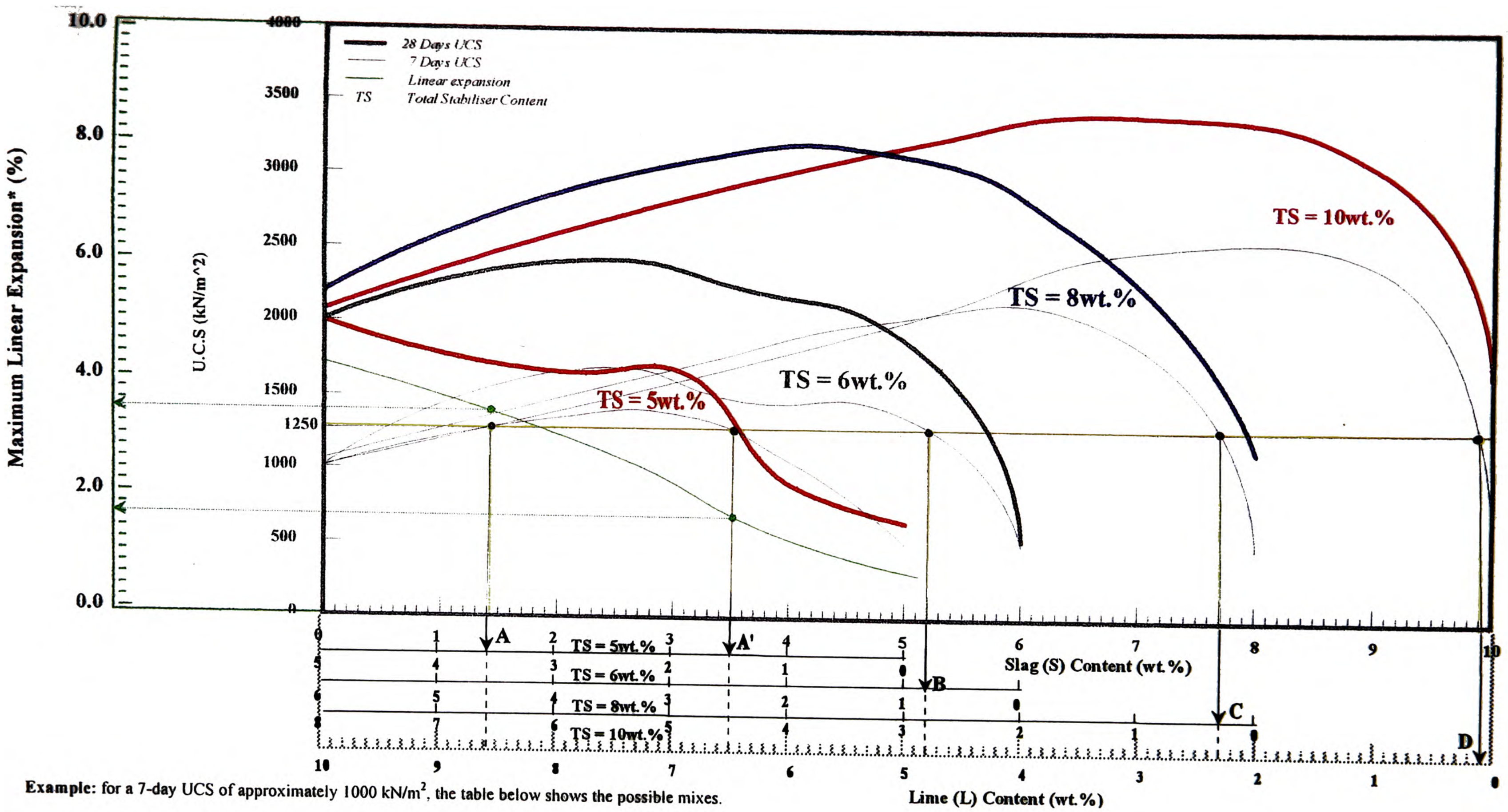
Gypum content (wt.%)	0	2		4		6	
Point on Nomograph	None	A	A'	B	B'	C	C'
Mix compositions	None	4.4L1.6S	0.2L5.8S	3.5L2.5S	0.3L5.7S	3.2L2.8S	0.4L5.6S
Maximum linear expansion (%)	-	< .5	< .5	2.5[e]	1.2	≈ 4.0	< 0.5 (2.5[e])
Expansion Compliance[a]	-	✓	✓	✓	✓	×	×[e]
Price (£/Tonne)[b]	-	3.28	2.44[d]	3.10	2.46	3.04	2.48
% Savings[c]	-	66	100	73	99	75	98

* Specimens for linear expansion were moist cured for 7 days prior to soaking in de-ionised water until no further expansion occurred beyond 30 days of soaking. [a] Assuming the DTp. allowable swelling of ≈ 4% (BS 1924).

[b] Per tonne of treated material, based on £40/Tonne of ggbs and £60/Tonne of lime (either CaO or $Ca(OH)_2$)).

[c] Based on the slag-free mix, capable of attaining the target strength (which is assumed to make 0% savings). (If none exists, savings are based on the least cost, non-expansive lime-ggbs mix (e.g. 0.2L5.8S, which is assumed to make 100% savings). [d] Least cost, non-expansive lime-ggbs mix. [e] Potentially expansive.

Figure 9.5-1 NOMOGRAPH FOR UCS AND LINEAR EXPANSION OF KAOLINITE-LIME-GGBS-GYPSUM MIXES



Example: for a 7-day UCS of approximately 1000 kN/m², the table below shows the possible mixes.

Total Stabiliser (TS) content (wt.%)	5	6	8	10
Point on Nomograph	A	B	C	D
Possible mix composisitions	0.9L4.1S	0.4L5.6S	0.2L7.8S	0L10S
Possible maximum expansion (%)	2.4	-	-	-
Expansion Compliance	✓	✓	✓	✓
Price (£/Tonne) [a]	2.18	2.48	3.24	4.00
% Savings [b]	27	17	-8	-33

NOTES

* Linear expansion was only conducted for TS=5wt.% only. Linear expansion figures are anticipated to be much lower at the other (higher) TS values. Specimens for linear expansion were moist cured for 7 days prior to soaking in de-ionised water until no further expansion occurred beyond 30 days of soaking.

[a] Per tonne of treated material, based on £40/Tonne of ggbs and £60/Tonne of lime (either CaO or $Ca(OH)_2$))

[b] Based on the slag-free mix of least TS value, capable of attaining the target strength ((i.e. 5L0S, which is assumed to make 0% savings). (If none exists, savings are based on the least cost, non-expansive lime-ggbs mix, which is assumed to make 100% savings).

[c] Least cost, non-expansive lime-ggbs mix.

Figure 9.5-2 **NOMOGRAPH FOR UCS OF KIMMERIDGE CLAY-LIME-GGBS MIXES**

Target 7-day UCS (kN/m^2)		Without Ggbs				With Ggbs						
		Gypsum Content (wt.%)				Gypsum Content (wt.%)						
		0	2	4	6	0	2		4		6	
500	Mix Composition (Lime-Ggbs)	6L0S	6L0S	6L0S	6L0S	0.3L5.7S	0.1L5.9S		0.1L5.9S^{d}		0.1L5.9S^{d}	
	Maximum Linear Expansion (%)	4.0	1.0	6.0	12.5	≈ 0	≈ 0		≈ 0 [4.0^{d}]		≈ [0 7.5^{d}]	
	Price (£/Tonne)^{a}	3.6^{c}	3.6^{c}	3.6^{c}	3.6^{c}	2.46	2.42		2.42		2.42	
	% Savings^{b}	0	0	0	0	32	33		33		33	
1000	Mix Composition (Lime-Ggbs)	NONE	NONE	NONE	NONE	NONE	4.4L1.6S	0.2L5.8S	3.5L2.5S	0.3L5.7S	3.2L2.8S	0.4L5.6S
	Maximum Linear Expansion (%)	-	-	-	-	-	<1.0	<0.5	2.5	<0.5 [≈ 1.5^{d}]	4	<0.5[≈ 2.5^{d}]
	Price (£/Tonne)^{a}	-	-	-	-	-	3.28	2.44^{c}	3.10	2.46	3.04	2.48
	% Savings^{b}	-	-	-	-	-	66	100	73	99	75	98
1500	Mix Composition (Lime-Ggbs)	NONE	NONE	NONE	NONE	NONE	1 0.7L4.3S	0.7L5.3S	NONE	NONE	NONE	NONE
	Maximum Linear Expansion (%)	-	-	-	-	-	< 0.5	< 0.5	-	-	-	-
	Price (£/Tonne)^{a}	-	-	-	-	-	2.74	2.54^{c}	-	-	-	-
	% Savings^{b}	-	-	-	-	-	92	100	-	-	-	-
2000	Mix Composition (Lime-Ggbs)	NONE	NONE	NONE	NONE	NONE	NONE	NONE	NONE	NONE	NONE	NONE
	Maximum Linear Expansion (%)	-	-	-	-	-	-	-	-	-	-	-
	Price (£/Tonne)^{a}	-	-	-	-	-	-	-	-	-	-	-
	% Savings^{b}	-	-	-	-	-	-	-	-	-	-	-

[a] Based on £40/Tonne of ggbs and £60/Tonne of lime (either CaO or $Ca(OH)_2$))

[b] Based on either:- (i) the estimated cost of the slag-free mix of least Total Stabiliser (TS) content, capable of attaining the target strength (which is assumed to make 0% savings), or if none exists, (ii) on the estimated cost of the least cost, non-expansive lime-ggbs mix (which is assumed to have already made 100% savings).

[c] Cost of control mixes for the computation of savings.

[d] Potentially expansive due to possible long-term slag hydration.

Table 9.5-1 - Cost analysis for 7-day UCS of Kaolinite-lime-ggbs-gypsum mixes.

Target 7-day UCS (kN/m^2)		Without Ggbs				With Ggbs						
		Total Stabil				Total Stabiliser (TS) (wt.%)						
		5	6	8	10	5	6		8		10	
500	Mix Composition (Lime-Ggbs)	5L0S	6L0S	8L0S	10L0S	0L5S	0L6S		0L8S		0L10S	
	Maximum Linear Expansion (%)	0.7	-	-	-	-	-		-		-	
	Price (£/Tonne)^a	3^c	3.6	4.8	6	2	2.4		3.2		4	
	% Savings^b	0	-20	-60	-100	33	33		33		33	
1000	Mix Composition (Lime-Ggbs)	5L0S	6L0S	8L0S	10L0S	0.9L4.1S	0.4L5.6S		0.2L7.8S^d		0.1L9.9S^d	
	Maximum Linear Expansion (%)	1.2	-	-	-	-	-		-		-	
	Price (£/Tonne)^a	3^c	3.6	4.8	6	2.18	2.48		3.24		4.02	
	% Savings^b	0	-20	-60	-100	27	17		-8		-34	
1500	Mix Composition (Lime-Ggbs)	NONE	NONE	NONE	NONE	NONE	4.9L1.1S	2.1L3.9S	6L2S	0.5L7.5S	7.5L2.5S	0.2L9.8S
	Maximum Linear Expansion (%)	-	-	-	-	-	-	-	-	-	-	-
	Price (£/Tonne)^a	-	-	-	-	-	3.38	2.82^c	4.4	3.30	5.50	4.04
	% Savings^b	-	-	-	-	-	80	100	44	83	5	57
2000	Mix Composition (Lime-Ggbs)	NONE	NONE	NONE	NONE	NONE	NONE	NONE	3.4L4.6S	1.4L6.6S	5L5S	0.5L9.5S
	Maximum Linear Expansion (%)	-	-	-	-	-	-	-	-	-	-	-
	Price (£/Tonne)^a	-	-	-	-	-	-	-	3.88	3.48^c	5.00	4.10
	% Savings^b	-	-	-	-	-	-	-	89	100	56	82

[a] Based on £40/Tonne of ggbs and £60/Tonne of lime (either CaO or Ca(OH)$_2$))

[b] Based on either:- (i) the estimated cost of the slag-free mix of least Total Stabiliser (TS) content, capable of attaining the target strength (which is assumed to make 0% savings), or if none exists, (ii) on the estimated cost of the least cost, non-expansive lime-ggbs mix (which is assumed to have already made 100% savings).

[c] Cost of control mixes for the computation of savings.

[d] Potentially expansive due to possible long-term slag hydration.

Table 9.5-2 - Cost analysis for 7-day UCS of Kimmeridge clay-lime-ggbs mixes

CHAPTER 10 - CONCLUSIONS AND RECOMMENDATIONS

10.1 CONCLUSIONS

The main objectives of the current work were to establish the fundamental material property changes of lime-stabilised kaolinite in the presence of metal sulphates, to explain the mechanisms involved, and finally to establish whether inclusion of ground granulated blastfurnace slag (GGBS), which is used in Portland Cement (PC) and PC-blends to combat sulphate attack in concrete, would impart similar resistance in lime-stabilisation of clay soil. These have been achieved, perhaps even more widely than initially intended. Thus;

- It is now demonstrably clear how the sulphates of calcium, magnesium, sodium and potassium affect the engineering properties of lime-stabilised kaolinite with respect to Atterberg limits, compaction, unconfined compression strength (UCS), swelling and swelling pressure generation.
- Arguments have been presented, based on the observations, which explain the mechanisms involved in these material property changes as the amounts of metal sulphates are varied.
- It has been shown that that it is possible to suppress the swelling caused by sulphates, by incorporating ground granulated blastfurnace slag (GGBS), in the lime - clay mix. Using the results of phase analysis and microstructural analysis, an

explanation has been put forward as to how replacement of lime by slag reduces or eliminates expansion due to sulphates.

The achievement of these objectives has been made after drawing specific conclusions from observations made during the investigations on each of the engineering properties studied. The principal conclusions, in relation to the different engineering properties are:

1. **Consistency:** Added sulphates in general lower the liquid limit of lime-stabilised kaolinite. The magnitude of lowering depends on the nature of the cation(s) in the sulphate, the monovalent cations lowering the liquid limit to a larger degree than the divalent ones. On the other hand, different sulphates have different effects on the plastic limit of lime-stabilised kaolinite, the divalent cations raising it while the monovalent ones lower it. However, the overall effect in both cases is that the plasticity index of lime-stabilised kaolinite is lowered. From work done using gypsum, this lowering of the index is greater on mellowing. The practical implications of these findings is that added sulphates are beneficial to the reduction of plasticity (and hence improvement on workability) of lime-stabilised clay soil. In these circumstances, as well as in natural sulphate bearing clay soils, mellowing is strongly recommended for further material improvements.
2. **Compaction:** The effects of sulphates on the compaction properties of lime-stabilised kaolinite are similar to those produced by the addition of lime to the kaolinite. They, generally, (further) lower the maximum dry density (MDD) and (further) raise the optimum moisture content (OMC). The sulphates containing divalent cations lower the MDD and raise the OMC by bigger magnitudes than those containing monovalent cations. Practically, the overall significance of this is that

the presence of sulphates would imply consumption of more water during mixing operations and relatively lower field densities are anticipated compared with the sulphate free material.

3. **Strength:** Only gypsum is beneficial in terms of strength enhancement. The maximum strength enhancement occurs at approximately 6wt.% gypsum (2.79% SO_3) for the kaolinite-6wt.% lime mix. The sulphates of magnesium and potassium are the most deleterious to strength development. At 14 weeks the sulphate free stabilised material (control mix) has higher strength than specimens containing any level of these sulphate types. However, minor quantities of sodium sulphate (below 1.86% SO_3) slightly enhanced the long-term (20 weeks) strength of lime-stabilised kaolinite used in the study.

   Thus, further research is required to establish any possible benefit of using these other sulphates (besides gypsum), particularly with the incorporation of slag which has appeared to enhance the performance of lime-stabilised gypsum-containing kaolinite.

4. **Swelling:** Systems containing gypsum and magnesium sulphate produce the most expansive material. The swelling due to gypsum, despite the significant material cementation is as a result of ettringite formation and high osmotic pressure while that due to magnesium sulphate is due to low strength coupled with high osmotic pressure. The sulphates containing monovalent cations show low swelling, despite low strength, because of the lower osmotic pressure. Sodium sulphate in small concentrations may reduce swelling possibly because it reduces the solubility of any gypsum that is likely to form in the system, thus inhibiting ettringite formation. Therefore, high swelling should be anticipated when significant quantities of

gypsum and or magnesium sulphate (≥ 4wt.% (1.9% SO_3)) are encountered during soil lime-stabilisation. In these circumstances, prolonged moist curing is strongly recommended to lower the swelling potential (although this might be difficult to do in practice).

5. **Swelling pressure:** Maximum swelling pressure in confined material is likely to be generated at approximately the same sulphate concentrations where maximum strength develops, suggesting a correlation between specimen rigidity and swelling pressure build-up. The construction implications of this are that even for strong mixes such as those containing gypsum, the increase in swelling pressure is still a problem despite the high strength development. This swell pressure build-up is likely to cause heave and subsequent cracking of overlying structures. The long-term pressure build-up may be prevented by prolonged moist curing in order to exhaust future ettringite formation/osmotic pressure potential.
6. **Composition:** The partial substitution of lime with GGBS in compacted clay - lime mixes produces a number of changes to the engineering properties of the mixes.

    (i) the Atterberg limits of both the mellowed and unmellowed kaolinite - lime mixes are not significantly altered in the absence of gypsum as long as there are small quantities of lime. In the presence of gypsum, inclusion of GGBS significantly increases both the liquid limit and the plastic limit of the mellowed material, as long as there are significant quantities of lime. This results in a significant drop in the plasticity index as a result of a higher increase in plastic limit compared to that occurring for liquid limit. Partial substitution of lime with GGBS in compacted lime - Kimmeridge Clay mixes have similar effects as for kaolinite - lime - gypsum mixes. Thus, even when GGBS is included, mellowing is still beneficial and is recommended during lime-stabilisation of sulphate bearing clay soils.

(ii) there is no significant reduction in the MDD of kaolinite - lime mixes both in the presence and in the absence of gypsum. For compacted Kimmeridge Clay - lime mixes (which inherently contain gypsum), the MDD is also unaffected when lime is partially substituted with GGBS. The OMC of lime-stabilised kaolinite is marginally increased by the presence of GGBS both with and without gypsum. In contrast for Kimmeridge Clay mixes, the OMC appears to be lowered by GGBS. Therefore, inclusion of GGBS is not likely to cause any problems in the achievement of the prescribed field compaction. Water consumption may however vary, depending on the clay type. Initial field trials would establish the prevailing situation.

(iii) strength at both 7 and 28 days increases with increasing slag as long as lime is present in significant amounts (depending on the clay type) so as to activate the slag. Despite the slow nature of slag hydration (relative to Portland Cement (PC) hydration), clay - lime - GGBS mixes have a faster rate of strength enhancement than clay-lime mixes, due to the extreme slowness of the pozzolanic reaction in the latter. The presence of gypsum is beneficial as strength is further enhanced without significant increase in linear expansion. The strength development of the ensuing clay - lime - GGBS - gypsum system increases with slag/lime ratio, gypsum content and curing period, the limiting values depending on the clay type. The total stabiliser content (slag + lime) must be at the necessary level to provide the required bearing capacity and strength. Overall, the benefit, in terms of strength, of inclusion of GGBS is firmly established.

(iv) gypsum accelerates slag hydration, and hence strength development, in the presence of lime particularly during the initial stages. In the absence of slag, gypsum also accelerates the strength development but to a lesser degree. Gypsum may also accelerate the slag hydration of some clay - GGBS mixes in the absence of lime depending on the mineralogy of the clay but it does not appear to initiate slag hydration. Kimmeridge Clay is one good example of such a clay. Kimmeridge Clay is slightly alkaline and contains gypsum and therefore even with clay slag mixes, there is some strength development as the slag is mildly activated. Gypsum does not however accelerate the GGBS - pure kaolinite mix because of the acidic environment. Thus, the identification of mineral phases in the soil is an inevitable starting point when the involvement of GGBS, lime and sulphates is anticipated.

(v) the resistance to sulphate expansion increases with the slag/lime ratio, although unreacted slag may be an indirect source of available Al_2O_3 and a system with such slag is potentially expansive. It is clear from the observations in this study that if lime activated slag stabilisation of sulphate bearing clay soils is to be used without potential problems of further heave when the clay becomes saturated with water, the clay must achieve a fully stable condition during the moist curing process. Thus the amount of lime added, relative to the slag, must be sufficient to activate the slag such that any long term slag hydration and release of calcium is avoided. It must also however not be too great such that excess lime is freely available over an extended period because of the low consumption rate of lime due to the slow pozzolanic reaction between the lime and the clay. That is, any expansive reactions involving sulphates must be exhausted during the initial curing period prior to any possible inundation by water.

7. Clear evidence of commercial implications have emerged, upon the understanding of the fundamental material reaction and subsequent behaviour when the amount and type of reactants and curing time are varied in clay - lime - GGBS - sulphate systems. Environmental considerations and viable economic savings, accruing as a result of strength enhancement, reduction in permeability and in the subsequent expansion of hitherto unsuitable sulphate bearing material, by incorporating GGBS, have attracted immediate response from the industry and there are on-going pilot trials. In general, the savings increase with:
    - inclusion of GGBS,
    - increasing GGBS/lime ratio,
    - increasing target strength, and
    - presence of gypsum.

10.2 RECOMMENDATIONS FOR FURTHER WORK

Notwithstanding the achievements highlighted in the previous section, there are, however, further recommended studies on clay - lime - slag - sulphate systems. These include:

1. More investigations on the long term strength and swelling behaviour of the clay-lime-GGBS system in conjunction with SEM (and more sensitive XRD analysis) to study the microstructure with and without the other sulphates studied in the current work, particularly $MgSO_4$ and Na_2SO_4, in a bid to establish :-
    - whether these sulphates can also promote slag hydration such that long-term strength is maintained or even enhanced,
    - if and the conditions under which delayed expansion may occur,
2. Further investigations on the critical lime and slag contents for effective stabilisation. There are several warnings of overdosing the slag in alkali-activated GGBS hydration by adding excess lime (Daimon, 1980; Douglas *et al.,* 1991; Talling, 1989). Here, very low lime levels have been found to activate the slag, the slag hydration being retarded above these levels. This needs further analysis to establish the relevance of the warning in clay - lime - GGBS systems. These investigations should include a much wider range of clay soils than have currently been studied in order to establish the general applicability of the processes involved.
3. Further studies on the nature and magnitude of delayed swelling in clay - lime - GGBS - sulphate systems, the time at which it occurs both in the presence and in the absence of lime and the significance of available lime, GGBS and sulphate. Analysis employing micro-analytical methods and using a wider range of compositions should be conducted in order to fully benefit from the commercial implications of the current work. However, XRD analysis alone is insufficient for monitoring hydration of clay-lime-GGBS mixes especially those of high slag-low lime composition where crystalline products are unlikely to form. Thus, XRD analysis should be accompanied by other analytical methods such as thermogravimetry and/or SEM.

4. The assessment of the commercial implications of the use of lime-activated slag stabilisation in other sectors (in addition to the highways and structural construction sector), such as the control of pH in agriculture and stabilisation of industrial wastes and by-products in the agricultural and in the environmental control sectors respectively.

o

REFERENCES.

ABDI, M. R. (1992) Effects of calcium sulphate on lime stabilised kaolinite. *Ph.D thesis* 1992.

ABSTRACTS (1994) *SCI Construction Materials Group and Cement & Concrete Group of the Institute of Materials,* Belgrave Square, London SW1X 8PS.

AGARWAL, K. B. & SHARMA, S. C. (1973) A method for measuring swelling pressure of an expansive soil. *3rd International Conference on Expansive Soils.*

AKPOKODJE, J. G. (1985) The stabilisation of some arid zone soils with cement and lime. *Q. J. Eng. Geol.* London,1985, **18**, 173 - 180.

AMERICAN CONCRETE INSTITUTE (1995) Ground granulated blast furnace slag as a cementitious constituent in concrete, *ACI Materials Journal,* Committee Report, **ACI.IR-87**, Title No. 84-M34, May-June 1995, 321 - 322.

AMERICAN CONCRETE INSTITUTE (1995) Ground granulated blast furnace slag as a cementitious constituent in concrete. *ACI Materials Journal,* Committee Report, **ACI.226.IR-87**, Title No. 84-M34, July-August 1995, 327 - 341.

ARABI, M & WILD, S. (1986) Microstructural development in cured soil-lime composites. *Journal of Materials Science*, **21**, 497 - 503.

ARABI, M. & WILD, S. (1989) Property changes in clay soils when using lime stabilisation.
Ph.D thesis and also, *Municipal Engineer*, **6** , 85-99.

ARABI, M., WILD, S. & ROWLANDS, G. O. (1989) Frost resistance of lime stabilised clay soil. *Transportation Research Record 1219*, 93 - 102.

BAILEY, J. E. & CHESCOE, D. (1978) *Proceedings of the British Ceramic Society.* **28**, 165 - 177.

BAILEY, J. E. & CHESCOE, D. (1980) A progress report on analytical electron microscopy of the hydration of tricalcium aluminate. *Proceedings 7th Int. Con. on chemistry of cements, Paris,* Vol. **IV**, 595 - 598.

BARBOUR, S. L. & FREDLUND, D. G. (1989) A mechanism of osmotic flow and volume change in clay soils. *Can. Geotech. J.* **26**, 551 - 562.

BARR, T. L., SEAL, S. , HE, H. & KLINOWSKI, J. (1995) X-ray photoelectron spectroscopic studies of kaolinite and montmorillonite: X-Ray photoelectron spectroscopic studies. *Pergamon, 0042-207X(95)00159-X*, **46**, 1391 - 1395.

BARSHAD, I. (1955) Adsorptive and swelling properties of clay-water system. *1st Nat. Conf. Clay & Clay Technology*, Div. of Mines, San Fransisco, **169**, 70 -77.

BAYKAL, G., ARMAN, A. & FERRELL, R. (Year unknown) Accelerated curing of fly ash-lime soil mixtures. *Transportation Research Record.* **1219**, 82 - 92.

BELL, F. G. (1987) Lime stabilisation and clay mineralogy. *Proc. of Foundations and Tunnels*, **II**, 1 - 7.

BELL, F. G. (1988A) Stabilisation and treatment of clay soils with lime Parts I - Basic Principles. *Ground Engineering.* January, **20**, 10-15.

BELL, F. G. (1988B) Stabilisation and treatment of clay soils with lime Part II - Some applications. *Ground Engineering.* March, **22**, 22-30.

BELL, F. G. & COULTHARD J. M. (1990) Stabilisation of clay soils with lime. *Mun. Engr.*, **7**, 125 - 140.

BEN SHALOM, A. (1973) Identification, Mineralogy, Structure, Soil Modification. *3rd International Conference on Expansive Soils,* **Session 1, Division I,**

BENTUR, A. (1976) Effect of gypsum on the hydration and strength of C_3S pastes. *Journal of the American Ceramic Society,* **59**, 210 - 213.

BEST, G. et. al (1996) Distribution of pore sizes in white cement paste from proton nmr spin-lattice relaxation. *Advances in Cement Research*, **8**, No. 32, 163 - 166.

BIJEN, J. G. VAN DER WEGEN & R. VAN SELST (1989) Carbonation of Portland blast furnace slag cement with fly ash. *Proc. SP114 - 31,* Trodheim. 645 - 668.

BIJEN, J. G. (1996) Blast Furnace Slag Cement ISBN 90 - 71806 24 - 3. Association of the Netherlands Cement Industry (VNC).

BLAND, C. H., SHARP, J. H. & BARKER, A. P. (1991/92) Electron probe microanalysis of galsifier slag cement pastes. *Advances in Cement Research*, **4**, No. 16, 159 - 166.

BOLAN, N. S., SYERS, J. K. & SUMMER, M. E. (1993) Calcium-induced sulphate adsorption by soils. *Soil Science Society of America (SSSA),* **57**, 691-696.

BONEN, D. (1993) A microstructural study of the effect produced by magnesium sulphate on plain and silica fume-bearing portland cement. *Cement and Concrete Research*, **23**, 541 - 553.

BRACKLEY, I. J. (1973) Swell pressure and free swell in a compacted clay. *3rd International conference on expansive soils*, 169 - 176..

BROWN, G. (1984) Crystal structures of clay minerals and related phyllosilicates. *Phil. Trans. R. Soc. Lond.* A **311**, 221 - 240.

BRITISH STANDARD (BS) 1377 (1990) Methods of test for Soils for civil engineering purposes.

BRITISH STANDARD (BS) 1924 (1990) Stabilised materials for civil engineering purposes.

BUXTON LIME INDUSTRIES Ltd. (1990) Lime stabilisation services & lime stabilisation manual 2nd Edition.

CAIJUN SHI & DAY, R. L. (1993) Chemical activation of blended cements made with lime and natural pozzolans. *Cement and Concrete Research.* **23**, 1389 - 1396.

CALDARONE, M., GRUBER, K. A. & BURG, R. G. (1994) High reactivity metakaolin: A new generation mineral admixture. *Concrete International*, November 1994. pp. 37.

CIVIL & MARINE SLAG CEMENT LIMITED (1993) Ground granulated blastfurnace slag: manufacture, Specification and Quality. *Fact Sheet 1*, September 1993.

CIVIL & MARINE SLAG CEMENT LIMITED (1993) The effects of ground granulated blastfurnace slag in concrete. *Fact Sheet 2*, September 1993.

CIVIL & MARINE SLAG CEMENT LIMITED (1994) Prevention of ASR using ground granulated blastfurnace slag. *Fact Sheet 3*, June 1994.

CIVIL & MARINE SLAG CEMENT LIMITED (1994) Concrete for marine and highway structures. *Fact Sheet 1*, July 1994.

COBBE, M. I. (1988) Lime-modification of kaolinite-illite clays. *Civil Engineering Technology*, Feb. 1988. 9 - 15.

COLLEPARDI, M., BALDINI, G. & PAURI, M. (1978) Tricalcium aluminate hydration in the presence of lime, gypsum or sodium sulphate. *Cement and Concrete Research*, **8**, 571 - 580.

CROFT, J. B. (1964) The pozzolanic reactivities of some New South Wales flyashes and their application to soil stabilization. *Proc. ARRB, Australia,* 1964, Vol. **2**, Part **2**, Paper No. 120, 1144 - 1167.

DAIMON, M. (1980) Mechanism and kinetics of slag cement hydration. *7th International Congress on the Chemistry of Cement, Paris, France,* Sub-Theme III-2, Vol. I, pp. III-2/1 - III- 2/9.

DENG MIN & TANG MINGSHU (1994) Formation and expansion of ettringite crystals *Cement and Concrete Research.* **24**, 119 - 126.

DEPARTMENT OF TRANSPORT (DTp.) (1994) Design manual for roads and bridges. Vol. 4 - Geotechnics and drainage.

DE SILVA, P. S. & GLASSER, F. P. (1992) Pozzolanic activation of metakaolin. *Advances in Cement Research,* **4**, 167 - 178.

DIAMOND, S. (1996) Delayed ettringite formation - Process and problems. *Cement and Concrete Composites,* **18**, 205 - 215.

DOUGLAS, E., BILODEAU, A. & BRANDSTETR, J. (1991) Alkali activated ground blast-furnace slag concrete: Preliminary investigation. *Cement and Concrete Research,* **21**, 101 - 108.

EDGE, R. A. & TAYLOR, H. F. W. (1971) Crystal Structure of Thaumasite, $[Ca3Si(OH)_6.12H_2O](SO_4)(CO_3)$. *Acta Cryst.* B**27**, 594 - 601.

ENTROY, H. C. (1992) The effect on compressive strength of the glass content of blastfurnace slag when used as a cementitious constituent. *ZEMENK-KALK-GIPS.* Nr. **10**/1992 (45 Jahrgang) 533 - 535.

ESCARIO,V., SAEZ, J. & FISICAS, L. C. (1973) Measurement of the properties of swelling and collapsing soils under controlled suction. *3rd International conference on expansive soils,* 195 - 199.

FANNING, D. S., RABENHORST, M. C. & BIGHAM, J. M. (1993) Colors of acid sulfate soils. *Soil Science Society of America,* SSSA Special Publication No. **31**.

FREARSON, J. P. H. & UREN, J. M. (1986) Investigation of a ground granulated blastfurnace slag containing merwinitic crystllization. *Proc. 2nd International Conference,* Madrid, Spain, 1986. Vol. **2**, SP 91-69, 1401 - 1420.

GABRISOVA, A., HAVLICA, J. & SAHU, S. (1991) Stability of calcium sulphoaluminate hydrates in water solutions with various pH values. *Cement and Concrete Research,* **21**, 1023 - 1027.

GEORGE, S. Z., PONNIAH, D. A. & LITTLE, J. A. (1992) Effect of temeprature on lime-soil stabilisation. *Construction & Building Materials.* **6**, No. 4, 247 - 252.

GEORGE, W. O. & STEELE, D. (1995) Computing applications in molecular spectroscopy. *The Royal Society of Chemistry,* ISBN 0-85404-519-8.

GJORV, O. E. (1989) Alkali activation of a Norwegian granulated blastfurnace slag. *American Concrete Institute, Detroit. Procceedings of the Third International Conference Trondheim, Norway, 1989,* **2**, SP 114 - 73, 1501 - 1517.

GLASSER, F. P. (1996) The role of sulfate mineralogy and cure temperature in delayed ettringite formation. *Cement and Concrete Composites,* **18**, 187 - 193.

GOLDSTEIN, J. I. et al. (1981) Scanning electron microscopy and X-ray microanalysis: A text book for biologists, Materials Scientists, and geologists. Plenum Press, ISBN 0-306-40768-X

GOLLOP, R. S. & TAYLOR, H. F. W. (1992) Microstructural and microanalytical studies of sulfate attack. I:. Ordinary Portland Cement Paste. *Cement and Concrete Research.* **22**, 1027 - 1038.

GOLLOP, R. S. & TAYLOR, H. F. W. (1996) Microstructural and microanalytical studies of sulfate attack. IV: Reaction of a slag cement paste with sodium and magnesium sulfate solutions. *Cement and Concrete Research.* **26**, 1013 - 1028.

GOLLOP, R. S. & TAYLOR, H. F. W. (1996) Microstructural and microanalytical studies of sulfate attack. V: Comparison of different slag blends. *Cement and Concrete Research.* **26**, 1029 - 1044.

GROUNDS, T., NOWELL, D. V. & WILBURN, F. W. (1995) The Influence of Temperature and Different Storage on the Stability of Supersulphated Cement. *Journal of Thermal Analysis*, **45**. 385 - 394.

GRIM, R. E. (1960) Applied Clay Mineralogy., *McGraw Hill Book Company.*

GRIM, R. E. (1968) Clay Mineralogy, 2nd. Edition. *McGraw Hill Book Company.*

HAKKINEN, T. (1993) The Influence of slag content on the microstructure, permeability and mechanical properties of concrete Part I: Microstructural studies and basic mechanical properties. *Cement and Concrete Research*, **23**, 407 - 421.

HALL, C. & CULLEN, D. C. (1996) Scanning force microscopy (SFM) of gypsum dissolution and crystal growth: Materials, interfaces and electrochemical phenomena. *AIChE Journal*, **42**, 232 - 238.

HAMPSON, C. J. & BAILEY, J. E. (1982) On the structure of some precipitated calcium alumino-sulphate hydrates. *Journal of Materials Science*, **17**, 3341 - 3346.

HAMPSON, C. J. & BAILEY, J. E. (1983) The microstructure of the hydration products of tri-calcium aluminate in the presence of gypsum. *Journal of Materials Science*, **18** , 404 - 410.

HAYNES, H., O'NEIL, R. & MEHTA, P. K. (1996) Concrete deterioration from physical attack by salts. *Concrete International,* January. 1996, 63 - 68.

HELLER, L. & BEN-YAIR, M. (1964) Effect of sulphate solutions on normal and sulphate-resisting portland cement. *J. appl. Chem,* **14**, 20 - 30.

HESTERBERG, D. & PAGE, A. L. (1993) Rheology of sodium and potassium illite suspensions in relation to colloidal stability. *Soil Science Society of America (SSSA),* **57**, 697-704 May/June 1993.

HIGGINS, D., KINUTHIA, J. M. & WILD, S. (1998) Soil stabilisation using lime-activated ground granulated blastfurnace slag. Proceedings of the Sixth CANMET/ACI/JCI International Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, Bangkok, Thailand, 31st May – 5th June, 1998, Vol. 2, pp. 1057 - 1074.

HOLLAS, J. M. (1996) Modern Spectroscopy. Third Edition. John Wiley & Sons. ISBN 0 471 96522 7 (or 0 471 96523 5).

HOWARTH, O. (1973) Theory of spectroscopy: An elementary Introduction. Thomas Nelson and Sons Ltd. ISBN 0 17 761035 2/7

HUNTER, D. (1988) Lime-induced heave in sulphate bearing clay soils. *ASCE. J. Geot. Eng.,* No. **114**, No. 2, February 1988, 150 - 167.

INGLES, O. G. & METCALF, J. B. (1972) Soil Stabilization : Principles and Practice. *Butterworths Publishers* 1972.

JACQUES, L., MARC-ANDRÉ, B & MARC CHOQUETTE (1990) Laboratory investigations on the lime stabilisation of sensitive clays: shear strength development. *Can. Geotech. J.* **27**, pp 294 - 304.

JOLICOEUR, C. ET AL. (Year Unknown) Chemical activation of blastfurnace slag: An overview and systematic experimental investigations. 471 - 502.

KALOUSEK, G. L. & BENTON, E. J. (1970) Mechanism of sea water attack on cement pastes. *J. Amer. Conc. Inst. (ACI) Proc. Paris,* **67**, 646 - 648.

KASSIFF, G., BAKER, R. & OVADIA, Y. (1973) Swell-pressure relationships at constant suction changes. *3rd International conference on expansive soils.* 201-208.

KRAHN, J. & FREDLUND, D. G. (1972) On total, matric and osmotic suction. *Soil science,* **114**, 339 - 348.

KUKKO, H. & MANNONEN, R. (1982) Chemical and mechanical properties of alkali-activated blastfurnace slag (F-concrete). *Nord. Concr. Res.* **1**, 16.1 - 16.16.

KUTTI, T. & MALINOWSKI, R. (1982) Influence of the curing conditions on the flexural strength of alkali activated blastfurnace slag mortar. *Nord. Concr. Res.,* **1**, 17.1

KUZEL, H. -J (1996) Initial hydration reactions and mechanisms of delayed ettringite formation in Portland cements. *Cement and Concrete Composites,* **18**, 195 - 203.

LAMBE, T. W., MICHAELS, A. S & MOH, Z. C. (1960) Improvement of soil with alkali metal compounds. *Highway Res. Board Bull.* **241**, 67 - 108.

LANGE, F. (VON) & MÖRTEL, H. (1995) The effect of additions of ultra-fine cement on the strength characteristics of mortars. *ZKG INTERNATIONAL* -Nr. **12**/1995 (48. Jahrgang) 661-666.

LEES, G., ABDELKADER, M. O. & HAMDANI, S. K. (1982) Sodium chloride as an additive in lime-soil stabilisation. *Journal of the Institution of Highway and Transportation*, December 1982, 2 - 8.

LEES, G., ABDELKADER, M. O. & HAMDANI, S. K. (1983) Reactions in lime-sodium chloride treated soils. *Journal of the institution of highway and transportation*, December 1983, 8 - 16.

LI, G., LE BESCOP, P & MORANVILLE, M. (1996A) The U-Phase Formation in Cement-Based Systems Containing High Amounts of Na_2SO_4. *Cement and Concrete Research*, **26**, No.1, 27 -33.

Ll, G., LE BESCOP, P & MORANVILLE, M. (1996B) Expansion mechanism associated with the secondary formation of the U-Phase Formation in Cement-Based Systems Containing High Amounts of Na_2SO_4. *Cement and Concrete Research*, **26**, No.2, 195 - 201.

LITTLETON, I. (1991) Some research trends with lime stabilisation (*Unpublished work*).

LITTLETON, I. & WILLAVISE, G. (1992) Some observations on the use of lime to stabilise Kimmeridge Clay. *Buxton Lime Industries Report Reference No. **91**.*

MACPHEE, D. E., ATKINS, M. & GLASSER, F. P. (1989) Phase development and pore solution chemistry in ageing blastfurnace slag-portland cement blends. *Materials Research Society Symposium Proceedings,* **127**, pp. 475 - 480.

MACTAVISH, J. C. et al (1996) Nuclear magnetic resonnance study of hydration of synthetic white cement: continuous quantitative monitoring of water and $Ca(OH)_2$ during hydration. *Advances in Cement Research*, **8**, No. 32, 155 - 161.

MARTYN, S. R. (1988) Engineering Experimentation : Ideas, Techniques and Presentation. *McGraw-Hill Publishers, London (1988).*

MATSUSHITA, I., SUZUKI, T., MORIGA, T., ASHIDA, T. NAKABAYASHI, I. & METSON, J. (1993) XPS study on the carbonation process of $CA(OH)_2$. *Journal of the Ceramic Society of Japan, Int. Edition.* Vol. **101**, 707 - 709.

McCALLISTER, L. D. & PETRY, T. M. (1992) Leach tests on lime-treated clays. *Geotechnical Testing Journal, GTJODJ,* **15**, No. 2, 106 - 114.

MEHTA, P. K. (1973A) Effect of Lime on Hydration of Pastes Containing Gypsum and Calcium Aluminates or Calcium Sulphoaluminates. *Journal of The American Ceramic Society,* **56**, 315 - 319.

MEHTA, P. K. (1973B) Mechanism of Expansion Associated with Ettringite Formation. *Cement and Concrete Research,* **3**, 1 - 6.

MEHTA, P. K. (1976) Scanning Electron Micrographic Studies of Ettringite Formation. *Cement and Concrete Research,* **6**, 169 - 182, 1976.

MEHTA, P. K. (1983) Mechanism of sulphate attack on Portland cement. *Cement and Concrete Research,* **13,** 401 - 406.

MITCHELL, J. K. (1973) Recent advances in the understanding of the influences of mineralogy and pore solution chemistry on the swelling and stability of clays. *3rd International Conference on Expansive Soils.* Vol. 2. 11-25.

MITCHELL, J. K. (1986) Practical problems from surprising soil behaviour. The twentieth Karl Terzaghi Lecture, ASCE *J. Geotech. Eng.,* **112,** No. 3. , March 1986.

MITCHELL, J. K. (1990) Clay soil heave caused by lime-sulfate reactions. ASTM Symposium on innovations and users of lime. San Fransisco, June, 1990.

ODLER, I. & YAOXIN CHEN (1996) On the delayed expansion of heat cured Portland cement pastes and concretes. *Cement and Concrete Composites,* **18**, 181 - 185.

OBIKA, B. & FREER-HEWISH, R. J. (1990) Soluble salt damage to thin bituminous surfacings of roads and runways. *Australian Road Research,* **20**, 24 - 41.

PACHENKO, A. I. (1990) Control of expansion and structure formation of expansive cement., *Cement and Concrete Research,* **20**, pp. 602 - 609.

PERRY, J., SNOWDON, R. A. & WILSON, P. E. (1995) Site investigation for lime stabilisation of highway works. *Extracts from Highway Agency, DOT conducted by Transport Research Laboratory, Road Engineering and Environmental Division,* Crown Copyright 1995, London.

REGOURD, M. (1980) Structure and behaviour of slag Portland cement hydrates. *7th International Congress on the Chemistry of Cement, Paris, France,* Sub-Theme III-2, Vol. I, pp. III - 2/10 - III - 2/26.

RICHARDSON, I. G., BROUGH, A. R., GROVES, G. W. & DOBSON, C. M. (1994) The characterization of hardened alkali-activated blast-furnace slag pastes and the nature of the calcium silicate hydrate (C-S-H). *Cement and Concrete Research,* **24**, 813 - 829.

ROBBINS, J. (1990) .... Just Add Lime. *New Civil Engineer (NCE),* Roads Supplement, May 1990.

ROBBINS, J. (1990) New M40 faces rebuild as lime base heaves. *New Civil Engineer*, **5** July 1990.

ROGERS, C. D. F. (1988) Lime stabilisation. *Ground Engineering*, April 1988, 7 - 10.

ROSSATO, G., NINIS, N. L. & JARDINE, R. J. (1992) Properties of some kaolin-based clay soils. *American Society for Testing and Materials Geotech. Testing Journal*, **GTJODJ, 15**, June 1992, 166 - 179.

SAKIYAMA, M. & MITSUDA, T. (1977) Hydrothermal reaction between C-S-H and kaolinite for the formation of tobermorite at 180°C. *Cement and Concrete Research*, **7**, 681 - 686.

SATO, K. & KOIBUCHI (1986) Properties of very fine blastfurnace slag prepared by classification. *Nippon Kokan K.K and Dai-ichi Cement Co. Ltd. Kawasaki, Japan.*

SCOTT, V. D. & LOVE, G. (1983) Quantitative Electron-Probe Microanalysis. First Published by Ellis Horwood Ltd., Distributed by John Wiley & Sons Ltd. ISBN 0-85312-514-7 (or 0-85312-672-0 or 0-470-27510-3).

SHAO-DONG WANG, XIN-CHENG PU, SCRIVENER, K. L. & PRATT, P. L. (1995) Alkali-activated slag cement and concrete: a review of properties and problems. *Advances in Cement Research*, 7, July 1995, 93 - 102.

SHAYAN, A. & IVANUSEC, I. (1996) An Experimental clarification of the association of delayed ettringite formation with alkali-aggregate reaction. *Cement and Concrete Composites*, **18**, 161 - 170.

SHERWOOD, P. T. (1962) Effect of sulphates on cement- and lime-stabilised soils. *Building and Highway Research Board.* **353**, 98-107.

SHERWOOD, P. T. (1992) Stabilised capping layers using either lime, or cement, or lime and cement. *Contractor Report* **No. 151**; *Transport Research Laboratory 1992.*

SINGH, N. B. & ABHA, K. M. (1983) Effect of sodium carbonate on the hydration of tricalcium silicate. *Journal of the American Ceramic Society*, **66**, 308 - 310.

SIVAPULLAIAH, P. V., SRIDHARAN, A. & RAMESHI, H. N. (1987) Effects of sulphate on the volume change behaviour of lime treated kaolinitic soils. *Unknown Publication*, 140 - 159.

SLOANE, R. L. (1965) Early reactions in the kaolinite-hydrated lime-water system. *Proc. 6th Int. Conf. Soil Mech. & Found. Eng.; Montreal*, **1**, 121 - 125.

SMITH, R. W. & NARIMATSU, Y. (1993) Electrokinetic behaviour of kaolinite in surfactant solutions as measured by both the microelectrophoresis and streaming potential methods. *Minerals Engineering.* **6**, 753 - 763.

MITH, C. J., PEOPLES, M. B., KEERTHISINGHE, G., JAMES, T. R., GARDEN, . L. & TUOMI, S. S. (1994) Effect of surface applications of lime, gypsum and ıosphogypsum on the alleviating of surface and subsurface acidity in a soil under ısture. *Aust. J. Soil Res.*, **32**, 995-1008.

MOLCZYK, H. G. (1980) Slag structure and identification of slags. *Proc. 7th Int. onf. on the Chemistry of Cement", Paris. France,* pp III - 1/3 - III - 1/17.

NEDKER, E. A. & TEMPORAL, J. (1990) M40 Motorway Banbury IV Contract - ime Stabilisation. *Highway and Transportation,* **December, 1990.** 7 - 8.

RIDHARAN, A., RAO, A. S. & SIVAPULLAIAH, P. V. (1986) Swelling pressure of ays. *Geotechnical Testing Journal,* (ASTM) **GTJODJ, 9,** 24 - 33.

TREVENS, G. & LITTLETON, I. (1989) The Influence of Sulphate on Lime tabilised Gault Clay. *ICI General Chemicals Rep.* **No. 8886**. June, 1989.

WAMY, R. N. & BOUKNI, A. (1990) Some engineering properties of slag concrete as ıfluenced by mix proportioning and curing. *Technical Paper, ACI Materials Journal,* **7-M23**, 210 - 220.

ALLING, B. (1989) Effect of curing conditions on alkali-activated slags. 1989 rondheim Conference, SP 114-72, pp. 1485 - 1499.

AYLOR, H. F. W. (1973) Crystal structure of some double hydroxide minerals. *lineralogical Magazine*, **39**, 377 - 389.

AYLOR H. F. W. (1990) Cement Chemistry, *Academic Press Inc.* Harcourt Brace ɔnovich Publishers, 1990, **ISBN 0-12-683900-X.**

AYLOR H. F. W. (1993) Nanostructure of C-S-H: Current structure. *Advanced Cement ased Materials,* **1**, 38-46.

AZAWA, E.; MIGAZAWA, S. & KASAI, T. (1995) Chemical shrinkage and ıtogeneous shrinkage of hydrating cement paste. *Cement and Concrete Research,* **25,** o.2 288 - 292.

RANSPORTATION RESEARCH RECORD (1993) Environmental Issues Related to laterials and Stabilisation. Transportation Research Board, National Research Council. ecord No. 1424 - Soils, Geology and Foundations

AN LIER, J. A, DEBRUTN, P. L. & OVERBEEK, J. T. G. (1960) The solubility of uartz. *J. of Physical Chemistry*, 64, 1960.

IJAYVERGIYA, V. N. & GHAZZALY, O. I. (1973) Prediction of swelling potential ɪr natural clays. *3rd International Conference on Expansive Soils*, 227 - 236.

WALTER, C. McRONE & JOHN GUSTAV DELLY The electron microscopy atlas: An encyclopaedia of techniques for small particle identification, Vol. I - IV, Second Edition, Ann *Arbor Science Publishers.*

WANG LAN & GLASSER, F. P. (1996) Hydration of Calcium Sulphoaluminate Cements. *Advances in Cement Research,* **8**, 127 - 134.

WARKETIN, B. P. & SCHOFIELD, R. K. (1962) Swelling pressure of Na-Montmorillonite in NaCl solutions. *Journal of Soil Science,* **13**, 98 - 105.

WASWA, B., WILD, S., JONES, G. I. & WEBB, D. T. W. (1993) The potential of lime-stabilised murram soil as a building material in Kenya. *Building and Research Information,* **21**. 288 - 295.

WESLEY, Wm WENDLANDT (1986) Thermal Analysis. *3rd Edition John Wiley & Sons.*

WILD, S., ARABI, M. & LENG WARD, G. (1986) Soil-lime reaction and microstructural development at elevated temperatures. *Clay Minerals,* **21**, 279 - 292.

WILD, S., ARABI, M. & ROWLANDS, G. O. (1987) Relation between pore size distribution, permeablility, and cementitious gel formation in cured clay-lime systems. *Materials Science Technology,* **3**, 1987.

WILD, S., HADI, M. & LENG WARD, G. (1990A) Expansion mechanisms and cementation in cured PFA-lime composites.
Part 2: Microstructural development, cementation and reaction mechanism. *Advances in Cement Research,* **3**, 63 - 74.

WILD, S., HADI, M. & LENG WARD, G. (1990B) The influence of gypsum content on microstructural development, strength and expansion of cured PFA-lime mixes. *J. Advances in Cement Research,* **3**, 153 - 166.

WILD, S., ABDI, M. R., & LENG WARD, G. (1993A) Sulphate expansion of lime-stabilised kaolinite. Part I - Physical characteristics. *Clay Minerals* , **28**, 555 - 567.

WILD, S., ABDI, M. R. & LENG WARD, G. (1993B) Sulphate expansion of lime-stabilised kaolinite. Part II - Reaction Products and Expansion. *Clay Minerals,* **28**, 569 - 583.

WILD, S., KINUTHIA, J. M., ROBINSON, R. B. & HUMPHREYS, I. (1996) Effects of ground granulated blastfurnace slag (ggbs) on the strength and swelling properties of lime stabilised kaolinite in the presence of sulphates. *Clay Minerals,* **31**, 423 - 433.

WILD, S. & KHATIB, J. M. (1997) Portlandite consumption in metakaolin cement pastes and mortars. *Cement and Concrete Research,* **127**, 137 - 146.

XUEQUAN WU, WEIMIN JIANG & ROY, D. M. (1990). Early activation of slag cement. *Cement and Concrete Research*, **20**, 961 - 974.

YAN FU, JIAN DING & BEAUDOIN, J. J. (1996) Effect of different calcium aluminate hydrates on ettringite formation and expansion of high alumina cement-based expansive cement pastes. *Cement and Concrete Research*, **26**, 417 - 426.

APPENDICES

APPENDIX 1 - SULPHATE CONVERSIONS

The formula weights for the four sulphates are:-

Calcium sulphate (gypsum) $CaSO_4.2H_2O$ = 40 + 32 + 4 x 16 + 2 x (18) = 172 g

Magnesium sulphate ($MgSO_4$) = 24 + 32 + 4 x 16 = 120 g

Sodium sulphate (Na_2SO_4) = 2 x 23 + 32 + 4 x 16 = 142 g

Potassium sulphate (K_2SO_4) = 2 x 39 + 32 + 4 x 16 = 174 g

For each of these sulphates, the sulphate content may be presented as SO_3 or as SO_4

e.g. for gypsum,

SO_3 content = (32 + 3 x 16)/172= 0.465 ; SO_4 = (32 + 4 x 16)/172=0.558

Therefore for gypsum, the SO_3:SO_4 ratio is 1:1.2

Table 1 - Amount of sulphate as SO_3 or as SO_4 for various sulphates per gram of sulphate.

	SO_3	SO_4
Calcium sulphate	0.465	0.558
Magnesium sulphate	0.667	0.800
Sodium sulphate	0.563	0.676
Potassium sulphate	0.460	0.552

In other words, 1 g of gypsum would provide 0.465g of sulphate as SO_3 or 0.558g as SO_4, while 1 g of magnesium sulphate would provide 0.667 or 0.800 as SO_3 or SO_4 respectively. Therefore to provide a given SO_3 or SO_4 concentration, a larger quantity (weight) of gypsum would have to be added than magnesium sulphate. The table below shows the quantities of the various sulphates to be added in order to provide the equivalent of 2, 4, 6 and 8 wt.% of gypsum.

TABLE 2

Amount aimed at in (wt.% Gypsum)	2	4	6	8
Equivalent in % SO_3	0.93	1.86	2.79	3.72
% SO_4	2.79	2.23	3.348	4.464
wt.% $MgSO_4$	1.394	2.790	4.183	5.577
wt.% Na_2SO_4	1.651	3.310	4.956	6.607
wt.% K_2SO_4	2.020	4.040	6.065	8.087

ETTRINGITE AND MONOSULPHATE FORMATION

In the formation of ettringite (see Chapter 3),

$$\mathbf{2Al(OH)_4^- + 3Ca^{2+} + 3Ca^{2+}\ 3SO_4^{2-} + 26H_2O + 4OH^- \longrightarrow AFt.}$$

or $3Ca(OH)_2$ combines with $3CaSO_4.2H_2O$ to form AFt. Thus, to form ettringite,

3[40 + (17)x2] g of hydrated lime combines with 3[40 +32 + 16x4 + 2(18)]g of gypsum i.e. 222g of hydrated lime and 516g of gypsum.

Therefore for 6wt.% lime, 516/222 x 6 wt.% of gypsum would be required to fully react and form ettringite. i.e. **13.946** wt.% gypsum. From Table 1, this would be equivalent to **7.782** wt.% SO_4 and **6.48** wt.% SO_3.

Likewise, 4wt.% and 2wt.% lime would require **4.33**wt.% and **2.16**wt.% SO_3 respectively.

From the reaction of ettringite to form monosulphate, 1 unit of ettringite yields 3 units of monosulphate. i.e.

$$\mathbf{AFt + 4Al(OH)_4^- + 6Ca^{2+} + 8OH^- \longrightarrow 3AFm + 8H_20}$$

Therefore, the formation of monosulphate would require one third of the sulphate required for ettringite formation i.e **4.649** wt.% gypsum [or **2.59** wt.% SO_4 or **2.16** wt.% SO_3]

APPENDIX 2 - SAMPLE MATERIAL COMPUTATIONS

Sample material components were computed from the MDD and OMC obtained from the proctor tests together with the pre-determined sample dimensions.

Example

For a sample of dimensions 53 mm in diameter (d) × 103 mm in height (h), and for MDD (ρ_d) = 1.49 Mg/m^3 and OMC (ω) = 24.8%,

$$\text{Sample volume (V)} = \frac{\pi d^2 h}{4} = \frac{\pi \text{ x } 0.053^2 \text{ x } 0.103}{4} = 0.000227 \text{ m}^3$$

Sample bulk density $\rho_b = \rho_d\,(1 + \omega)$

$$= 149 \times (1 + 0.248) = 1.86 \text{ Mg/m}^3$$

Weight of sample = Volume × density = 0.000227 × 1.86 Mg

= 422 g

Assuming a sample contains 6wt.% lime and 4wt.% gypsum, and K is the weight (in g) of clay (say kaolinite) alone, then

$$K + 0.06K + 0.04K + 0.248(K + 0.06K + 0.04K) = 422 \text{ g}$$

$$\therefore K = 307.40 \text{ g}$$

$\therefore$ Clay (say Kaolinite) = 307.40 g,

Lime = 0.006K = 18.44 g,

Gypsum = 0.004K = 12.30 g,

& Water = 0.248 x 1.1K = 84.86 g

TOTAL = 422.00 g

APPENDIX 3 - INITIAL CONSUMPTION OF LIME & ATTERBERG LIMITS

Kaolinite-Lime system	Amount of Kaolinite (g)	Amount of Lime (%)	Observed pH at T = 22°C	Corrected pH to T = 25°C	pH after calibration
1	20.0	0	4.83	4.74	4.89 (7.43)*
2	20.0	2	11.84	11.75	12.11 (10.22)
3	20.0	3	11.90	11.81	12.17 (10.33)
4	20.0	4	11.99	11.90	12.27 (12.37)
5	20.0	5	12.02	11.93	12.30 (12.4)
6	20.0	6	12.11	12.02	12.39 (12.4)
7	0.0	100	12.12	12.03	12.40 (12.4)

Table A 3-1 pH readings for various kaolinite-lime-water systems.

[( ) Results obtained using Kimmeridge Clay*]*

* Results from an independent and better calibration of the pH meter gave these values as5.9 and 9.6 respectively.

ATTERBERG LIMITS

	Lime Content (%)	Sulphate Content (Wt.% SO_3)	Liquid Limit (LL) (%)	Plastic Limit (PL) (%)	Plasticity Index (PI) (%)
Kaolinite Only	0	0	61	32	29
Kaolinite - Lime	3	0	72	39	33
	6	0	73	41	32
	14	0	73	41	32
	20	0	71	44	27
Kaolinite - Lime - Calcium Sulphate (Gypsum ($CaSO_4.2H_2O$))	6	0.93	71	40	31
		1.86	68	39	29
		2.79	67	45	22
Kaolinite - Lime - Magnesium Sulphate ($MgSO_4$)	6	0.93	70	41	29
		1.86	67	43	24
		2.79	65	45	20
Kaolinite - Lime - Sodium Sulphate ($Na_2SO_4.10H_2O$)	6	0.93	59	33	26
		1.86	58	34	24
		2.79	58	34	24
Kaolinite - Lime - Potassium Sulphate (K_2SO_4)	6	0.93	61	35	26
		1.86	62	34	28
		2.79	64	36	28
Kimmeridge Clay Only	0	1.73	(65)	(33)	(32)
Kimmeridge Clay - Lime	4	1.73	(70)	(43)	(27)
	5	1.73	(66)	(42)	(23)
	6	1.73	(71)	(47)	(24)

( ) Results after mellowing for 3 days (72 hours)

Table A 3-2 Atterberg limits (% moisture content) for kaolinite - lime and Kimmeridge Clay - lime mixes with varying amounts of different metal sulphates *(Lumpy Standard Porcelain).*

ATTERBERG LIMITS

	Lime Content (%)	Slag Content (%)	Sulphate Content (Wt.% SO_3)	Liquid Limit (LL)(%)	Plastic Limit (PL)(%)	Plasticity Index (PI) (%)
Kaolinite*-Lime-Slag TS = 6 WT.%	6	0	0	84 (82)	40 (45)	44 (37)
	5	1	0	84 (83)	40 (41)	44 (42)
	4	2	0	85 (84)	40 (36)	45 (48)
	3	3	0	84 (83)	38 (38)	46 (45)
	2	4	0	83(83)(84)	38(36)(36)	45(47)(48)
	1	5	0	83 (80)	35 (35)	48 (45)
	0	6	0	54 (57)	28 (30)	26 (27)
	0	0	0	60	31	29

(a)

	Lime Content (%)	Slag Content (%)	Sulphate Content (Wt.%SO_3)	Liquid Limit (LL) (%)	Plastic Limit (PL) (%)	Plasticity Index (PI) (%)
Kaolinite*-Lime-GGBS-Gypsum TS = 6 WT.%	6	0	3.72	86 (91)	40 (41)	46 (50)
	5	1	3.72	85 (89)	39 (44)	46 (45)
	3	3	3.72	81 (94)	35 (57)	46 (37)
	2	4	3.72	92 (107)	40 (59)	52 (48)
	1	5	3.72	85 (87)	35 (54)	50 (33)
	0	6	3.72	66 (66)	28 (30)	38 (36)

(b)

Kimmeridge Clay - Lime-GGBS	1	4	1.73	(79)	(43)	(37)
	2	3	1.73	(75)	(50)	(25)
	3	2	1.73	(70)	(50)	(20)
	5	0	1.73	(66)	(42)	(24)

(c)

TS Total stabiliser content ( ) Results after mellowing for 3 days (72 hours)

Table A 3-3 Atterberg limits (% moisture content) for (a) kaolinite - lime - GGBS, (b) kaolinite - lime - GGBS - gypsum and (c) Kimmeridge Clay - lime - GGBS mixes.

* *(Powdery Standard Porcelain).*

APPENDIX 4 - PROCTOR (BS) COMPACTION

	Lime Content (%)	Sulphate Content (Wt.% SO_3)	Maximum Dry Density (MDD) (Mg/m^3)	Optimum Moisture Content OMC) (%)
Kaolinite Only	0	0	1.545	24.0
Kaolinite - Lime	6	0	1.490	25.0
	14	0	1.470	27.0
	20	0	1.440	28.0
Kaolinite - Lime - Calcium Sulphate (Gypsum ($CaSO_4.2H_2O$))	6	0.93	1.420	27.8
		1.86	1.412	28.4
		2.79	1.420	29.0
Kaolinite - Lime - Magnesium Sulphate ($MgSO_4$)	6	0.93	1.400	28.0
		1.86	1.390	29.2
		2.79	1.378	30.0
Kaolinite - Lime - Sodium Sulphate ($Na_2SO_4.10H_2O$)	6	0.93	1.465	24.8
		1.86	1.490	26.6
		2.79	1.483	24.8
Kaolinite – Lime – Potassium Sulphate (K_2SO_4)	6	0.93	1.425	27.6
		1.86	1.445	26.4
		2.79	1.470	26.0

Table A 4-1 Maximum dry density (MDD) and optimum moisture content (OMC) for various kaolinite - lime - sulphate systems *(Lumpy Standard Porcelain).*

PROCTOR (BS) COMPACTION

	Lime Content (%)	Slag Content (%)	Added Gypsum Content (Wt.% SO_3)	Optimum Moisture Content (OMC) (%)	Maximum Dry Density (Mg/m^3) (%)
Kaolinite- Lime - Slag	6	0	2.79 (6wt.%)	30	1.420
	5	1	2.79	30.5	1.410
	3	3	2.79	31	1.400
	2	4	2.79	31	1.430
	6	0	0	29	1.460
	5	1	0	30.6	1.400
	3	3	0	30	1.423
	2	4	0	31	1.410
	0	0	0	26	1.500

(a)

	Lime Content (%)	Slag Content (%)	Inherent Gypsum Content (% SO_3)	Optimum Moisture Content (OMC) (%)	Maximum Dry Density (Mg/m^3) (%)
Kimmeridge Clay - Lime - Slag	0	0	1.73	22.32	1.570
	4	0	1.73	27.60	1.360
	5	0	1.73	24.20	1.430
	6	0	1.73	28.00	1.370
	1	4	1.73	20.50	1.430
	2	3	1.73	21.70	1.420
	3	2	1.73	25.20	1.410

(b)

Table A 4-2 Maximum dry density (MDD) and optimum moisture content (OMC) for various (a) Kaolinite - lime - slag - gypsum and (b) Kimmeridge Clay - lime - slag systems.

SULPHATE CONTENT (% SO_3)	CURING TIME (Weeks)								
	0	1	2	3	4	5	6	10	20
0	806.24	849.8	1015.3	1355.48	-	1419.83	1340.79	2013.64	2362.92
0.93	784.70	1282.07	1575.03	1223.6	1581.13	1536.11	1198.83	2263.86	2160.58
1.86	697.57	1063.20	2070.67	2173.71	2062.59	2185.21	2327.42	2547.46	2715.60
2.79	630.56	1199.07	1512.12	1751.01	2591.52	2342.40	2371.72	3346.36	3237.84
3.72	599.66	1194.4	1510.70	1863.13	2383.70	1948.29	2049.13	2592.98	3190.68

TABLE A5-1 Average Unconfined Compressive Strength (UCS (kN/m^2)) of kaolinite - 6wt.% lime - Gypsum system.

SULPHATE CONTENT (% SO_3)	CURING TIME (Weeks)								
	0	**1**	**2**	**3**	**4**	**5**	**6**	**10**	**20**
0	806.24	849.8	1015.3	1355.48	-	1419.83	1340.79	2013.64	2362.92
0.93	-	1411.55	1432.30	1597.05	1362.09	1864.34	1835.46	1937.76	1883.18
1.86	992.26	1393.91	1431.80	1751.50	1267.37	1855.93	1749.30	2167.84	1773.53
2.79	1136.17	1364.78	1611.50	1474.19	1447.02	1475.66	1288.90	1331.01	1498.42
3.72	1094.63	1711.36	1855.77	1551.78	1658.98	1377.33	1715.26	1319.75	1498.09

TABLE A5-2 Average Unconfined Compressive Strength (UCS (kN/m^2)) of kaolinite-6wt.%lime - Magnesium Sulphate system.

SULPHATE CONTENT (% SO_3)	**CURING TIME (Weeks)**								
	0	**1**	**2**	**3**	**4**	**5**	**6**	**10**	**20**
0	806.24	849.8	1015.3	1355.48	-	1419.83	1340.79	2013.64	2362.92
0.93	669.17	1330.51	1612.97	1618.84	1581.13	1829.82	1904.70	2421.16	2377.11
1.86	309.38	1499.90	1797.03	2210.67	2062.59	2431.69	2111.79	2597.23	2694.80
2.79	358.33	1731.65	1498.91	2025.14	2591.52	1497.44	2149.74	2346.76	2165.96
3.72	329.45	1096.60	1097.82	1824.93	2383.70	1841.74	1758.86	1784.06	1765.21

TABLE A5-3 Average Unconfined Compressive Strength (UCS (kN/m^2)) of kaolinite - 6wt.%lime - Sodium Sulphate system.

SULPHATE CONTENT (% SO_3)	**CURING TIME (Weeks)**								
	0	**1**	**2**	**3**	**4**	**5**	**6**	**10**	**20**
0	806.24	849.8	1015.3	1355.48	-	1419.83	1340.79	2013.64	2362.92
0.93	-	1168.22	1146.46	1420.58	1499.40	1470.77	1493.00	1888.82	1930.05
1.86	-	1334.70	1544.43	1669.51	1746.62	1798.49	2123.54	1793.85	2198.58
2.79	-	1221.39	1312.90	1576.74	1951.71	2218.99	2086.33	2162.24	2274.80
3.72	-	1227.01	1294.29	1665.34	1815.88	1963.46	1993.58	2099.60	2111.79

TABLE A5-4 Average Unconfined Compressive Strength (UCS (kN/m^2)) of kaolinite - 6wt.%lime - Potassium Sulphate system.

UNCONFINED COMPRESSIVE STRENGTH (UCS)

Gypsum Content (wt.%)	1 week curing	4 weeks curing
0 %	6L0S0G 555.12 5L1S0G 495.64 3L3S0G 611.41 2L4S0G 652.04 1L5S0G 776.38 0L6S0G 124.876	6L0S0G 699.52 5L1S0G 804.28 3L3S0G 963.374 2L4S0G 1272.26 1L5S0G 1907.66 0L6S0G 116.51
2 %	6L0S2G 823.86 5L1S2G 764.48 3L3S2G 1304.57 2L4S2G 1412.75 1L5S2G 1708.42 0L6S2G 121.89	6L0S2G 1112.19 5L1S2G 1260.51 3L3S2G 1417.65 2L4S2G 1609.05 1L5S2G 1915.98 0L6S2G 145.88
4 %	6L0S4G 591.83 5L1S4G 822.88 3L3S4G 1074.98 2L4S4G 1132.26 1L5S4G 1445.55 0L6S4G 107.69	6L0S4G 1677.10 5L1S4G 1656.78 3L3S4G 1737.30 2L4S4G 1702.35 1L5S4G 1874.37 0L6S4G 126.79
6 %	6L0S6G 723.26 5L1S6G 734.28 3L3S6G 1039.74 2L4S6G 1021.39 1L5S6G 1311.42 0L6S6G 120.13	6L0S6G 1365.26 6L4S6G 2650.26 5L1S6G 1638.18 3L3S6G 1674.16 2L4S6G 1716.74 1L5S6G 1767.65 0L6S6G 102.80

6L0S6G ... 6 wt.% lime, 0 wt.% slag, 6 wt.% gypsum

Table A5-5 Average Unconfined compressive strength (UCS) for kaolinite - lime - GGBS - gypsum system for mixes with a total stabiliser (TS) content of 6 wt.%

UNCONFINED COMPRESSIVE STRENGTH (UCS)

Total Stabiliser Content	1 week curing	4 weeks curing
5 %	5L0S 1006.94 3L2S 1352.05 2L3S 1384.36 1L4S 1061.28 0L5S 505.67	5L0S 2000.67 3L2S 1667.58 2L3S 1690.31 1L4S 911.97 0L5S 653.02
6 %	6L0S 1012.33 3.6L2.4S 1697.16 2.4L3.6S 1473.45 1.2L4.8S 1431.35 0L6S 491.48	6L0S 2002.62 3.6L2.4S 2418.72 2.4L3.6S 2229.76 1.2L4.8S 1985.49 0L6S 534.07
8 %	8L0S 1058.34 4.8L3.2S 1727.51 3.2L4.8S 2019.76 1.6L6.4S 2069.20 0L8S 475.81	8L0S 2191.56 4.8L3.2S 3101.59 3.2L4.8S 3158.38 1.6L6.4S 2638.51 0L8S 1141.56
10 %	10L0S 1014.28 6L4S 2021.71 4L6S 2502.42 2L8S 2405.50 0L10S 586.93	10L0S 2072.14 6L4S 3203.41 4L6S 3424.19 2L8S 3078.10 0L10S 1676.60

Table A5-6 Average Unconfined compressive strength for Kimmeridge Clay at various stabiliser contents

APPENDIX 6 - LINEAR EXPANSION DURING MOIST CURING AND DURING SOAKING

	KAOLINITE - 6WT.% LIME		KAOLINITE ONLY
	MOIST CURING	SOAKING	
Day			
1	0.019	0.066	-0.013
2	-0.015	0.048	-0.142
3	-	0.028	-0.259
4	-	0.011	-
5	-0.044	-	-
6	-0.045	-	-0.421
7	-0.048	-0.163	-0.422 Moist Curing
	-	SOA	KING
8	-	3.283	COLLAPSE
9	-	3.361	
10	-	3.406	
11	-	3.435	
12	-	-	
13	-	-	
14	-0.071	3.442	
15	-	3.475	
16	-	3.489	
17	-	3.499	
18	-	3.508	
19	-	-	
20	-0.086	-	
21	-	3.514	
22	-	-	
23	-	3.523	
24	-	3.526	
25	-	-	
26	-	-	
27	-0.097	-	
28	-	3.540	
29	-	-	
30	-	-	
31	-	3.550	
32	-	-	
33	-	-	
34	-0.107	-	
35	-	-	
36	-	-	
37	-	-	
38	-	-	
39	-	-	
40	-	-	
41	-	-	
42	-	3.567	
43	-	-	
44	-0.122	-	
45	-	-	
46	-	3.588	
47	-		
48	-		
49	-		
54	-		
55	-0.132		
56			

Table A6-1 Linear expansion during moist curing for kaolinite - 6wt.% lime and during soaking for kaolinite only.

LINEAR EXPANSION DURING MOIST CURING

Sulphate level (% SO_3)	GYPSUM				MAGNESIUM SULPHATE			
	0.93	1.86	2.79	3.72	0.93	1.86	2.79	3.72
Day								
1	0.640	0.607	0.062	0.166	0.511	0.427	-0.057	-0.046
2	0.905	-	0.168	0.328	0.717	-	0.019	0.009
3	-	-	0.236	0.422	-	-	0.085	0.049
4	-	1.186	0.320	0.526	-	0.932	0.154	0.101
5	1.232	1.332	0.386	0.604	1.029	1.087	0.217	0.150
6	1.229	1.429	0.460	0.681	1.059	1.199	0.292	0.205
7	1.224	1.546	0.522	0.744	1.061	1.338	0.358	0.256
8	1.217	1.628	-	-	1.061	1.445	-	-
9	1.208	-	-	-	1.091		-	-
10	-	-	0.717	0.924	-		0.571	0.413
11	-	1.888	0.783	0.987	-	1.789	0.644	0.467
12	1.165	1.978	0.851	1.05	1.029	1.912	0.717	0.517
13	1.155	2.03	-	-	1.026	2.003	-	-
14	1.152	2.068	0.980	1.175	1.015	2.118	0.851	0.607
15	1.136	2.075	-	-	1.011	2.208	-	-
16	1.127	-	-	-	1.004	-	-	-
18	-	2.072	-	-	-	2.353	-	-
19	1.099	2.072	-	-	0.994	2.374	-	-
20	1.092	2.065	1.410	1.575	0.983	2.388	1.295	0.746
21	1.083	2.060	-	-	0.981	2.395	-	-
22	1.078	2.060	-	-	0.978	2.398	-	-
23	1.073	-	-	-	0.975	-	-	-
25	-	2.060	-	-	-	2.405	-	-
26	1.059	2.059	-	-	0.969	2.406	-	-
27	1.058	2.059	1.621	1.942	0.967	2.407	1.484	0.761
28	1.058	2.059	-	-	0.966	2.403	-	-
29	1.049	2.059	-	-	0.963	2.395	-	-
30	1.046	-	-	-	0.955	-	-	-
32	-	2.059	-	-	-	2.393	-	-
33	1.046	2.060	-	-	0.954	2.393	-	-
34	1.046	2.062	1.616	2301	0.954	2.393	1.524	0.749
35	1.046	2.064	-	-	0.953	2.392	-	-
36	1.046	-	-	-	0.954	-	-	-
41	-	2.066	1.604	2.535	-	2.390	1.524	0.727
42	1.046	2.069	-	-	0.954	2.391	-	-
43	1.046	2.071	-	-	0.956	2.391	-	-
44	1.046	-	1.605	2.584	0.959	-	1.518	0.718
47	-	2.071	-	-	-	2.391	-	-
48	1.046	-	-	-	0.961	-	-	-
49	-	2.071	-	-	-	2.391	-	-
50	1.046	-	-	-	0.964	-	-	-
53	-	2.074	-	-	-	2.390	-	-
54	1.047	-	-	-	0.965	-	-	-
55	-	2.083	1.608	2.617	-	2.396	1.510	0.703
56	1.051	-	-	-	0.969	-	-	-
57	-	2.085	-	-	-	2.397	-	-
58	1.051	-	-	-	0.971	-	-	-
60	-	2.090	-	-	-	2.398	-	-
61	1.052	-	-	-	0.972	-	-	-
62	-	2.099	1.617	2.610	-	2.403	1.494	0.688
63	1.058	-	-	-	0.977	-	-	-
64	-	2.105	-	-	-	2.405	-	-
65	1.058	-	-	-	0.978	-	-	-
68	-	2.117	-	-	-	2.408	-	-
69	1.061	-	-	-	0.982	-	-	-
71	-	2.122	-	-	-	2.412	-	-
72	1.065	-	1.648	2.609	0.984	-	1.476	0.672
78	-	2.138	-	-	-	2.419	-	-
79	1.071	-	1.668	2.614	0.994	-	1.467	0.666
86	-	-	1.692	2.620	-	-	1.460	0.656
95	-	-	1.735	2.641	-	-	1.465	-

Table A6-2 **Linear expansion during moist curing for Gypsum and Magnesium Sulphate**

LINEAR EXPANSION DURING MOIST CURING

Sulphate level (% SO$_3$)	SODIUM SULPHATE				POTASSIUM SULPHATE			
	0.93	1.86	2.79	3.72	0.93	1.86	2.79	3.72
Day								
1	0.601	0.712	0.015	0.159	0.607	0.792	0.139	0.024
2	0.671	-	0.027	0.225	0.652	-	0.230	0.014
3	-	-	0.063	0.285	-	-	0.286	-0.006
4	-	0.926	0.176	0.469	-	0.975	0.449	-0.004
5	0.676	0.990	0.302	0.661	0.652	1.013	0.607	0.066
6	0.694	1.044	0.400	0.807	0.657	1.049	0.758	0.191
7	0.711	1.112	0.445	0.850	0.663	1.103	0.878	0.302
8	0.727	1.152	-	-	0.675	1.139	-	-
9	0.740	-	-	-	0.679	-	-	-
10	-	-	0.471	0.885	-	-	1.105	0.617
11	-	1.210	0.476	0.906	-	1.255	1.135	0.676
12	0.762	1.217	0.477	0.926	0.689	1.284	1.149	0.705
13	0.773	1.218	-	-	0.708	1.301	-	-
14	0.780	1.226	0.484	0.977	0.725	1.318	1.164	0.727
15	0.789	1.228	-	-	0.734	1.324	-	-
16	0.794	-	-	-	0.746	-	-	-
18	-	1.232	-	-	-	1.338	-	-
19	0.808	1.237	-	-	0.775	1.344	-	-
20	0.814	1.238	0.497	1.094	0.784	1.349	1.176	0.732
21	0.819	1.247	-	-	0.790	1.350	-	-
22	0.824	1.248	-	-	0.796	1.351	-	-
23	0.827	-	-	-	0.800	-	-	-
25	-	1.251	-	-	-	1.357	-	-
26	0.840	1.252	-	-	0.814	1.360	-	-
27	0.844	1.252	0.503	1.140	0.817	1.362	1.182	0.734
28	0.847	1.256	-	-	0.820	1.365	-	-
29	0.853	1.256	-	-	0.827	1.362	-	-
30	0.850	-	-	-	0.825	-	-	-
32	-	1.256	-	-	-	1.367	-	-
33	0.856	1.256	-	-	0.833	1.368	-	-
34	0.859	1.259	0.508	1.150	0.860	1.372	1.187	0.733
35	0.861	1.261	-	-	0.840	1.375	-	-
36	0.866	-	-	-	0.842	-	-	-
41	-	1.267	0.498	1.151	-	1.390	1.1997	0.734
42	0.879	1.275	-	-	0.854	1.395	-	-
43	0.885	1.277	-	-	0.856	1.396	-	-
44	0.887	-	0.492	1.152	0.861	-	1.194	0.728
47	-	1.283	-	-	-	1.407	-	-
48	0.893	-	-	-	0.855	-	-	-
49	-	1.284	-	-	-	1.411	-	-
50	0.899	-	-	-	0.857	-	-	-
53	-	1.290	-	-	-	1.420	-	-
54	0.905	-	-	-	0.853	-	-	-
55	-	1.295	0.488	1.150	-	1.427	1.204	0.729
56	0.913	-	-	-	0.865	-	-	-
57	-	1.296	-	-	-	1.431	-	-
58	0.918	-	-	-	0.873	-	-	-
60	-	1.298	-	-	-	1.437	-	-
61	0.921	-	-	-	0.882	-	-	-
62	-	1.299	0.488	1.154	-	1.441	1.213	0.730
63	0.930	-	-	-	0.888	-	-	-
64	-	1.299	-	-	-	1.444	-	-
65	0.931	-	-	-	0.892	-	-	-
68	-	1.306	-	-	-	1.452	-	-
69	0.941	-	-	-	0.901	-	-	-
71	-	1.311	-	-	-	1.459	-	-
72	0.946	-	0.485	1.158	0.907	-	1.230	0.735
78	-	1.327	-	-	-	1.484	-	-
79	0.958	-	0.484	1.164	0.910	-	1.240	0.740
86	-	-	0.484	1.166	-	-	1.248	0.740
95	-	-	0.489	1.177	-	-	1.258	0.747

Table A6-3 **Linear expansion during moist curing for Sodium Sulphate and Potassium Sulphate.**

LINEAR EXPANSION DURING SOAKING

Sulphate level (% SO_3)	GYPSUM				MAGNESIUM SULPHATE			
	0.93	1.86	2.79	3.72	0.93	1.86	2.79	3.72
Day								
1	0.417	0.394	0.400	0.397	0.288	0.152	0.124	0.085
2	0.607	0.546	0.553	0.571	0.442	0.241	0.199	0.145
3	0.691	0.603	0.613	0.632	0.523	0.291	0.239	0.179
4	-	-	-	-	-	-	-	-
5	-	-	-	-	-	-	-	-
6	0.690	0.696	0.715	0.720	0.534	0.424	0.375	0.293
7	0.591	0.723	0.748	0.749	0.492	0.431	0.395	0.317
8	3.343	5.635	6.203	5.222	5.648	5.881	5.688	5.648
9	3.483	8.700	9.260	8.317	5.969	7.646	7.478	7.530
10	3.498	9.971	9.274	9.608	6.046	9.056	8.837	8.989
11	-	-	-	-	-	-	-	-
12	-	-	-	-	-	-	-	-
13	3.531	12.325	13.001	12.201	-	-	-	-
14	3.536	13.023	13.807	13.030	6.117	13.178	12.744	13.237
15	3.539	13.493	14.608	13.861	6.139	14.028	13.589	13.960
16	3.539	13.590	15.193	14.449	6.144	14.832	14.415	14.699
17	3.540	13.609	15.820	15.087	6.154	15.699	15.358	15.324
18	-	-	-	-	-	-	-	-
19	-	-	-	-	-	-	-	-
20	3.541	13.611	17.074	16.396	6.168	17.747	17.409	16.521
21	3.539	13.611	17.675	17.012	6.178	18.045	17.860	16.762
22	3.540	13.611	18.147	17.514	6.190	18.177	18.266	16.958
23	3.539	13.611	18.573	17.970	6.200	18.208	18.526	17.101
24	3.539	13.611	18.925	18.389	6.209	18.218	18.740	17.233
25	-	-	-	-	-	-	-	-
26	-	-	-	-	-	-	-	-
27	3.540	13.611	19.471	19.508	6.215	12.221	19.023	17.412
28	-	-	-	-	6.217	18.224	19.066	17.439
29	3.545	13.611	19.499	20.105	-	-	-	-
30	3.550	13.615	19.514	20.283	-	-	-	-
31	3.554	13.612	19.512	20.425	6.229	18.225	19.157	17.499
32	-	-	-	-	-	-	-	-
33	-	-	-	-	-	-	-	-
34	-	-	-	-	-	-	-	-
35	3.561	13.613	19.510	20.659	6.249	18.231	19.194	17.529
36	3.562	13.613	19.510	20.692	-	-	-	-
37	-	-	-	-	-	-	-	-
38	-	-	-	-	6.263	18.233	19.206	17.540
39	-	-	-	-	-	-	-	-
40	-	-	-	-	-	-	-	-
41	3.568	13.614	19.507	20.766	6.286	18.235	19.214	17.551
42	-	-	-	-	6.287	18.237	19.217	17.554
43	-	-	-	-				
44	-	-	-	-				
45	-	-	-	-				
46	-	-	-	-				
47	-	-	-	-				
48	3.583	13.617	19.505	20.805				
49	-	-	-	-				
50	-	-	-	-				
51	-	-	-	-				
52	-	-	-	-				
53	-	-	-	-				
54	-	-	-	-				
55	3.595	13.618	19.505	20.805				
56								
57								
58								
59								
60								

Table A6-4 Linear expansion during moist soaking for Gypsum and Magnesium Sulphate.

LINEAR EXPANSION DURING SOAKING

Sulphate level (% SO_3)	SODIUM SULPHATE				POTASSIUM SULPHATE			
	0.93	1.86	2.79	3.72	0.93	1.86	2.79	3.72
Day								
1	0.466	0.553	0.643	0.671	0.474	0.514	0.487	0.614
2	0.333	0.480	0.555	0.627	0.503	0.670	0.723	0.863
3	0.184	0.239	0.523	0.638	0.404	0.653	0.779	0.982
4	0.065	0.154	0.518	0.668	-	-	-	-
5	-	-	-	-	-	-	-	-
6	-	-	-	-	0.240	0.599	0.770	1.064
7	-0.151	-0.050	0.439	0.645	0.174	0.578	0.779	1.098
8	0.235	1.638	9.676	10.908	1.341	2.482	8.261	9.568
9	0.313	1.929	10.038	11.237	1.399	2.561	8.826	10.287
10	0.349	2.031	10.164	11.361	1.426	2.595	8.924	10.483
11	0.376	2.094	10.227	11.429	-	-	-	-
12	-	-	-	-	-	-	-	-
13	-	-	-	-	1.454	2.626	8.964	10.632
14	0.459	2.197	10.369	11.635	1.468	2.637	8.969	10.640
15	0.470	2.220	10.432	11.676	-	-	-	-
16	0.493	2.236	10.479	11.731	1.482	2.640	8.970	10.643
17	0.529	2.346	10.620	11.580	1.487	2.642	8.972	10.645
18	-	-	-	-	-	-	-	-
19	-	-	-	-	-	-	-	-
20	-	-	-	-	-	-	-	-
21	0.575	2.362	10.636	11.621	1.505	2.646	8.970	10.644
22	-	-	-	-	-	-	-	-
23	-	-	-	-	-	-	-	-
24	-	-	-	-	1.510	2.648	8.966	10.643
25	0.621	2.378	10.636	11.648	-	-	-	-
26	-	-	-	-	-	-	-	-
27	-	-	-	-	1.515	2.649	8.966	10.643
28	0.653	2.409	10.668	11.648	-	-	-	-
29	-	-	-	-	-	-	-	-
30	-	-	-	-	-	-	-	-
31	-	-	-	-	1.525	2.650	8.962	10.641
32	0.703	2.441	10.699	11.678	-	-	-	-
33	-	-	-	-	-	-	-	-
34	-	-	-	-	1.533	2.652	8.959	10.640
35	0.728	2.465	10.715	11.676	-	-	-	-
36	-	-	-	-	-	-	-	-
37	-	-	-	-	-	-	-	-
38	-	-	-	-	1.551	2.657	8.956	10.640
39	0.767	2.488	10.715	11.648	-	-	-	-
40	-	-	-	-	-	-	-	-
41	-	-	-	-	1.560	2.659	8.952	10.639
42	-	-	-	-	-	-	-	-
43	-	-	-	-	-	-	-	-
44	-	-	-	-	-	-	-	-
45	-	-	-	-	1.584	2.665	8.952	10.640
46	1.262	2.929	11.124	12.046	-	-	-	-
47					-	-	-	-
48					1.599	2.668	8.952	10.640
49					1.605	2.669	8.952	10.641
50								

Table A6-4 **Linear expansion during moist soaking for Sodium Sulphate and Potassium Sulphate**

APPENDIX 6 - LINEAR EXPANSION DURING 7 DAYS OF MOIST CURING AND DURING SUBSEQUENT SOAKING.

Day	6L0S0G	5L1S0G	3L3S0G	2L4S0G	0L6S0G
1	0.066	0.046	0.022	-0.017	-0.221
2	0.048	0.007	-0.039	-0.099	-0.492
3	0.028	-0.042	-0.105	-0.207	-0.778
4	0.011	-0.080	-0.186	-0.242	-1.008
7	-0.163	-0.284	-0.384	-0.545	-1.481
8	3.283	2.543	0.885	0.203	-0.149
9	3.361	2.612	0.911	0.222	-0.116
10	3.406	2.647	0.928	0.240	-0.095
11	3.435	2.670	0.942	0.254	-0.084
14	3.442	2.676	0.937	0.250	-0.088
15	3.475	2.701	0.955	0.270	-0.067
16	3.489	2.713	0.963	0.279	-0.063
17	3.499	2.720	0.971	0.284	-0.057
18	3.508	2.730	0.980	0.289	-0.051
21	3.514	2.738	0.988	0.293	-0.050
23	3.523	2.747	0.998	0.299	-0.044
24	3.526	2.750	1.003	0.303	-0.039
28	3.540	2.764	1.018	0.310	-0.028
31	3.550	2.774	1.024	0.316	-0.019
42	3.567	2.795	1.036	0.323	-0.011
46	3.588	2.7810	1.047	0.334	0.008
78	3.610	2.832	1.068	0.359	0.047

Table A6-5 - Linear expansion during moist curing and during subsequent soaking for kaolinite - lime - GGBS cylinders containing no Gypsum.

APPENDIX 6 - LINEAR EXPANSION DURING 7 DAYS OF MOIST CURING AND DURING SUBSEQUENT SOAKING.

Day	6L0S2G	5L1S2G	3L3S2G	2L4S2G	0L0S2G
1	0.785	0.593	0.523	0.552	0.139
2	0.999	0.708	0.557	0.543	0.011
3	0.917	0.586	0.437	0.449	-0.129
7	0.358	0.035	0.097	0.205	-0.730
8	0.786	0.472	0.513	0.657	1.491
9	0.811	0.496	0.582	0.699	1.857
10	0.820	0.516	0.607	0.716	2.060
13	0.839	0.537	0.622	0.729	2.271
14	0.843	0.539	0.622	0.729	2.289
15	0.844	0.544	0.624	0.731	2.313
16	0.845	0.547	0.626	0.732	2.326
17	0.847	0.549	0.629	0.736	2.340
20	0.848	0.557	0.631	0.737	2.365
21	0.850	0.560	0.633	0.740	2.370
24	0.860	0.570	0.635	0.746	2.034
28	0.869	0.579	0.641	0.748	2.057
31	0.874	0.584	0.641	0.749	2.069
34	0.886	0.593	0.644	0.750	2.082

Table A6-6 - Linear expansion during moist curing and during subsequent soaking for kaolinite - lime - GGBS cylinders containing 2wt.% Gypsum (0.93% SO_3).

APPENDIX 6 - LINEAR EXPANSION DURING 7 DAYS OF MOIST CURING AND DURING SUBSEQUENT SOAKING.

Day	6L0S4G	5L1S4G	3L3S4G	2L4S4G	0L0S4G
1	0.645	0.680	0.660	0.610	-0.001
2	0.770	0.809	0.769	0.717	-0.188
3	0.798	0.839	0.785	0.667	-0.379
4	0.806	0.846	0.790	0.604	-0.609
7	0.704	0.790	0.675	0.479	-1.105
8	3.969	3.540	4.231	1.817	1.511
9	4.008	3.601	4.349	1.961	1.900
10	4.017	3.620	4.373	2.005	2.081
11	4.025	3.627	4.384	2.030	2.190
14	4.037	3.631	4.399	2.070	2.350
15	4.039	3.632	4.400	2.077	2.375
17	4.045	3.637	4.406	2.091	2.407
18	4.048	3.637	4.408	2.096	2.423
22	4.054	3.641	4.413	2.110	2.463
25	4.057	3.641	4.413	2.114	2.482
28	4.064	3.645	4.417	2.120	2.498
32	4.070	3.650	4.423	2.131	2.423
35	4.074	3.650	4.424	2.133	2.533

Table A6-7 - Linear expansion during moist curing and during subsequent soaking for kaolinite - lime - GGBS cylinders containing 4wt.% Gypsum (1.86% SO_3).

APPENDIX 6 - LINEAR EXPANSION DURING 7 DAYS OF MOIST CURING AND DURING SUBSEQUENT SOAKING.

Day	6L0S6G (1)	6L0S6G (2)	5L1S6G	3L3S6G	2L4S6G	0L0S6G
1	0.771	0.680	0.391	0.291	1.201	-0.187
2	1.203	0.872	0.559	0.384	1.253	-0.599
3	1.488	0.979	0.645	0.385	1.166	-0.951
4	-	1.065	-	-	-	-
6	2.000	-	0.795	0.310	0.930	-1.944
7	2.125	1.254	0.847	0.250	0.865	-2.301
8	6.508	5.717	4.856	2.986	2.011	0.227
9	8.906	8.183	7.117	3.332	2.214	0.585
10	10.788	9.698	8.419	3.410	2.254	0.861
11	-	11.016	-	-	-	-
13	12.381	-	9.024	3.471	2.290	1.012
14	12.382	12.182	9.034	3.480	2.298	1.022
15	12.383	12.186	9.041	3.489	2.305	1.034
16	12.383	-	9.045	3.498	2.312	1.041
17	12.384	12.188	9.047	3.504	2.317	1.046
18	-	12.190	-	-	-	-
20	12.387	-	9.050	3.517	2.329	1.049
22	12.390	12.193	9.052	3.525	2.336	1.050
23	12.391	-	9.053	3.529	2.339	1.050
25	-	12.194	-	-	-	-
27	12.394	-	9.053	3.536	2.345	1.050
28	-	12.194	-	-	-	-
30	12.400	-	9.058	3.545	2.352	1.049
32	-	12.199	-	-	-	-
35		12.200				
41	12.420		9.068	3.563	2.357	1.051
45	12.430		9.075	3.574	2.366	1.061

Table A6-8 - Linear expansion during moist curing and during subsequent soaking for kaolinite - lime - GGBS cylinders containing 6wt.% Gypsum (2.79% SO_3).

APPENDIX 6 - LINEAR EXPANSION DURING 7 DAYS OF MOIST CURING AND DURING SUBSEQUENT SOAKING.

Day	6L0S8G	5L1S8G	3L3S8G	2L4S8G	0L6S8G	0L0S8G
1	0.676	0.704	0.785	0.781	0.068	0.106
2	1.081	1.069	1.148	1.165	0.038	0.079
3	1.408	1.327	1.341	1.231	0.007	0.054
4	1.707	1.562	1.433	1.190	-0.03	0.029
7	2.310	2.077	1.395	1.141	-0.12	-0.08
8	5.661	5.218	4.994	2.804	6.931	3.165
9	7.770	7.261	5.574	3.005	7.418	***
10	9.051	8.376	5.694	3.055	***	
11	10.24	8.990	5.749	3.077		
14	11.74	9.357	5.802	3.109		
15	11.92	9.398	5.811	3.114		
16	11.93	9.398	5.811	3.118		
17	11.97	9.403	5.816	3.120		
18	11.99	9.411	5.820	3.124		
21	12.13	9.509	5.880	1.130		
22	12.13	9.510	5.883	3.163		
23	12.14	9.512	5.886	3.166		
24	12.14	9.513	5.888	3.138		
25	12.14	9.513	5.888	3.139		
28	12.14	9.516	5.890	3.141		
29	12.15	9.521	5.898	3.148		
30	12.15	9.521	5.898	3.148		
31	12.15	9.521	5.898	3.148		

Table A6-9 - Linear expansion during moist curing and during subsequent soaking for kaolinite - lime - GGBS cylinders containing 8wt.% Gypsum (3.72% SO_3) at 0.6 OMC. *(OMC=30.55%; All samples moist cured for the first 7 days before being soaked*
**** samples collapsed upon soaking).*

Day	6L0S8G	5L1S8G	3L3S8G	2L4S8G	0L6S8G	0L0S8G
1	0.317	0.294	0.196	0.095	-0.29	-0.40
2	0.336	0.313	0.217	0.114	-0.61	-0.46
3	0.423	0.397	0.334	0.210	-0.47	-0.60
4	0.487	0.445	0.404	0.227	-0.61	-0.65
7	0.595	0.478	0.433	0.214	-0.81	-0.85
8	7.620	7.743	4.655	5.301	3.600	6.020
9	9.344	9.046	4.763	6.388	3.776	6.910
10	10.51	9.965	6.402	6.852	***	***
11	11.51	10.76	6.963	6.997		
14	13.87	12.67	8.393	7.382		
16	15.05	13.60	9.060	7.469		
17	15.56	14.03	9.338	7.490		
18	16.16	14.52	9.666	7.509		
21	17.49	15.61	10.36	7.570		
22	17.89	15.94	10.51	7.585		
23	18.28	16.27	10.66	7.594		
24	18.62	16.55	10.78	7.599		
25	18.97	16.84	10.89	7.606		
28	20.01	17.89	11.16	7.606		

Table A6-10 - Linear expansion during moist curing and during subsequent soaking for kaolinite - lime - GGBS cylinders containing 8wt.% Gypsum (3.72% SO_3) at 0.8 OMC. *(OMC=30.55%; All samples moist cured for the first 7 days before being soaked*
**** samples collapsed upon soaking).*

APPENDIX 6 - LINEAR EXPANSION DURING 7 DAYS OF MOIST CURING AND DURING SUBSEQUENT SOAKING.

Day	6L0S8G	5L1S8G	3L3S8G	2L4S8G	0L6S8G	0L0S8G
1	0.383	0.383	0.311	0.329	-0.148	-0.07
2	0.576	0.574	0.472	0.521	-0.295	-0.18
3	0.650	0.642	0.507	0.570	-0.448	-0.29
4	0.682	0.662	0.507	0.572	-0.570	-0.36
7	0.745	0.682	0.493	0.463	-0.838	-0.57
8	5.815	4.717	4.093	3.532	-0.160	2.814
9	7.567	6.095	5.214	4.239	-0.152	3.308
10	9.058	7.227	6.178	4.483	-0.105	3.591
11	10.49	8.289	7.075	4.627	-0.105	3.785
14	13.72	10.64	8.843	4.804	-0.105	3.943
15	14.19	11.24	9.190	4.845	-0.105	3.960
16	15.33	11.80	9.375	4.870	-0.160	3.980
17	16.22	12.42	9.594	4.880	-0.162	3.987
18	16.96	12.95	9.781	4.892	-0.162	3.994
21	19.18	14.51	10.02	4.903	-0.177	4.023
22	19.82	14.95	10.06	4.903	-0.195	4.029
23	20.59	15.50	10.09	4.903	-0.197	4.032
24	21.19	15.92	10.09	4.906	-0.197	4.038
25	21.49	16.25	10.09	4.907	-0.197	4.042
28	23.13	17.13	10.10	4.907	-0.207	4.042
29	23.67	17.33	10.11	4.090	-0.210	4.042
30	24.07	17.46	10.12	4.909	-0.215	4.042
31	24.38	17.55	10.12	4.909	-0.219	4.042
32	24.73	17.61	10.12	4.909	-0.219	4.042
35	25.65	17.73	10.13	4.909	-0.219	4.042
36	25.85	17.75	10.13	4.909	-0.219	4.042
37	26.05	17.78	10.14	4.909	-0.219	4.042
38	26.22	17.79	10.14	4.917	-0.219	4.042
39	26.35	17.81	10.14	4.918	-0.162	4.043
43	26.10	17.84	10.14	4.918	1.13	4.044
44	26.64	17.84	10.13	4.918	2.05	4.046
45	26.67	17.85	10.13	4.918	3.16	4.048
46	26.68	17.85	10.13	4.918	3.95	4.048
48	26.73	17.87	10.14	4.927	6.92	4.048
49	26.75	17.87	10.15	4.935	7.68	4.051
50	26.76	17.88	10.16	4.937	8.41	4.054
51	26.77	17.89	10.16	4.941	9.08	4.058
52	26.78	17.89	10.16	4.946	9.63	4.059
55	26.78	17.89	10.16	4.948	11.16	4.060
56	26.78	17.89	10.17	4.954	11.43	4.061
57	26.79	17.90	10.17	4.959	11.68	4.063

Table A6-11 - Linear expansion during moist curing and during subsequent soaking for kaolinite - lime - GGBS cylinders containing 8wt.% Gypsum (3.72% SO_3) at OMC. *(OMC=30.55%; All samples moist cured for the first 7 days before being soaked *** samples collapsed upon soaking).*

APPENDIX 6 - LINEAR EXPANSION DURING 7 DAYS OF MOIST CURING AND DURING SUBSEQUENT SOAKING.

Day	6L0S8G	5L1S8G	3L3S8G	2L4S8G	0L6S8G	0L0S8G
1	0.570	0.563	0.396	0.470	-0.209	0.280
2	0.626	0.604	0.467	0.433	-0.481	0.02
3	0.597	0.571	0.444	0.375	-0.761	-0.20
6	0.483	0.428	0.289	0.167	-1.490	-0.78
7	0.448	0.390	0.223	0.103	-1.746	-0.99
8	5.020	4.421	2.258	0.898	-0.966	***
9	7.275	6.487	2.513	0.970	-0.951	
10	9.083	7.965	2.573	0.995	-0.947	
13	12.65	9.243	2.635	1.034	-0.935	
14	13.14	9.329	2.639	1.036	-0.934	
15	13.39	9..377	2.647	1.042	-0.931	
16	13.51	9.402	2.649	1.044	-0.930	
17	13.58	9.421	2.656	1.053	-0.930	
20	13.64	9.442	2.665	1.057	-0.921	
21	13.65	9.449	2.670	1.061	-0.919	
22	13.66	9.452	2.671	1.063	-0.917	
23	13.67	9.452	2.672	1.064	-0.917	
24	13.67	9.454	2.674	1.067	-0.917	
27	13.68	9.456	2.677	1.071	-0.916	
28	13.68	9.461	2.678	1.073	-0.914	
29	13.68	9.462	2.683	1.077	-0.913	
30	13.68	9.464	2.683	1.077	-0.869	
31	13.68	9.466	2.685	1.077	-0.432	

Table A6-12 - Linear expansion during moist curing and during subsequent soaking for kaolinite - lime - GGBS cylinders containing 8wt.% Gypsum (3.72% SO_3) at 1.2 OMC. *(OMC=30.55%; All samples moist cured for the first 7 days before being soaked *** samples collapsed upon soaking).*

APPENDIX 7 - SWELLING PRESSURE GENERATION

Symbols used in Table A7-1

Transducer calibration

T1: $P=-0.1592 + 2.4233\Delta R$

T2: $P=-2.2584 + 2.0429\Delta R$

T3: $P=-0.5303 + 1.8012\Delta R$

T4: $P=-0.7945 + 1.9410\Delta R$

T5: $P=-0.0295 + 1.6108\Delta R$

T6: $P=-3.3916 + 2.0670\Delta R$

T7: $P=-5.3899 + 3.9200\Delta R$

T8: $P=-4.5658 + 3.6518\Delta R$

T9: $P=-1.8241 + 17.8721\Delta R$ (or $P=-129.7779 + 327.3736\,\Delta R$ After damage)

T10: $P= 2.9430 + 17.7662\Delta R$ (or $P=-89.9724 + 248.2474\,\Delta R$ After damage)

Where:-

T1=Transducer No. 1 etc.	B= Brass Restraint
P= Pressure on 51mm diam sample (kN/m^2)	S=Sand Ring Restraint

R=Change in Transducer Reading (mV)

OP = Open Perspex Restraint

CP=Closed Perspex Restraint

JCP=Jubilee Clipped Perspex Restraint

<u>348.194</u>	End of soaking due to lack of change in pressure
<u>348.194TL</u>	Termination of soaking due to the transducer limit (TL).

Sulphate level(% so_3)		Control	Gypsum				Magnesium sulphate				Sodium sulphate				Potassium sulphate			
Trial		1	0.93	1.86	2.79	3.72	0.93	1.86	2.79	3.72	0.93	1.86	2.79	3.72	0.93	1.86	2.79	3.72
Transducer		T6	T6	T8	T7	T9	T3	T7	T8	T6	T7	T8	T8	T6	T6	T6	T7	T8
Restraint		OP	OP	OP	OP	OP	OP	OP	OP	JCP	OP	OP	OP	OP	OP	OP	OP	OP
Day																		
1	Curing	15.490	65.440	58.245	12.233	1.172	4.110	2.050	12.233	14.050	39.690	41.082	35.000	29.887	45.596	38.982	28.322	14.058
2		30.456	85.696	77.600	25.690	1.172	6.720	3.500	25.690	33.500	31.066	43.273	36.102	31.541	-	47.250	36.554	21.727
3		45.272	100.372	91.477	33.213	1.056	5.174	1.964	33.213	41.964	-	41.447	-	-	-	-	43.610	28.300
4		55.002	110.707	102.432	45.987	0.905	3.500	1.100	45.987	51.100	-	-	-	-	-	-	-	-
5		45.668	-	-	-	0.000	-	-	-	-	-4.606	-	-	-	15.211	42.909	-	-
6		-	-	-	-		-	-	-	-	-5.390	-	-	14.591	10.871	36.915	35.770	25.014
7		-	89.003	133.837	65.247		2.100	0.960	41.369	41.700	-6.174	37.795	34.231	16.658	8.184	18.932	31.850	18.806
8	Soaking	359.987	319.267	443.875	348.194	328.545	294.150	363.874	264.937	176.455	340.182	470.533	426.963	370.569	229.766	319.887	348.194	291.230
9		362.261	325.055	531.153	424.634	-	314.955	431.690	328.478	196.925	354.510	493.905	451.078	390.647	230.386	350.065	404.194	360.979
10		361.434	328.980	585.200	476.378	-	321.209	477.162	366.092	213.813	-	498.652	-	387.002	-	-	443.842	405.166
11		361.847	-	635.595	-	492.232	323.473	519.106	399.323	227.119	-	-	-	-	-	-	-	-
12		-	-	-	-	557.705	-	-	-	239.401	-	-	447.632	-	237.001	361.641	-	-
13		-	335.596	-	600.642	590.444	-	-	-	-	371.227	495.000	446.867	383.167	236.793	362.674	496.762	488.062
14		361.021	337.043	678.686	631.218	655.919	316.539	615.930	461.769	-	374.570	504.495	444.953	386.024	237.207	363.708	502.642	499.017
15		359.367	-	-	-	688.656	348.039	-	541.743	275.736	378.869	504.860	443.805	-	237.207	365.361	505.386	503.034
16		362.261	342.418	-	*715.106*	-	312.380	-	522.024	284.180	383.167	504.860	-	394.851	237.414	360.607	505.778	503.400
17		357.920	343.244	-	714.714	-	323.324	-	552.334	285.716	-	504.130	-	398.747	-	-	504.602	501.574
19			-	-	-	754.131	321.294	676.821	569.862	295.183	396.540	-	440.781	-	-	-	-	-
20			-	-	-	-	-	-	-	304.139	400.839	499.017	440.781	412.769	-	366.395	-	-
21			343.244	683.00	728.434	-	-	-	-	-	404.182	487.697	441.508	415.625	238.860	368.462	500.682	500.113
22			346.345	TL	TL	754.180	329.618	694.360	614.780	-	407.048		441.891	417.443	239.654	369.289	498.898	501.209
23						TL	-	-	-	326.145	-		435.384	419.521	239.481	369.909	499.506	501.574
23’							328.426	691.848	643.264	337.660	-		-	415.885	239.481	371.356	499.114	501.939
24							-	-	-	348.407	-		-	412.042	-	-	499.898	503.034
26							314.564	662.646	660.062	356.340	417.555		444.953	-	238.447	370.529	-	-
27							-	666.106	TL	382.183	420.421		445.336	387.061	240.928	370.322	498.722	498.287
28							-	710.794		384.998	424.242				241.135	370.115	504.994	503.400
29							-	-			426.630				242.375	-	504.602	503.765
30							341.700	719.810			424.242				242.581	368.668	-	-
33							TL								-	-	504.602	502.304
34															245.887	366.808	-	-
35															-	366.808	505.778	-
36															240.514	-	505.386	499.748
37																-	-	499.017
38																366.601	-	-
40																	505.386	-
41																		495.731

Table A7-2 Average Swelling Pressure generated (kN/m^2) by specimens containing various amounts of various metal sulphates.

APPENDIX 8 - X-RAY DIFFRACTION (XRD) ANALYSIS

Symbols used in Tables A8-1 - A8-5

Compound

E - Ettringite
G - Gypsum
H - Hydrogarnet (C_3AH_6)
L - Lime
K - Kaolinite
M - Mica (illite)
Ha - Haematite
Ca - Calcite
Q - Quartz
Mg - Magnetite
T - Tobermorite

S - Dicalcium aluminate silicate 8-hydrate (Gehlenite or Statling's compound) $Ca_2Al_2(OH)6(SiO_4).5H_2O$) or C_2ASH_8)

C2 - α-Tetracalcium aluminate 13-hydrate ($Ca_2Al(OH)_7.3H_2O$)

C3 - Tetracalcium aluminate carbonate 12-hydrate ($Ca_4Al_2(OH)_{12}(CO_3).6H_2O$ or $C_3A.CaCO_3.12H_2O$)

C4 - Tetracalcium aluminate 13-hydrate ($Ca_2Al(OH)_7.3H_2O$ or C_4AH_{13})

INTENSITY

VVS - Very very strong
VS - Very strong
S - Strong
45 - 45%
MS - Mildly strong
M - Medium
W - Weak

BRAGG'S LAW

$$d = \frac{\lambda}{2\sin 2\theta} = \frac{1.54179}{2\sin(\frac{2\theta + 0.33}{2})}$$

λ - Radiation wavelength
θ - Angle of radiation incidence

APPENDIX 8 - X-RAY DIFFRACTION (XRD) ANALYSIS

6L0S0G						6L0S6G					
CURING PERIOD (Weeks)						CURING PERIOD (Week)					
1			4			1			4		
IDENTIFIED PEAKS		LIKELY COMPOUNDS AND INTENSITY	IDENTIFIED PEAKS		LIKELY COMPOUNDS AND INTENSITY	IDENTIFIED PEAKS		LIKELY COMPOUNDS AND INTENSITY	IDENTIFIED PEAKS		LIKELY COMPOUNDS AND INTENSITY
2θ	d-spacing		2θ	d-spacing		2θ	d-spacing		2θ	d-spacing	
8.5	10.014	M_S	8.5	10.014	M_s	8.5	10.014	M_S	8.5	10.014	M_S
11.5	7.481	K_{100}	11.9	7.237	K_{100}	8.7	9.793	E100	8.8	9.718	E_{100}
17.4	5.002	$H_{S,}\ M_M$	17.4	5.002	H_S	11.4	7.544	G_{100}, T_S	12.0	7.178	K_{100}
17.7	4.920	$L_{vs(74)}$	17.7	4.920	$L_{VS(74)}$	12.1	7.121	K_{100}	15.4	5.644	E_{76}
19.6	4.455	$K_{35,} M_{VS}, H_S$	19.5	4.477	M_{VS}, K_{35}	17.8	4.893	$L_{VS(74)}$	17.3	5.039	M_M, E_{12}, L_{74}, H_S
19.9	4.389	K_{60}, H_S	20.0	4.368	M_W, H_S, K_{35}	19.7	4.433	K_{35}, H_S, M_{VS}	17.5	4.983	L_{74}
20.9	4.185	K_{35}, Q_S, S_S	20.8	4.204	K_{35}, S_S, Q_S	20.2	4.326	K_{60}	18.5	4.713	E_{17}
22.7	3.862	K_{60}	22.7	3.862	K_{60}	20.5	4.264	G_{100}, Q_S	19.5	4.477	M_{VS}, K_{35}
24.6	3.572	K_{80}	23.4	3.749	K_{45}, M_M	21.1	4.146	K_{35}	20.0	4.368	K_{60}, H_S
26.3	3.347	Q_{VVS}, M_{VS}, K_{35}	24.6	3.572	K_{80}	22.8	3.845	K_{40}, E_{31}, C_4A	20.4	4.285	G_{100}, Q_S
28.4	3.110	L_{23}, T_{VVS}	26.3	3.347	Q_{VVS}, M_{VS}, K_{35}	24.7	3.558	K_{80}	21.0	4.166	K_{45}
33.8	2.627	$L_{VVS(100)}$	28.3	3.118	G_{23}, L_{23}, T_{VVS}	26.4	3.335	Q_{VVS}, M_{VS}	22.7	3.867	M_M, E_{31}, K_{40}, C_4
34.7	2.561	K_{35}, M_S	29.5	2.998	T_S, M_S, Ca_{VVS}, H_M	28.8	3.065	$G_{75}, K_{20}, T_{VVS}, C_{aVVS}$ H_S	23.4	3.749	M_M, K_{25}, G_{17}
35.1	2.533	K_{35}	33.8	2.627	$L_{VVS(100)}$				24.5	3.586	K_{80}
35.6	2.499	K_{45}, H_M	34.7	2.561	K_{35}, M_S	30.9	2.864	$G_{45}, Ca_M, T_S, C_4A_{VVS}$	25.2	3.493	E_{23}
37.3	2.390	K_{25}, S_S	35.1	2.533	K_{35}	33.9	2.620	$E_{16}, L_{VVS(100)}, Ha_{VVS}$	26.2	3.360	M_{VS}, Q_{VVS}
38.3	2.331	K_{40}	35.6	2.499	K_{45}, H_M, S_S	34.7	2.561	K_{25}, E_{29}, M_{VS}	32.0	2.769	M_M, H_S
38.8	2.302	K40 , T_{MS}	37.4	2.384	K_{25}	35.2	2.527	K_{35}, Ha_{VS}	34.7	2.561	M_{VS}, E_{29}, K_{25}
			38.1	2.342	K_{40}	35.7	2.493	K_{45}, G_{11}, H_M	35.1	2.533	$K_{35},$
			38.9	2.296	K_{40}, T_{MS}, H_M	37.5	2.378	K_{25}	35.6	2.499	K_{45}, G_{11}, H_M
						38.2	2.336	K_{40}	37.3	2.390	K_{25}
						39.2	2.280	$K_{35}, E_{22}, H_M, T_{MS}, Ca_S$	38.1	2.342	K_{40}
									38.9	2.296	$K_{35}, E_{22}, H_M, T_{MS}, Ca_S$

TABLE A8 -1 - XRD results for 6L0S0G and 6L0S6G specimens at 1 and 4 weeks of moist curing at 30°C and 100% relative humidity

APPENDIX 8 - X-RAY DIFFRACTION (XRD) ANALYSIS

5L1S0G						5L1S6G					
CURING PERIOD (Weeks)						CURING PERIOD (Week)					
1			4			1			4		
IDENTIFIED PEAKS		LIKELY COMPOUNDS AND THEIR INTENSITIES	IDENTIFIED PEAKS		LIKELY COMPOUNDS AND THEIR INTENSITIES	IDENTIFIED PEAKS		LIKELY COMPOUNDS AND THEIR INTENSITIES	IDENTIFIED PEAKS		LIKELY COMPOUNDS AND THEIR INTENSITIES
2θ	d-spacing		2θ	d-spacing		2θ	d-spacing		2θ	d-spacing	
8.7	9.793	M_S	8.6	9.902	M_S	8.5	10.014	M_S	8.5	10.014	M_S
12.3	7.008	K_{100}	12.0	7.178	K_{100}	8.8	9.686	E_{100}	8.7	9.793	E_{100}
17.6	4.955	M_M ,H_S	17.5	4.983	M_M ,H_S	11.5	7.481	G_{100} ,	12.1	7.121	K_{100}
17.9	4.874	L_{74}	19.6	4.455	K_{35} , M_{VS}	12.2	7.064	K_{100}	15.4	5.644	E_{76}
19.7	4.433	M_{VS}	20.1	4.347	K_{60} ,H_S	17.7	4.920	$L_{VS(74)}$,E_{12} ,M_M	17.6	4.947	E_{12} , M_M , $L_{VS(74)}$
20.3	4.316	K_{60} , H_M	21.2	4.127	K_{45}	19.7	4.433	K_{35} , M_{VS}	19.7	4.433	M_{VS} , K_{35}
20.7	4.224	K_{45}	22.6	3.878	K_{40}	20.1	4.347	K_{60} , H_S	20.1	4.347	K_{60} , H_S
21.0	4.166	K_{35}	23.5	3.734	K_{25} ,M_M	20.5	4.264	G_{100} , Q_S	20.4	4.285	G_{100} , Q_S
23.0	3.813	K_{40}	24.5	3.586	K_{80} ,	21.1	4.146	K_{35}	20.8	4.204	K_{45}
24.7	3.558	K_{80}	26.3	3.347	K_{35} , M_{VS} , Q_{VVS}	23.0	3.813	K_{40} ,E_{31} , C_4A_{MS}	21.1	4.146	K_{35}
26.4	3.335	M_{VS}, K_{35} , Q_{VVS}	29.5	2.995	M_S , T_{VVS} , H_M	24.8	3.544	K_{80}	22.8	3.845	K_{40} , E_{31} , C_{3S}
34.0	2.612	L_{100}	34.7	2.561	K_{35} , M_S	26.4	3.335	K_{35} , M_{VS}, Q_{VVS}	23.5	3.733	Ha_S
34.8	2.554	M_{VS} , K_{25} ,	35.2	2.527	K_{35}	29.0	3.045	G_{75} K_{20},T_S,Ca_{VVS},H_S	24.6	3.572	K_{80}
35.2	2.527	Ha_{VVS}	35.7	2.493	K_{45}	31.0	2.855	G_{45} , C_4 , T_S	25.4	3.462	E_{23}
35.8	2.486		37.5	2.378	K_{40} , M_{SM}	34.8	2.554	$K_{25/35}$, E_{29}	26.5	3.323	M_{VS} ,K_{35} , Q_{VVS}
37.5	2.378		38.2	2.336	K_{40}	35.3	2.520	K_{35} , H_S	29.7	2.976	T_S
38.3	2.331	K_{40}	38.9	2.296	K_{35} ,T_{MS}	35.8	2.486	K_{45}, G_{11}	34.8	2.554	$K_{25/35}$, M_{VS} , E_{29}
39.1	2.285	K_{35} , T_{MS} , H_M	39.7	2.252	K_{20} ,T_{MS} , H_M	37.6	2.372	K_{25}	35.2	2.527	K_{35} , Ha_{VS}
						38.3	2.331	K_{40}	35.8	2.486	K45 , G_{11}
						39.1	2.285	K_{35} , E_{22} ,T_S ,S_S, H_M	37.6	2.372	K_{25}
									38.3	2.331	K_{40}
									39.2	2.280	K_{35} ,E_{22}, T_S , H_M , Ca_S

TABLE A8-2 - XRD results for 5L1S0G and 5L1S6G specimens at 1 and 4 weeks of moist curing at 30^{0}C and 100% relative humidity

APPENDIX 8 - X-RAY DIFFRACTION (XRD) ANALYSIS

3L3S0G						3L3S6G					
CURING PERIOD (Weeks)						CURING PERIOD (Week)					
1			4			1			4		
IDENTIFIED PEAKS		LIKELY COMPOUNDS AND THEIR INTENSITIES	IDENTIFIED PEAKS		LIKELY COMPOUNDS AND THEIR INTENSITIES	IDENTIFIED PEAKS		LIKELY COMPOUNDS AND THEIR INTENSITIES	IDENTIFIED PEAKS		LIKELY COMPOUNDS AND THEIR INTENSITIES
2θ	d-spacing		2θ	d-spacing		2θ	d-spacing		2θ	d-spacing	
8.7	9.793	M_S	8.4	10.129	M_S	8.5	10.014	M_S	8.6	9.902	M_S
12.2	7.060	K_{100}	12.0	7.178	K_{100}	11.4	7.544	G_{100}	11.5	7.481	G_{100} , E_9
17.6	4.947	M_M , L_{74}	17.4	5.011	M_M , H_S	12.2	7.092	K_{100}	12.2	7.064	K_{100}
19.7	4.433	K_{35} , M_{VS}	19.6	4.455	K_{35} , M_{VS}	19.6	4.466	M_{VS} , K_{35}	19.7	4.433	K_{35} ,M_{VS}
20.3	4.305	K_{60}	20.0	4.368	K_{60} , H_S	20.1	4.347	K_{60} , H_S	20.3	4.305	G_{100} , K_{60} ,Q_S
21.1	4.146	K_{35}	20.8	4.204	K_{45} , S_S , Q_S	20.5	4.264	G_{100} , K_{45}	20.7	4.224	G_{100} , K_{45} ,S_S
23.0	3.813	K_{40}	22.7	3.862	K_{40}	21.0	4.166	$K_{45/35}$,S_S	21.1	4.146	$K_{45/35}$,S_S
23.6	3.718	K_{25}	23.4	3.749	K_{25} , M_M	22.0	3.981	C_{4M}	22.8	3.845	K_{40} , E_{31} , C_{3MS}
24.8	3.544	K_{80}	24.6	3.572	K_{80}	22.5	3.895	M_M , C_{2M}	23.7	3.703	K_{25} , G_{17} , E_4
26.5	3.323	K_{35} , M_{VS} , Q_{VVS}	26.3	3.347	M_{VS} , K_{35} , Q_{VVS}	22.7	3.862	C_{2MS}	24.7	3.558	K, E_7
29.7	2.976	M_S , H_M , T_{VVS}	34.7	2.565	K_{35} , M_{VS}	23.1	3.797	M_M , C_{2M} , C_{3MS}	26.6	3.311	M_{VS}
34.8	2.554	K_{35}	35.1	2.533	K_{35}	23.6	3.726	M_M	29.0	3.045	G_{75} , H_M , T_{VVS}
35.8	2.486	K_{45}	35.6	2.499	K_{45} , H_S	24.6	3.572	K_{80}	29.7	2.976	M_S
37.6	2.372	K_{25}	37.4	2.384	K_{25}	25.3	3.482	E_{23}	34.7	2.561	K_{35} ,M_{VS}
38.3	2.331	K_{40}	38.1	2.342	K_{40}	26.4	3.335	M_{VS} , K_{25}	35.3	2.520	K_{10}
39.0	2.291	K_{35} , T_{MS} , H_M	38.9	2.296	K_{35} , T_{MS} , H_M	28.9	3.055	G_{75} , H_S , T_{VVS}	35.7	2.493	K_{45},G_{11},C_{4VS} , S_S , H_M
						34.8	2.554	M_{VS}	37.5	2.378	K_{25-45}
						35.2	2.530	K_{35} , H_M	38.3	2.331	K_{40}
						35.7	2.493	K_{45} , G_{11} ,C_{4S}	39.1	2.285	K_{25},H_M ,T_{MS} ,H_M , Ca_S
						37.5	2.378	K_{25-45}			
						38.2	2.336	K_{40} , Ca_4A_{VS}			
						39.1	2.288	K_{25} , H_M , T_{VS}			

TABLE A8-3 - XRD results for 3L3S0G and 3L3S6G specimens at 1 and 4 weeks of moist curing at 30°C and 100% relative humidity

APPENDIX 8 - X-RAY DIFFRACTION (XRD) ANALYSIS

2L4S0G						2L4S6G					
CURING PERIOD (Weeks)						CURING PERIOD (Week)					
1			4			1			4		
IDENTIFIED PEAKS		LIKELY COMPOUNDS AND THEIR INTENSITIES	IDENTIFIED PEAKS		LIKELY COMPOUNDS AND THEIR INTENSITIES	IDENTIFIED PEAKS		LIKELY COMPOUNDS AND THEIR INTENSITIES	IDENTIFIED PEAKS		LIKELY COMPOUNDS AND THEIR INTENSITIES
2θ	d-spacing		2θ	d-spacing		2θ	d-spacing		2θ	d-spacing	
8.5	10.014	M_S	8.5	10.071	M	8.4	10.129	M_S	8.5	10.014	M_S
11.9	7.237	K_{100}	11.9	7.237	K_{100}	11.2	7.708	G_{100}	11.3	7.609	G_{100}
17.3	5.030	H_S ,M_M	17.3	5.030	H_S , M_M	12.0	7.178	K_{100}	12.0	7.178	K_{100}
19.5	4.477	M_S , K_{35}	19.5	4.488	M_S , K_{35}	17.4	5.002	M_M , H_S	17.4	5.002	M_M , H_S
20.0	4.368	M_M , H_S	19.9	4.389	K_{60} , H_S	19.4	4.500	M_{VS} , K_{35}	19.5	4.477	M_{VS} , K_{35}
20.6	4.244	K_{35} , M_{VS}	20.9	4.195	K_{45} , S_S	20.0	4.368	K_{60} ,H_S	20.0	4.368	K_{60} , H_S
20.8	4.204	K_{60} , S_S , Q_S	21.2	4.127	K_{35}	20.3	4.305	M_W, G_{100}	20.4	4.285	G_{100}
21.2	4.137	K_{45}	22.7	3.862	K_{40}	20.8	4.204	K_{45} , S_S	20.8	4.204	K_{45} , S_S
22.1	3.964	C_{4M}	24.5	3.586	K_{80}	22.6	3.878	E_{31}, K_{40} , C_{2MS}	22.6	3.878	K_{40} , E_{31} , C_{2MS}
22.7	3.862	K_{40} , C_{2MS}	26.0	3.385	K_{35}	24.4	3.600	K_{80}	23.5	3.734	K_{25} , G_{17}
23.4	3.749	K_{25} , M_M	26.3	3.347	M_M , Q_{VVS}	26.3	3.351	M_{VS}, K_{35}	24.5	3.586	K_{80}
24.5	3.586	K_{80}	27.2	3.267	M_{VS} , H_M	28.8	3.071	M_S,Ca_{VVS},T_{VVS}, H_M, G_{75}, Mg_{VS}	25.2	3.489	E_{23}
26.3	3.347	K_{35} , M_{VS} ,Q_{VVS}	29.5	2.995	M_S , H_M , T_S	34.6	3.569	K_{35} , E_{29} , M_{VS}	26.3	3.347	M_{VS} , K_{35}
29.5	2.995	M_S , H_M , T_S	34.7	2.561	K_{35} , M_{VS}	35.0	2.540	K_{35} , Mg_{VVS}	28.7	3.076	G_{75}, M_S, H_M, Mg_{VS}, T_{VVS}, Ca_{VVS}, S_S
34.6	2.569	M_{VS} , K_{35}	35.0	2.540	K_{25}	35.5	2.506	K_{45} ,G_{11} , S_S	30.9	2.864	G_{45}, T_S, C_{4VS}, C_{3M}
35.0	2.540	K_{35} ,C_{2M}	35.6	2.503	K_{45} , S_S ,H_M	37.3	2.390	K_{25}	34.7	2.561	M_{VS} , K_{35} , E_{29}
35.6	2.499	M_W,S_S,C_{4MS},K_{45} ,H_M	37.3	2.390	S_M , K_{25}	38.1	2.345	K_{40}	35.1	2.533	K_{35} , Mg_{VVS}
37.4	2.384	K_{25} , S_M	38.1	2.345	K_{40} , S_M	39.0	2.291	K_{25}, T_{MS}, Ca_S , H_M	35.6	2.499	K_{45} , G_{11} ,H_M, S_S
38.0	2.348	K_{40} , S_M	38.9	2.299	K_{20} ,T_{MS} , H_M				37.3	2.390	K_{25}
38.8	2.302	K_{40}							38.1	2.345	K_{40}
									39.0	2.291	K_{35} , T_{MS}, Ca_S ,H_M

TABLE A8-4 - XRD results for 2L4S0G and 2L4S6G specimens at 1 and 4 weeks of moist curing at 30°C and 100% relative humidity

APPENDIX 8 - X-RAY DIFFRACTION (XRD) ANALYSIS

OL6S0G						0L6S6G					
CURING PERIOD (Weeks)						CURING PERIOD (Week)					
1			4			1			4		
IDENTIFIED PEAKS		LIKELY COMPOUNDS AND THEIR INTENSITIES	IDENTIFIED PEAKS		LIKELY COMPOUNDS AND THEIR INTENSITY	IDENTIFIED PEAKS		LIKELY COMPOUNDS AND INTENSITIES	IDENTIFIED PEAKS		LIKELY COMPOUNDS AND INTENSITIES
2θ	d-spacing		2θ	d-spacing		2θ	d-spacing		2θ	d-spacing	
8.4	10.129	M_S	8.3	10.246	M_S	8.4	10.129	M_S	8.4	10.129	M_S
11.9	7.237	K_{100}	11.8	7.296	K_{100}	11.2	7.708	G_{100} , C_3	11.2	7.675	G_{100} , C_3
17.4	5.016	M_M , H_S	17.4	5.016	M_M , H_S	11.8	7.296	K_{100}	11.9	7.236	K_{100}
19.5	4.488	K_{35} ,M_{VS}	19.4	4.500	K_{35} , M_{VS}	17.3	5.030	M_M , H_S	17.3	5.030	M_M , H_S
19.9	4.389	K_{60} , H_S	19.9	4.389	K_{60} , H_S	19.5	4.488	K_{35} , M_{VS}	19.4	4.500	M_{VS} , K_{35}
20.4	4.285	M_W	20.8	4.204	K_{45} , S_S , Q_S	20.0	4.368	K_{60} , H_S	20.0	4.368	K_{60} , H_S
20.8	4.204	K_{45}	22.7	3.862	K_{40}	20.3	4.305	G_{100} , Q_S	20.3	4.305	G_{100} , Q_S
22.1	3.964	C_{4M}	23.4	3.749	K_{25} , M_M	20.8	4.204	K_{45} , S_S	20.8	4.204	S_S , K_{45}
22.6	3.878	M_M , K_{40} ,C_{2MS}	24.4	3.600	K_{80}	22.7	3.862	K_{40} , C_2, M_M	22.7	3.870	K_{40} , M_M, C2
23.4	3.749	K_{25} , M_M	29.4	3.010	M_S , H_M , T_S	23.3	3.765	K_{25} , G_{17} , M_M C_{3MS}	23.0	3.813	Ca_4A
24.5	3.593	K_{80}	26.2	3.360	K_{35} , M_{VS}	23.8	3.688	Ha_S	23.5	3.734	K_{25} ,G_{17}, M_M
26.3	3.353	K_{35} , M_{VS}	34.6	2.572	K_{35} , M_S	24.3	3.614	K_{100}	24.5	3.586	K_{100}
29.4	3.010	M_S , H_M , T_S	35.0	2.540	K_{35}	26.3	3.347	K_{35} , M_M	26.3	3.347	M_M , K_{35}
34.6	2.572	K_{35}	35.5	2.506	K_{45}, H_M ,S_S	28.7	3.081	G_{75} , H_M	28.7	3.076	G_{75} , Mg_{VS} , T_{VVS}
35.6	2.503	K_{45} , S_S , H_M	37.3	2.390	K_{25}	29.3	3.015	Mg_{VS} , T_{VVS} , Ca_{VVS}	29.5	2.995	M_S , G_{75} ,T_S, Ca_{VVS}
37.3	2.390	K_{25}	38.1	2.345	K_{40} , S_M	30.7	2.882	G_{45}, C_{4VS}, T_S, C_{3M} ,C_{2VS} , K_{45} , S_{VS}	30.8	2.873	G_{45}, C_{4VS}, T_S, C_{3M} ,C_{2VS} , K_{45} , S_{VS}
38.1	2.342	K_{40}	38.9	2.296	K_{35} , T_{MS}	32.9	2.696	G_{35}	33.0	2.688	G_{35}
38.8	2.302	K_{25}	39.7	2.252	K_{20} , H_M	34.5	2.576	K_{35}, M_{VS}	34.5	2.576	M_{VS} , K_{35}
45.1	1.996	K_{35} , H_{MS}				35.0	2.544	K_{35} , Mg_{VVS}	34.9	2.547	Mg_{VVS}
						35.5	2.506	G_{11},K_{45} ,S_S,H_M	35.5	2.506	S_S ,K_{45} ,G_{11}, H_M
						37.3	2.390	K_{25} , S_M	37.3	2.393	S_M , K_{25}
						38.0	2.348	K_{40}	38.1	2.342	K_{40}
						38.8	2.302	K_{40}	38.8	2.302	K_{40}

TABLE A8-5 - XRD results for 0L6S0G and 0L6S6G specimens at 1 and 4 weeks of moist curing at 30°C and 100% relative humidity

X-RAY ANALYSIS

2θ	d-spacing Å)	Intensity (%)	2θ	d-spacing Å)	Intensity (%)
12.335	7.17	100	45.378	1.997	35
19.810	4.478	36	45.619	1.987	35
20.324	4.366	60	45.937	1.974	20
21.208	4.186	45	46.485	1.952	20
21.451	4.139	35	46.815	1.939	35
23.101	3.847	40	47.280	1.921	20
23.740	3745	25	47.675	1.908	5b
24.858	3.579	80	47.915	1.897	25
26.033	3.420	5	48.652	1.870	20
26.379	3.376	35	49.355	1.845	25
28.263	3.155	20	49.555	1.838	35
28.709	3.107	20	50.375	1.810	20
32.485	2.754	20	51.008	1.489	25
34.939	2.566	35	53.547	1.710	25
35.122	2.553	25	54.267	1.689	25
35.380	2.535	35	54.547	1.681	25
35.612	2.519	10	54.972	1.669	40
38.966	2.495	45	55.296	1.660	40
37.686	2.385	25	55.441	1.656	10
38.320	2.347	40	55.697	1.649	40
38.473	2.338	40	56.291	1.633	30
39.046	2.305	5	56.783	1.620	70
39.259	2.293	35	57.285	1.607	30
39.995	2.253	20	57.796	1.594	10
40.284	2.237	5	58.115	1.586	60
40.644	2.218	10	58.683	1.572	10
41.050	2.197	20	59.472	1.553	30
41.266	2.186	20	59.812	1.545	40
41.524	2.173	5	60.155	1.537	40
41.969	2.151	10	61.166	1.514	5
42.340	2.133	20	61.571	1.505	5
42.697	2.116	10	62.306	1.489	90b
43.189	2.093	10			
43.473	2.080	5			
43.827	2.064	20			

Table A8-6 X-ray peaks for a typical kaolinite - Kaolinite 1A (Aluminium Silicate Hydroxide ($Al_2Si_2O_5(OH)_5$); Specimen from Scalby, Yorkshire, England, UK).

X-RAY ANALYSIS

Calcium Hydroxide (Ca(OH)$_2$			Calcim Oxide (CaO)		
2θ	d-spacing (Å)	Intensity (%)	2θ	d-spacing (Å)	Intensity (%)
18.089	4.9	74	32.204	2.777	30
28.662	3.112	23	37.347	2.4059	100
34.089	2.628	100	53.856	1.7009	54
36.697	2.447	3	64.154	1.4505	16
47.124	1.927	42	67.375	1.3888	16
50.795	1.796	36	79.665	1.2026	6
54.337	1.687	21	88.525	1.1037	6
56.253	1.634	1	91.459	1.0758	16
59.304	1.557	3	103.631	0.9819	12
62.540	1.484	13	112.631	0.9257	6
64.228	1.449	13	129.879	0.8504	6
71.779	1.314	8	142.643	0.8131	10
77.699	1.228	1	147.776	0.8018	16
79.001	1.211	1			
81.825	1.1762	3			
84.724	1.1432	11			
86.187	1.1275	2			
93.232	1.0599	12			
95.993	1.0366	5			
98.830	1.0143	7			
107.513	0.9551	4			
110.607	0.9369	1			
118.285	0.8979	1			
121.285	0.8838	2			
123.125	0.8760	1			
126.584	0.8623	0			
120.125	0.8495	4			
142.281	0.8140	2			

Table A8-7 X-ray peaks for synthetic limes.

X-RAY ANALYSIS

2θ	d-spacing (Å)	Intensity (%)	2θ	d-spacing (Å)	Intensity (%)
9.091	9.72	100	49.440	1.842	5
9.987	8.85	1	49.786	1.830	3
12.283	7.20	1	50.375	1.810	4
15.784	5.61	76	51.161	1.784	1
17.832	4.97	12	51.721	1.766	4
18.243	4.859	6	52.391	1.745	2
18.911	4.689	17	53.112	1.723	2
20.050	4.425	<1	53.717	1.705	2
22.111	4.017	3	54.688	1.677	3
22.944	3.873	1	55.223	1.662	5
24.212	3.673	4	55.296	1.660	5
24.724	3.598	7	56.783	1.620	8
25.614	3.475	23	57.637	1.598	2
27.284	3.266	5	58.236	1.583	3
27.507	3.240	21	58.601	1.574	3
28.766	3.101	1	59.179	1.560	1
29.645	3.011	4	60.328	1.532	<1
31.867	2.806	6	61.481	1.507	2
32.268	2.772	25	62.075	1.494	1
32.977	2.714	1	63.736	1.459	1
33.204	2.696	7	65.341	1.422	<1
33.459	2.676	<1	66.123	1.412	<1
34.277	2.614	16	67.417	1.380	1
35.023	2.560	29	69.173	1.357	1
35.568	2.522	2	70.238	1.339	1
36.116	2.485	2	71.779	1.314	<1
36.963	2.430	1	72.224	1.307	2
37.185	2.416	1	73.330	1.290	1
37.458	2.399	6	74.065	1.275	2
38.371	2.344	2	75.304	1.261	<1
40.416	2.230	8	75.941	1.252	2
40.875	2.206	22	77.926	1.225	2
41.325	2.183	5	78.459	1.218	<1
41.969	2.151	13	80.353	1.194	1
42.444	2.128	2	91.926	1.175	<1
42.591	2.121	5	83.395	1.158	<1
43.473	2.080	2	85.762	1.132	1
43.962	2.058	3	86.235	1.127	1
44.786	2.022	<1	88.592	1.103	2
45.306	2.000	<1	88.796	1.101	1
46.011	1.971	2	90.589	1.084	1
46.687	1.944	11	96.313	1.084	<1
47.755	1.903	1	96.937	1.029	>1
49.652	1.870	1			
49.212	1.850	3			

Table A8-8 X-ray peaks for ettringite.

APPENDIX 9 - A421 TINGEWICK BYPASS PILOT TRIAL MIX DESIGN RESULTS.

BINDER (%)			MCV	CBR (%)		Swell (mm)	Cube Strength (N/mm^2)		
Lime	OPC	GGBS		7 days (3+4)*	14 dys (3+11) *		7 days	14 dys	14 dys (7+7)
1.5	1.5	-	8	28	35	2.7	-	-	-
			12	60	55	3.1	-	-	-
1.5	-	2	8	50	65	0.2	-	-	-
			12	60	75	0.3	-	-	-
1.5	2.5	-	8	35	40	2.8	-	-	-
			12	60	80	2.0	-	-	-
1.5	-	3	8	70	90	0	-	-	-
			12	120	125	1.3	-	-	-
1.5	5.5	-	8	-	-	-	1.4	1.8	1
			12	-	-	-	1.9	1.7	1.1
1.5	-	5.5	8	-	-	-	2.2	2.5	2.2
			12	-	-	-	2.9	2	2.2
1.5	8.5	-	8	-	-	-	2.1	2.5	1.6
			12	-	-	-	2.6	2.6	1.5
1.5	-	8.5	8	-	-	-	2.7	3.4	3.3
			12	-	-	-	2.7	3.2	3.1

- Second number denotes soaking period.

Table A9-1 Mix design results for stabilisation of boulder clay.

(PL 20, LL 47, PI 27, total SO_3 content > 2%, SO_4 > 2.5%).

PUBLICATIONS

(June 1998)

1. **WILD, S., KINUTHIA, J. M., ROBINSON, R. B. and HUMPHREYS, I.** (1996) Effects of ground granulated blastfurnace slag (GGBS) on the strength and swelling properties of lime stabilised kaolinite in the presence of sulphates. *Clay Minerals,* 31, 423 - 433.]**ENCLOSED]**

2. **HIGGINS, D., KINUTHIA, J. M. and WILD, S.** (1998) Soil stabilisation using lime-activated ground granulated blastfurnace slag. *Proceedings of the Sixth CANMET/ACI/JCI International Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, Bangkok, Thailand, 31st May - 5th June, 1998,* Vol. 2, SP178-55, pp. 1057 - 1074.**[ENCLOSED]**

3. **WILD, S., KINUTHIA, J. M., JONES, G. I. AND HIGGINS, D. D.,** (1998) (in Press) effects of partial substitution of lime with ground granulated blastfurnace slag (GGBS) on the strength properties of lime-stabilised sulphate-bearing clay soils. *Journal of Engineering Geology. Elsevier Science, Amsterdam.*

4. **WILD, S., KINUTHIA, J. M., JONES, G. I. And HIGGINS, D. D.,** 1998 (in press). Suppression of swelling associated with ettringite formation in lime-stabilised sulphate bearing clay soils by partial substitution of lime with ground granulated blastfurnace slag (GGBS)". *Journal of Engineering Geology. Elsevier Science, Amsterdam.*

5. **KINUTHIA, J. M., WILD, S., and JONES, G. I.** (1998) (in Press) Effects and of monovalent and divalent metal sulphates on consistency and compaction of lime-stabilised kaolinite. *J. Applied. Clay Science, Elsevier Science, Amsterdam.*

6. **KINUTHIA, J. M., WILD, S., and JONES, G. I.** (1998) (in Press) Compressive strength of lime-stabilised kaolinite in the presence of monovalent and divalent metal sulphates. *Clay Minerals Journal.*

Clay Minerals (1996) **31**, 423–433

EFFECTS OF GROUND GRANULATED BLAST FURNACE SLAG (GGBS) ON THE STRENGTH AND SWELLING PROPERTIES OF LIME-STABILIZED KAOLINITE IN THE PRESENCE OF SULPHATES

S. WILD, J. M. KINUTHIA, R. B. ROBINSON AND I. HUMPHREYS

Department of Civil Engineering and Building, University of Glamorgan, Pontypridd, Mid Glamorgan, South Wales, CF37 1DL, UK

(*Received 13 July 1995; revised 4 December 1995*)

ABSTRACT: The use of ground granulated blast furnace slag (ggbs) is well established in many cement applications where it provides enhanced durability, including high resistance to chloride penetration, resistance to sulphate attack and protection against alkali silica reaction (ASR). The use of ggbs in soil stabilization is, however, still a novel process in the UK although it has been used in South Africa. This paper reports on efforts to extend the use of ggbs to highway and other foundation layers by determining the beneficial effect which it has on the reduction of expansion due to the presence of sulphates. The paper describes the results of laboratory tests on lime-stabilized kaolinite containing different levels of added sulphate to which different amounts of ggbs have been added. The tests determine the strength development of compacted cylinders, moist cured in a humid environment at 30°C, and the linear expansion of these moist cured cylinders on soaking in water. The results illustrate that small additions of ggbs to sulphate containing clays which are stabilized with lime reduce substantially their expansion when exposed to water and have no significant deleterious effect on strength development.

INTRODUCTION

Lime ($Ca(OH)_2$) stabilization of clay soil has been widely used in highway and foundation layers as an economic method of providing suitable pavement and fill material whilst avoiding the generally more expensive process of transporting in large quantities of granular fill. In a number of reported cases, however, (Mitchell, 1986; Hunter, 1988; Snedker & Temporal, 1990), serious problems of swelling and heave have occurred where sulphates were present in the soil and this swelling has been associated with ettringite formation. Mitchell (1986) and Hunter (1988) reported very large amounts of heave, in excess of 100%, leading to pavement failure in the Stewart Avenue lime treated subbase in Las Vegas, Nevada, USA. Snedker & Temporal (1990), on the other hand, reported at least 60% heaving on the Banbury IV contract, part of the M40 motorway between Oxford and Birmingham. In both cases, the heave-induced failures were shown to be related to sulphate reactions when water gained access to the treated sulphate-bearing clay, leading to the formation of highly crystalline materials — ettringite and thaumasite.

In the case of lime-treated kaolinite, in the presence of gypsum, a swelling mechanism has been proposed by Wild *et al.* (1993) which involves an osmotic process associated with initial nucleation and growth of ettringite crystals on the surface of clay particles. Sulphate expansion associated with ettringite formation can also cause problems in Portland cement-based mortar and concretes and one method widely employed to prevent sulphate expansion in these systems is to replace the cement by ground granulated blast furnace slag (ggbs). Use of ggbs as a cementitious material blended with Portland cement is based on its activation with alkalis (mainly $Ca(OH)_2$) released from hydration of the Portland cement (Gjorv, 1989; Hakkinen, 1993). In addition, over recent years, there has been renewed interest in activation of ggbs cements with alkalis other than those from Portland cement, e.g. NaOH, Na_2CO_3 or Na_4SiO_4 (Gjorv, 1989).

TABLE 1. Engineering properties of kaolinite.

Test	Value
Specific gravity	2.57
pH value	4.6
Liquid limit	61%
Plastic limit	32%
Plasticity index	29%
Maximum dry density	1.56 mg/m^3
Optimum moisture content	24.0%

The reaction of ggbs with Portland cement and water is a complex process. When Portland cement hydrates, the principal hydration products are $Ca(OH)_2$ and C-S-H gel. The ggbs, due to its high alumina and silica content, produces somewhat more complex hydrates than ordinary Portland cement (OPC). Precipitates of calcium silicate hydrates and calcium aluminate hydrates result from the hydration reaction that ensues. This hydration reaction which is slower than the hydration of Portland cement has a 'pore-blocking' effect resulting in increased long-term hardening of the cement paste. The blocking of pores leads to higher strength and lower permeability (Macphee *et al.*, 1989) which, besides other improved binding and adsorptive effects, enhances resistance of ggbs concrete to attack from sulphates.

The formation of ettringite in such systems does not necessarily result in expansion and swelling. For example, expansion is not a problem in supersulphated cement in which 80–85% of the ggbs is blended with 10–15% of anhydrite and Portland cement is included as an activator, although ettringite is a principal hydration product and a substantial quantity of sulphate is present in the system.

The well established sulphate-resisting properties imparted to cements by blending them with ggbs suggests that by blending the lime with ggbs, the ggbs may impart similar sulphate-resisting properties to lime-stabilized clays. In both of these systems (i.e. hydrated sulphate-containing lime-clays and Portland cements), the principal phases present (i.e. portlandite, ettringite and C-S-H or C-A-S-H gels) are similar. The object of this work is to establish whether replacement of lime by ggbs in lime-stabilized clay provides increased sulphate resistance whilst maintaining or enhancing strength.

TABLE 2. Chemical and physical properties of lime (Buxton Lime Industries Ltd.).

Trade Name	'Limbux'
Chemical name	Hydrated lime or calcium hydroxide
Physical form	Dry white powder
Molecular formula	$Ca(OH)_2$
Melting/decomposition temperature	580°C
Bulk density	480 kg/m^3
Specific gravity	2.3 (water = 1 at 4°C)
Solubility in water	1.76 g/l sat. sol. at 10°C

EXPERIMENTAL PROCEDURE

Materials used

Hydrated lime and kaolinite (Trade names 'Limbux' and 'Standard Porcelain' respectively) were supplied by Buxton Lime Industries Ltd., Buxton, Derbyshire, UK and by ECC International, St. Austell, Cornwall, UK, respectively. The kaolinite supplied as 'Standard Porcelain' consisted of 84% kaolinite, 13% mica, 1% feldspar and 2% other minerals. The chemical and physical properties of kaolinite and lime are shown in Tables 1 and 2. Ground granulated blast furnace slag was supplied by Civil and Marine Slag Cement Ltd., Llanwern, Newport, UK. Table 3 shows its chemical composition and physical properties together with a typical ordinary Portland cement composition for comparison. Gypsum was supplied by Philip Harris Scientific Ltd. of Pentwyn, Cardiff.

TABLE 3. Chemical composition and physical properties of ggbs and Portland cement from Civil & Marine Slag Cement Ltd., UK.

Oxide	Composition	
	GGBS	Portland cement
CaO	41	63
SiO_2	35	20
Al_2O_3	11	6
Fe_2O_3	1	3
Insoluble residue	0.3	0.5
Relative density	2.9	3.15
Bulk density, kg/m^3	1200	1400
Colour	Off-white	Grey

Consistency limits and compaction tests

Consistency limits tests and standard Proctor compaction tests were performed on kaolinite, kaolinite-lime, kaolinite-lime-gypsum and on kaolinite-lime-gypsum-ggbs systems in order to characterize material behaviour in the presence of water (Table 4).

Composition of test samples

Generally, 1–3 wt% lime is needed for modifying soil properties and 2–8 wt% lime for stabilization, depending on the clay content. As the current work was carried out on 'pure' clay, a reference value of 6 wt% lime was chosen as a sensible addition to the kaolinite clay. Gypsum was included to monitor the effect of sulphate on swelling behaviour, and ggbs was included to establish whether incorporation of this material reduced swelling. Previous work by Wild *et al.* (1993) has shown that substantial swelling is experienced by compacted moist cured kaolinite–6 wt% lime mixes during subsequent soaking, when gypsum is incorporated in the mix at amounts in excess of 2 wt%. Hence, in the current work, a level of 4 wt% gypsum was taken as a reference value, for purposes of comparison. Using the kaolinite–6 wt% lime and the kaolinite–6 wt% lime–4 wt% gypsum mixes as controls, 4 wt% ggbs was also included to determine its effect on the swelling properties. In addition, to indicate the relative effect of each component of the lime-ggbs combination, mixes were made, varying the relative proportion of lime to ggbs but maintaining an overall total amount of 10 wt%.

Preparation of test samples and curing

Dry materials, enough to produce three compacted cylindrical test samples which are 50 mm in diameter and 100 mm in length, were thoroughly mixed in a variable speed Kenwood Chef Excell mixer for 2 min before slowly adding the calculated amount of water. Intermittent hand mixing with palette knives was necessary to achieve an 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 maximum dry density at optimum 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. The cylinders were labelled and placed in polythene bags before being placed on a platform in sealed plastic containers. Water was always maintained below the platform to ensure that there was no evaporation from the samples. The plastic containers were then placed in an environmental chamber capable of maintaining temperatures to

TABLE 4. Proctor and consistency limits results for kaolinite-lime-gypsum-ggbs systems.

	% Slag	% Lime	% Gypsum	Liquid limit (LL) (%)	Plastic limit (PL) (%)	Plasticity index (PI) (%)	Linear shrinkage (LS) (%)	Maximum dry density (MDD) (Mg/m^3)	Optimum moisture content (OMC) (%)
Control	0	0	0	61	32	29	6.0	1.560	24
Control	0	6	0	73	41	32	–	1.490	25
Sample 1	4	6	0	83	41	42	10.4	1.382	29
Sample 2	6	4	0	81	38	43	10.2	1.394	30
Sample 3	8	2	0	79	35	44	10.0	1.405	28
Control	0	6	4	65	29	36	5.1	1.520	25
Sample 4	4	6	4	87	42	45	8.5	1.394	31
Sample 5	6	4	4	85	39	46	8.4	1.404	30
Sample 6	8	2	4	83	35	48	8.3	1.419	30

– Not Determined

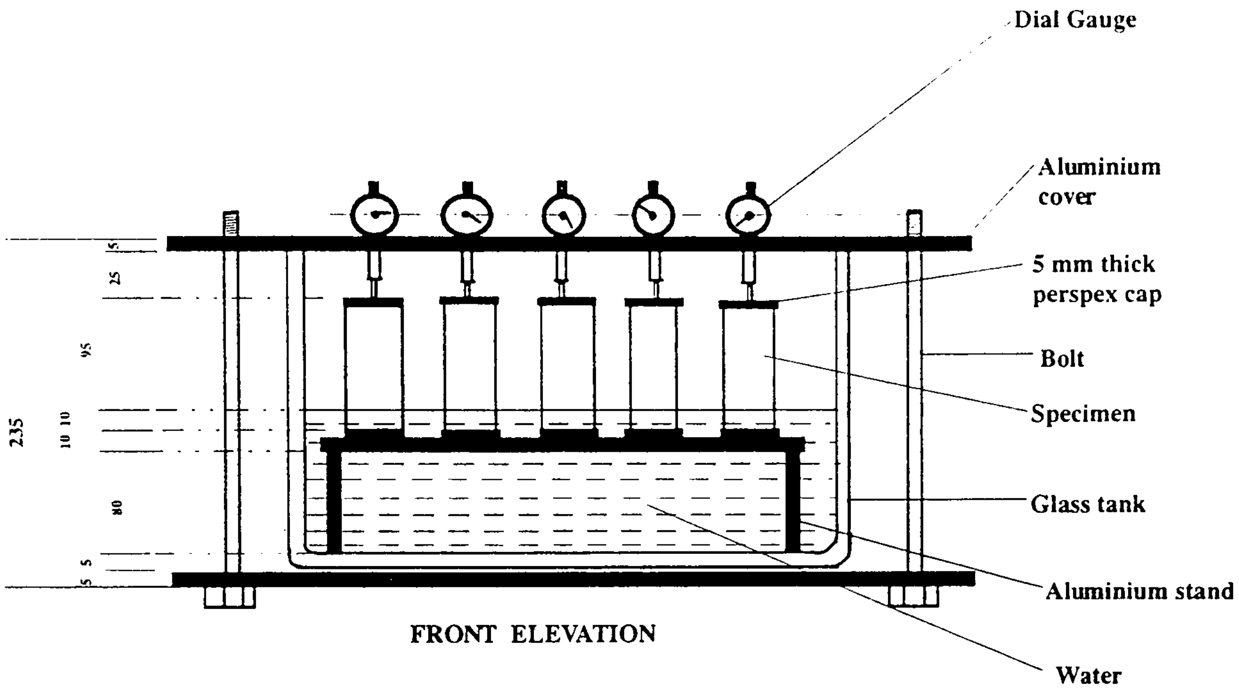


FIG. 1. Chamber employed to monitor the linear expansion during soaking of the previously moist-cured cylinders. (Not to scale; dimensions in mm.)

± 0.1°C and humidity to ± 2% relative humidity. The samples were moist cured for curing periods of 7 and 28 days at 30°C and 100% relative humidity.

Testing

At the end of each of the moist curing periods, three samples were removed from the environmental chamber. Any surface moisture on the cylinders was removed with paper tissue, prior to their being weighed. At this stage two cylinders were subjected to unconfined compressive strength (UCS) tests and one to swelling tests. The end surfaces of samples to be tested for UCS 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. After testing, a small quantity of material was taken from the interior of the tested sample for moisture content determination to establish the moisture condition at the end of each curing period. Previous work by Abdi & Wild (1993) on kaolinite–6 wt% lime–4 wt% gypsum mixes using identical materials and curing environment has shown that linear expansion during moist curing is small relative to that observed during subsequent soaking. This was confirmed by observations on the current mixes. Therefore detailed expansion measurements were only carried out during soaking.

Samples to be tested for swelling were placed on a platform in a glass tank and covered with a lid fitted with dial gauges (Fig. 1). The cylindrical samples were partially immersed in water to a depth of 10 mm above their base. The tank was placed in the environmental chamber where conditions were maintained at 30°C and 100% relative humidity. Linear axial swelling was monitored on a daily basis until no further expansion occurred.

Both the moist curing environment and the soaking environment were closed sealed systems to reduce the availability of carbon dioxide and prevent carbonation of the lime. Clearly excessive carbonation of the lime would reduce the amount of lime available for pozzolanic reaction and is, therefore, undesirable.

RESULTS

It is generally accepted that the addition of small amounts of lime to kaolinite produces a marked increase in the plastic limit. The liquid limit may

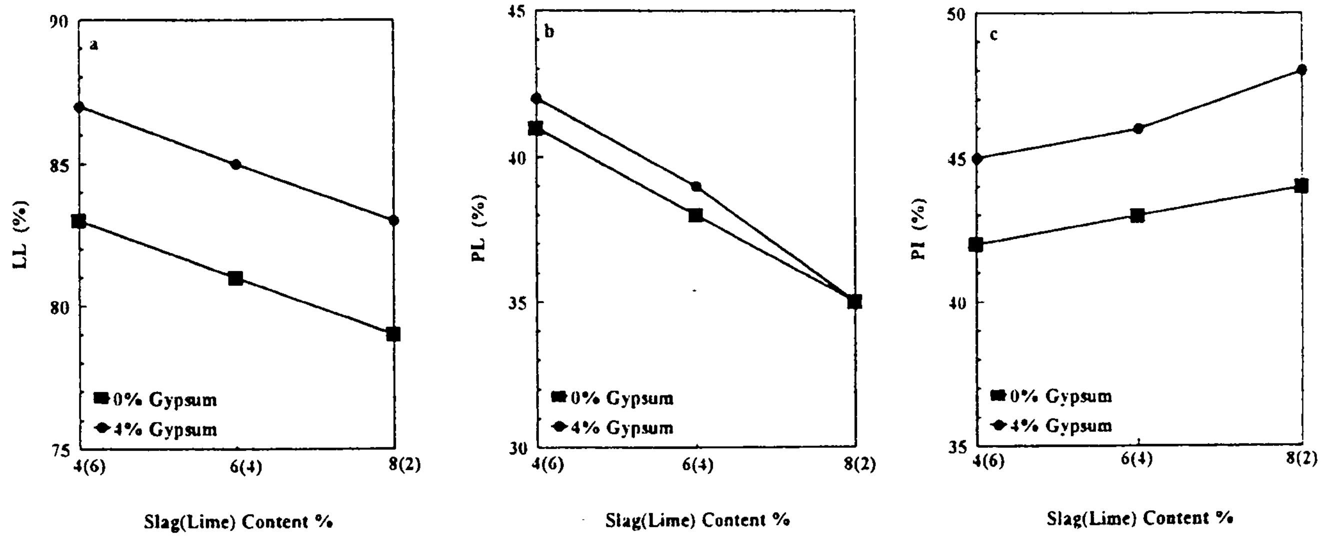


FIG. 2. Change in (a) liquid limit, (b) plastic limit and (c) plasticity index with composition, kaolinite–10 wt% (slag/lime) mixes with and without 4 wt% gypsum.

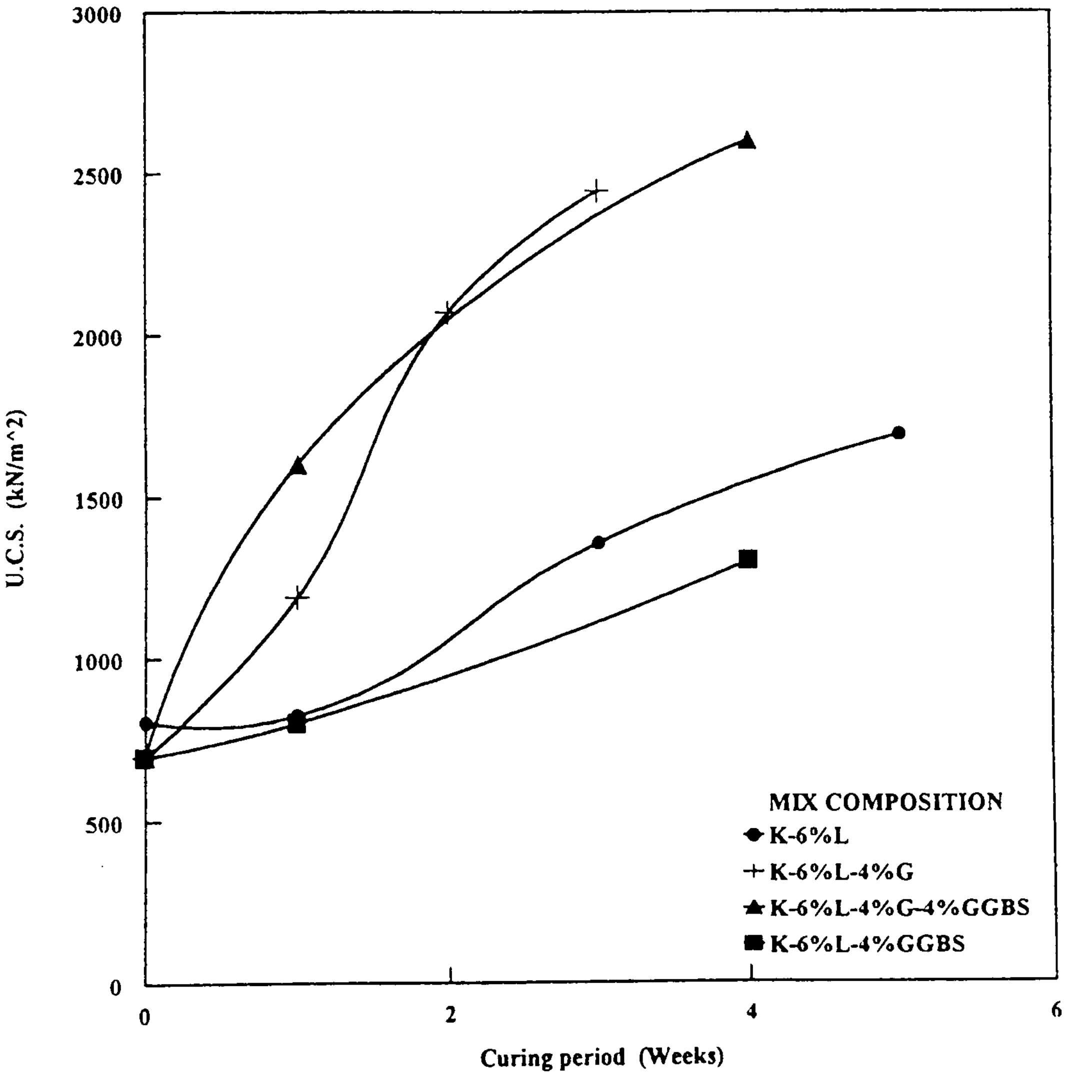


FIG. 3. Unconfined compressive strength *vs.* curing time for kaolinite–6 wt% lime cylinders containing 4 wt% gypsum and/or 4 wt% ground granulated blast furnace slag.

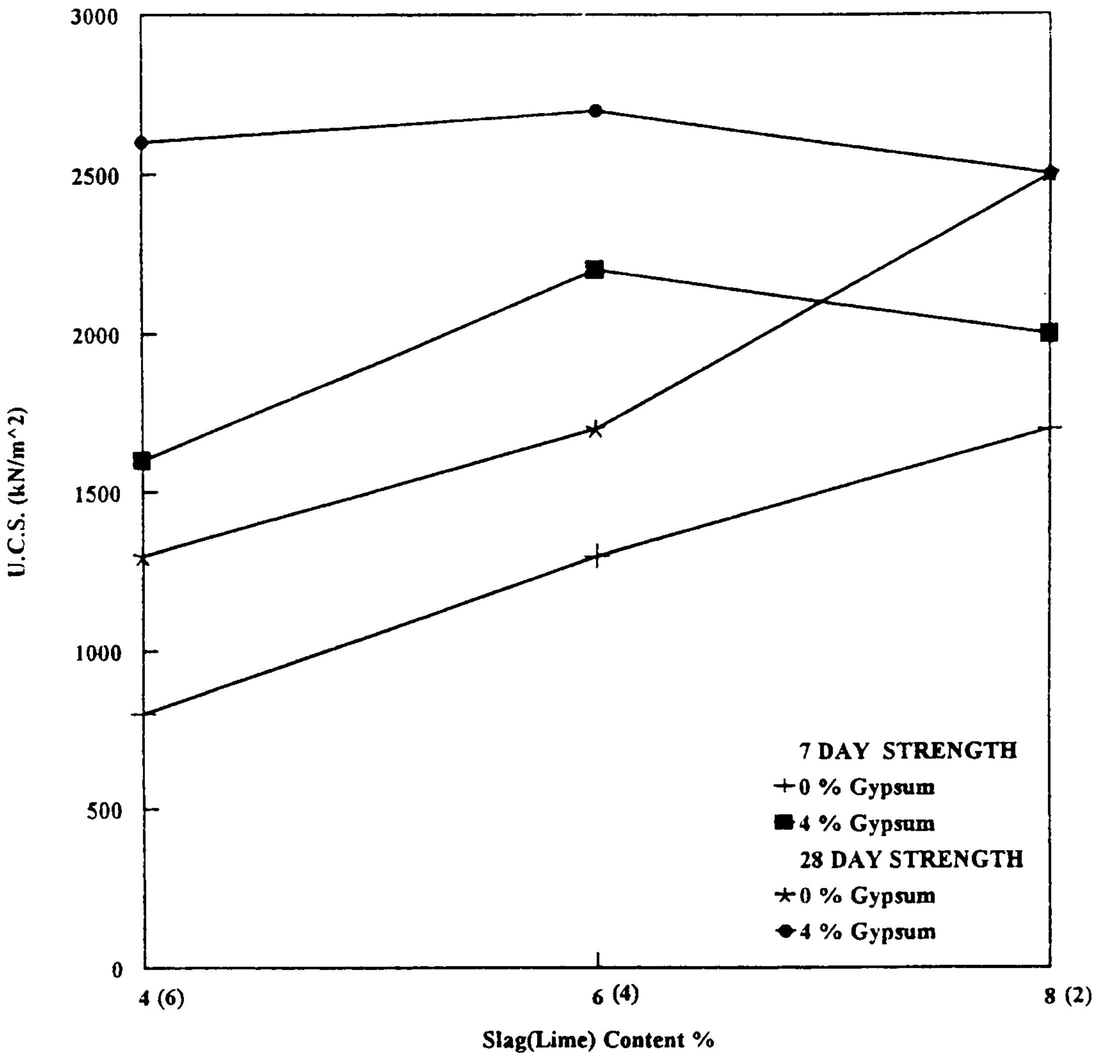


FIG. 4. Unconfined compressive strength (U.C.S.) *vs.* composition (slag/lime) for cylinders with and without gypsum (4 wt%) moist cured for 7 and 28 days.

increase or decrease but in such a way that there is an increase in the plasticity index with increasing lime content for lime contents up to 6 wt%. This is confirmed by the data given in Table 4. Figure 2 shows the effect of different lime-slag ratios on the Atterberg limits of kaolinite and kaolinite–4 wt% gypsum. This illustrates that as the lime to slag ratio decreases, there was a small reduction in liquid limit and a more marked decrease in the plastic limit thus producing an increase in the plasticity index. The effect of this decrease in lime to slag ratio on linear shrinkage (Table 4) was relatively minor producing a slight reduction. These trends were maintained when gypsum was present in the kaolinite (Fig. 2) but gypsum has the effect of producing slightly higher liquid limits and plasticity indices, and slightly lower shrinkage. The addition of lime to kaolinite produced a sharp reduction in maximum dry density corresponding to an increase in optimum moisture content (Table 4). However, a decrease in lime to slag ratio produced a slight increase in maximum dry density and a small but non-systematic variation in optimum moisture content. Similar trends were observed when gypsum was present, the effect of the gypsum being to produce a slightly greater maximum dry density and optimum moisture content.

Figure 3 shows compressive strength *vs.* curing period for compacted and moist-cured kaolinite–6 wt% lime cylinders containing 4 wt% gypsum, 4 wt% ggbs and 4 wt% gypsum plus 4 wt% ggbs. The addition of 4 wt% gypsum resulted in a significant increase in compressive strength in specimens both with and without ggbs. This is in agreement with previous reports (Waswa *et al.*, 1993) of the effect of gypsum on strength. The addition of 4 wt% ggbs produced a small reduction

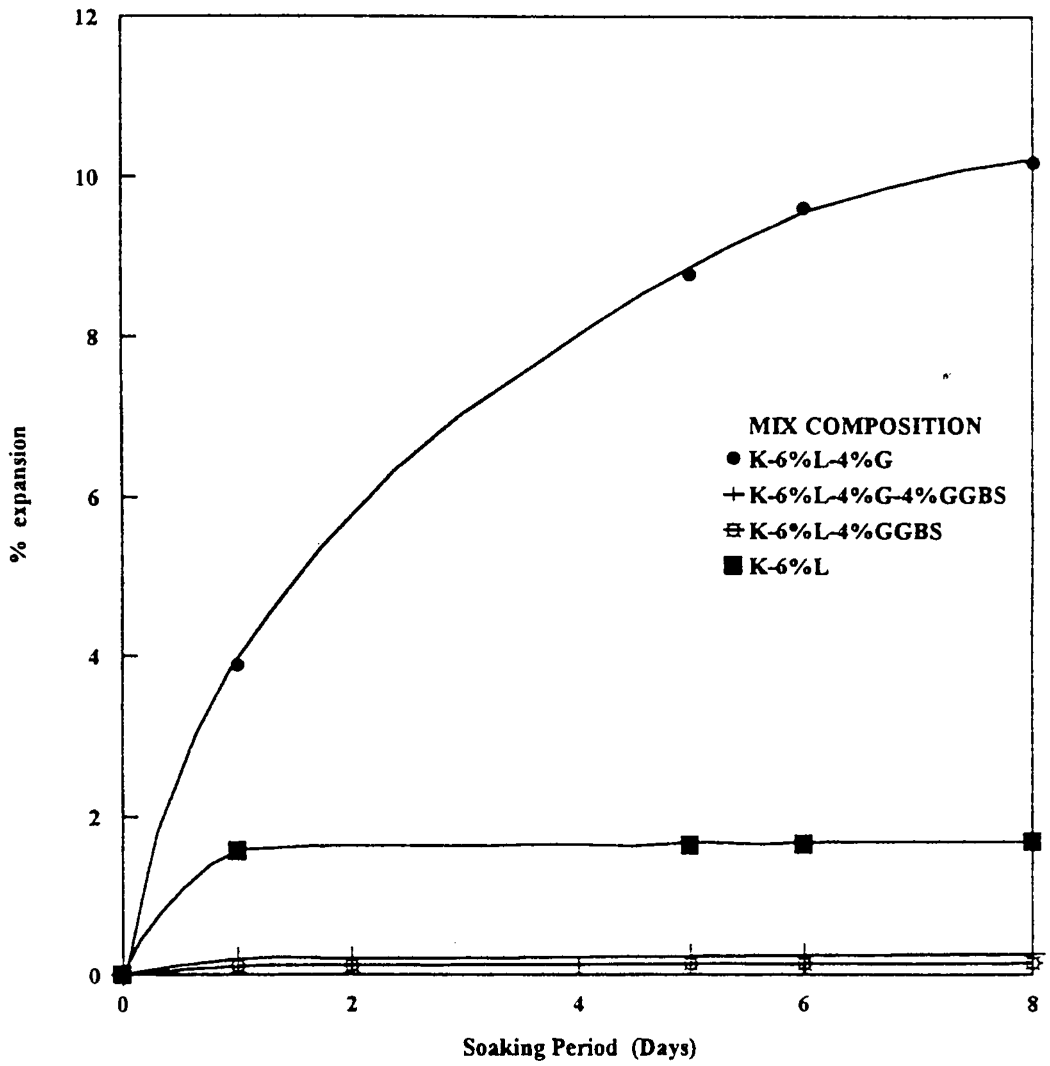


FIG. 5. Unconfined linear expansion *vs.* soaking time for 7-day moist-cured kaolinite–6 wt% lime cylinders containing 4 wt% gypsum and/or 4 wt% ground granulated blast furnace slag.

in strength when gypsum was absent, but resulted in an initial acceleration in strength development when gypsum was present.

Figure 4 shows the effect on the 7-day and 28-day strengths of changing the relative proportions of lime to slag both with and without added gypsum. Without added gypsum there was a consistent gain in strength as the slag to lime ratio increased. Significantly, when gypsum was added the strengths of the specimens with low lime to slag ratios did not increase greatly whereas specimens with high lime to slag ratios showed a substantial increase in strength. This suggests that gypsum had a much more profound effect on the lime-kaolinite reaction than it did on the hydration of the slag.

With regard to sulphate expansion, the stabilized soil might be expected to be in its most vulnerable state in the early stages of curing when negligible interparticle bonding had developed (Abdi & Wild, 1993). Therefore, swelling measurements during soaking were performed on specimens which had been moist cured for only 7 days and 28 days.

Figures 5 and 6 show the percent linear expansion on soaking of 7-day and 28-day moist-cured cylinders, respectively, for kaolinite–6 wt% lime compositions containing 4 wt% ggbs, 4 wt% gypsum, and 4 wt% ggbs plus 4 wt% gypsum. For 7-day cured specimens (Fig. 5), the effect of the slag on reducing expansion was dramatic, particularly when gypsum had been added, where expansion was reduced from over 10% to 0.26%. For 28-day cured specimens (Fig. 6) where expansion was very much less, the addition of ggbs still reduced expansion by a significant factor (i.e. from 1.45% to 0.23%). It is also of interest to

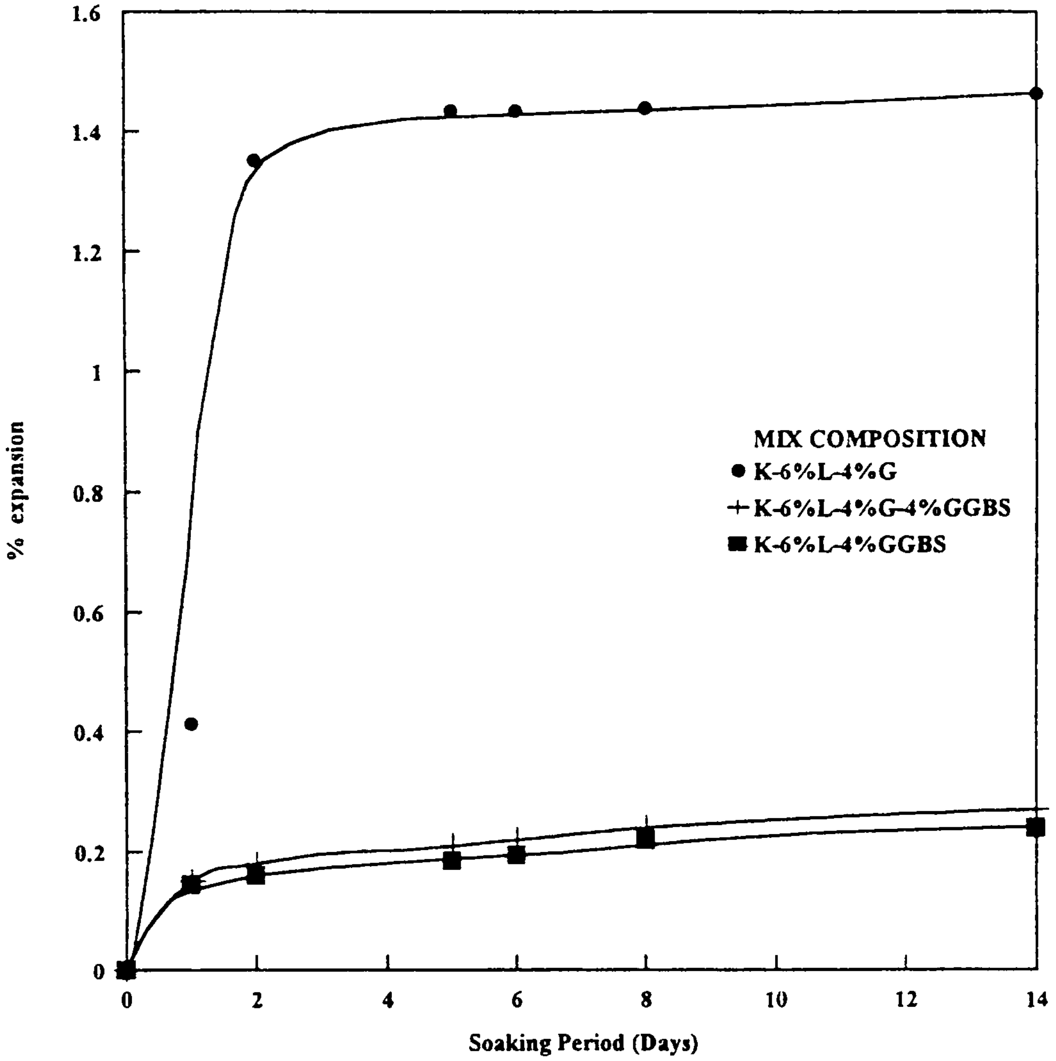


FIG. 6. Unconfined linear expansion *vs.* soaking time for 28-day moist-cured cylinders containing 4 wt% gypsum and/or 4 wt% ground granulated blast furnace slag.

note that the expansion of the kaolinite-lime specimens containing ggbs was virtually the same regardless of whether gypsum was or was not present, which suggests that the ggbs had in some way eliminated the expansive effect of the gypsum. The effectiveness of the slag in eliminating the effect of gypsum on expansion was also sensitive to the relative amount of slag to lime which was added.

Figures 7 and 8 show the effect of different slag to lime ratios on the swelling of 7-day and 28-day cured cylinders, respectively, when gypsum was and was not added. Because slag was present in all specimens the percent expansions were much smaller than the maximum observed in Figs. 5 and 6 at equivalent ages. Without added gypsum, changing the lime to slag ratio over the range chosen had little effect on the linear swell. However, when gypsum was present, there was a significant variation in percentage linear swell with changing lime to slag ratio and surprisingly it decreased as the lime to slag ratio increased. To what degree this trend continued is unknown at present, although the results do suggest that only relatively small additions of slag are required to eliminate the effect of sulphate expansion observed in the current work.

DISCUSSION

When clays such as kaolinite are subjected to moisture they show intercrystalline swelling (Arabi & Wild, 1989). Water, a few monolayers thick, is strongly adsorbed at the negatively charged particle surfaces. Beyond this, an extensive adsorbed layer is formed due to the concentration gradient between

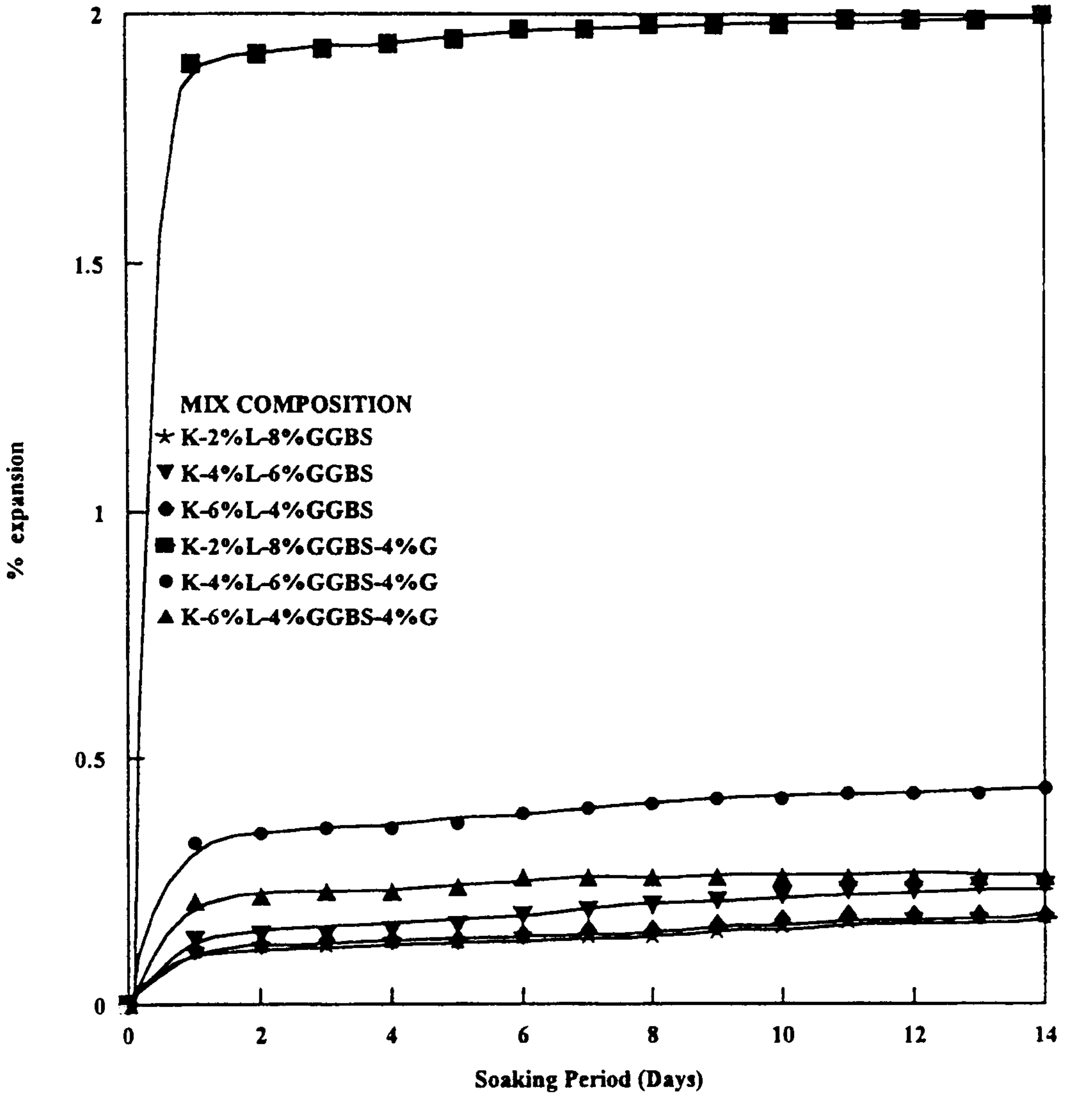


FIG. 7. Unconfined linear expansion *vs.* soaking time for 7-day moist-cured cylinders of different slag/lime ratios, with and without gypsum.

the bulk solution and the electrical double layer (consisting of water molecules and exchangeable cations). The addition of lime modifies the electrical double layer, reducing the thickness of the adsorbed water layer and thus reducing the swelling capacity. Flocculation also ocurrs. In addition to the rapid ion exchange reaction, on treatment with lime there is also a slow chemical reaction which produces cementitious C-A-S-H gel and in some cases crystalline calcium aluminate hydrate and calcium silicate aluminate hydrate phases. The cementing effect of these reaction products binds the clay particles together, further resisting swelling. Therefore, lime-clay specimens cured for long periods would be expected to show increased resistance to swelling. When sulphates are present in addition to lime, the reaction at the clay particle surfaces is modified. Ettringite crystals nucleate and grow on the surface of the kaolinite plates, within a colloidal C-A-S-*S*-H product, and the swelling capacity shows a dramatic increase. Wild *et al.* (1993) proposed that an osmotic mechanism, in which concentration gradients are generated within this surface colloidal layer, is responsible for the extreme swelling which occurs when sulphate (i.e gypsum) is present. In the current work the addition of ggbs to lime-stabilized kaolinite (Figs. 5, 6) dramatically reduced the swelling of specimens in contact with water. This, however, is not a result of increased interparticle bonding, as the addition of ggbs tends to produce a slight decrease in strength (Fig. 3) suggesting little or no improvement in interparticle bonding.

The hydration of slag in the presence of calcium sulphate is known from work on supersulphated cements (Taylor, 1990) to produce C-S-H gel and

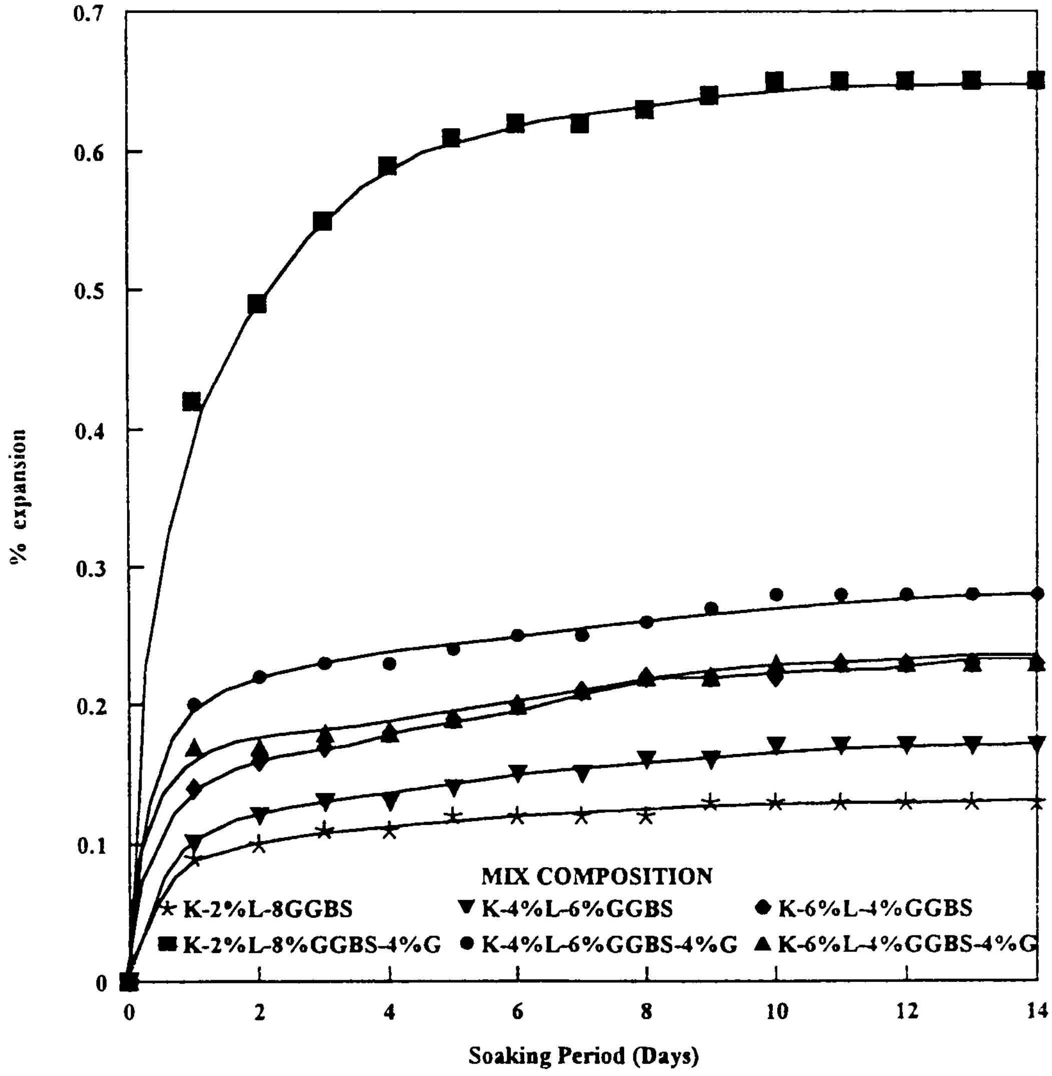


FIG. 8. Unconfined linear expansion *vs.* soaking time for 28-day moist-cured cylinders of different slag/lime ratios, with and without gypsum.

ettringite. The calcium sulphate is rapidly consumed (within a few days) and the slag particles provide nucleation sites on which well-developed ettringite crystals form. The manner in which the ettringite forms is such that little expansion occurs. In the current work, therefore, there will be competing reactions (i.e. slag hydration activated by lime in the presence of calcium sulphate to give C-S-H gel and ettringite, and kaolinite-lime aqueous reaction in the presence of calcium sulphate to give a colloidal C-A-S-*S*-H product plus ettringite) and also competing nucleation sites on the kaolinite particle surfaces and on the slag particle surfaces. Therefore, one possible explanation of the dramatic reduction in expansion, on addition of ggbs, is that the slag hydration reaction becomes the dominant reaction, and nucleation and growth of ettringite crystals on slag particles starves the kaolinite particles of the available sulphate. Thus, ettringite nucleation on the clay particle surfaces is prevented. The nature of the reaction product which forms on the clay particles is modified and the clay no longer undergoes extreme expansion when saturated with water.

When gypsum is not present, increasing the slag to lime ratio but keeping the total slag and lime constant (at 10%) results (see Fig. 4) in a systematic increase in strength. This indicates that the slag hydration reaction, which is activated by lime, is a more rapid reaction than the lime kaolinite reaction. Although for these specimens expansion is extremely small (<0.2%), it does, as might be expected, tend to decrease (see Fig. 8) as the strength and slag to lime ratio increases. The addition of gypsum enhances the strength development particularly at low slag to lime ratios (see Fig. 4) suggesting that gypsum has a greater accelerating effect on the lime-kaolinite reaction than it does on the slag hydration reaction. The acceleration (Wild *et al.*, 1993) is known to be due to rapid removal of Al from solution, by formation of ettringite. The expansion of the gypsum-containing specimens, although reduced dramatically by incorporation of slag, does vary quite widely (Figs. 7, 8) for different slag to lime ratios and is, in fact, substantially greater at higher slag to lime ratios. On the basis of the proposed hypothesis, the converse might be expected to occur. However, there may also be a small contribution to expansion from the nucleation and growth of ettringite on the slag which would become apparent at high slag to lime ratios. Clearly, much more detailed work is still required, employing micro-analytical methods, and using a wider range of compositions in order to verify the proposed hypothesis, and this will be the object of further study.

CONCLUSIONS

The following principal conclusions may be drawn from the current work. (1) Kaolinite clay containing gypsum and stabilized with lime, shows (when cured for short periods) very large levels of expansion when in contact with water. (2) The addition of ggbs to the clay-lime-gypsum system results in a dramatic reduction in this expansion whilst producing only a small variation in compressive strength. (3) Adjusting the ratio of lime to ggbs whilst maintaining a constant combined weight modifies both compressive strength and expansion. In the absence of gypsum, an increase in the slag to lime ratio produces an increase in strength and a decrease in expansion. With gypsum present, an increase in the slag to lime ratio produces an increase in expansion but a non-systematic variation in strength. (4) It is postulated that the marked reduction in expansion imparted by the ggbs results from the relative balance between competing hydration reactions. This is thought to inhibit the nucleation of ettringite on the surface of kaolinite particles, a process previously associated with extreme expansion. (5) Much more detailed work is required using a wider range of compositions and employing micro-analytical methods to confirm the proposed hypothesis. Also the work should be extended to include Na-, K- and Mg-sulphates.

ACKNOWLEDGMENTS

The authors would like to thank Dr D.D. Higgins of Civil and Marine Slag Cement Ltd. for his suggestion that we investigate slag as part of our lime-stabilization research programme and also for supply of the slag. The authors would also like to thank Buxton Lime Industries and ECC International for supplying the lime and the kaolinite, respectively. In addition, the authors would like to thank Prof. P.S. Coupe, Head of Department of Civil Engineering and Building and the technical staff in the Department for provision of facilities and assistance, and also to ODA for providing a scholarship for J.M. Kinuthia.

REFERENCES

ARABI M. & WILD S. (1989) Property changes induced in clay soils when using lime stabilization. *Municipal Engineer*, **6**, 85–99.

ABDI M.R. & WILD, S. (1993) Sulphate expansion of lime-stabilized kaolinite: I Physical characteristics. *Clay Miner.* **28**, 555–567.

GJORV O.E. (1989) Alkali activation of a Norwegian granulated blast furnace slag. *American Concrete Institute, Detroit. Proc. Third Int. Conf. Trondheim, Norway 1989*, **2**, SP114-73, 1501–1517.

HAKKINEN T. (1993) Influence of slag content on the microstructure, permeability and mechanical properties of concrete. *Cement Concrete Res.*, **23**, 407–421.

HUNTER D. (1988) Lime-induced heave in sulphate-bearing clay soils. *ASCE J. Geot. Eng.* **114**, 150–167.

MACPHEE D.E., ATKINS M. & GLASSER F.P. (1989) Phase development and pore solution chemistry in ageing blast furnace slag-portland cement blends. *Materials Res. Soc. Sym.*, **127**, 475–480.

MITCHELL J.K. (1986) Delayed failure of lime-stabilized pavement bases. *J. Geot. Eng.* **112**, 274–279.

SNEDKER E.A. & TEMPORAL J. (1990) M40 Motorway Banbury IV Contract – Lime Stabilization. *Highways Transportation*, Dec 7–8.

TAYLOR H.F.W. (1990) *Cement Chemistry*. Academic Press Inc., San Diego, **CA 92101**.

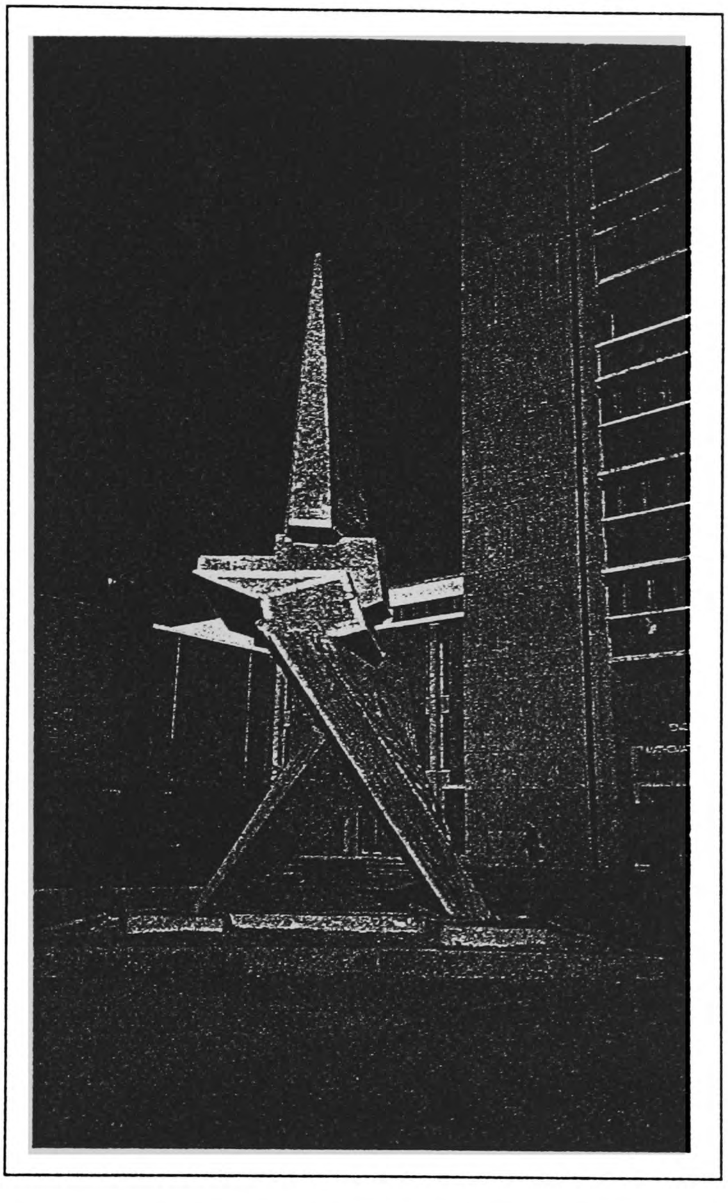
WASWA B., WILD S., JONES G.I. & WEBB D.T.W. (1993) The potential of lime-stabilized murram soil as a building material in Kenya. *Building Res. Information*, **21**, 287–295.

WILD S., ABDI M.R. & LENG WARD G. (1993) Sulphate expansion of lime-stabilized kaolinite: II Reaction products and expansion. *Clay Miner.* **28**, 569–583.

1998

SIXTH CANMET / ACI / JCI
SIXIÈME CANMET / ACI / JCI

INTERNATIONAL · CONFERENCE · INTERNATIONALE



FLY ASH, SILICA FUME, SLAG AND NATURAL POZZOLANS IN CONCRETE

CENDRES VOLANTES, FUMÉES DE SILICE, LAITIERS ET POUZZOLANES NATURELLES DANS LE BÉTON

VOLUME 2

EDITOR · **V.M. MALHOTRA** · RÉDACTEUR EN CHEF

SP 178-55

Soil Stabilization using Lime-Activated Ground Granulated Blast Furnace Slag

by D.D. Higgins, J.M. Kinuthia and S. Wild

Synopsis: Soil stabilisation with cement or lime, is a well established technique for use in highway or foundation construction. Extensive laboratory investigations and a full-scale trial have been carried out to evaluate the performance of ground granulated blastfurnace slag (ggbs) in combination with lime, for stabilising soils. This paper reports the results of laboratory tests for strength and swelling, and also describes the full-scale trial.

The applicability of lime / ggbs combinations has been demonstrated. In addition laboratory tests have shown a previously undemonstrated advantage where the incorporation of ggbs combats the deleterious swelling which can occur when sulphate-containing soils are stabilised with cement or lime.

Keywords: blast furnace slag; expansion; lime; roads; stabilization; strength; sulfates.

Denis Higgins is Director General of the UK Cementitious Slag Makers Association at Croudace House, Godstone Road, Caterham, Surrey, UK.

John Kinuthia was a PhD student at the School of the Built Environment, University of Glamorgan, Pontypridd, Mid Glamorgan, UK. This paper is mainly based on work carried out as part of his thesis.

Stan Wild is Professor of Construction Materials and Head of the Building Materials Research Unit, also in the School of the Built Environment, University of Glamorgan.

INTRODUCTION

Soil Stabilisation

Soil stabilisation techniques for road construction are used in most parts of the world. In densely-populated countries such as the UK, environmental factors and taxes encourage the upgrading of in-situ soil, by stabilisation as an alternative to its export to land-fill and replacement by imported granular fill.

Soil stabilisation is normally carried out using lime or cement and the main properties that may require alteration by stabilisation are:

a) strength - to increase the strength and bearing capacity
b) volume stability - to control the swell-shrink characteristics caused by moisture changes
c) durability - to increase the resistance to erosion, weathering or traffic loading.

In South Africa, ground granulated blastfurnace slag (ggbs) has been widely used in combination with lime, for stabilising soils. Prompted by this experience and the ready availability of ggbs an investigation was carried out to evaluate lime / ggbs for use in soil stabilisation in the UK. This investigation consisted of a full-scale site trial, combined with extensive laboratory investigations. The present paper reports on the trial and on the laboratory results for strength and swelling. Results for initial lime consumption, plastic limit, liquid limit, compaction and optimum moisture will be reported elsewhere. Some of the work has been reported previously (1).

Swelling in the presence of Sulphates

Lime and cement stabilisation of soil have been widely used in highway and foundation layers. However, in a number of reported cases (2-5) serious problems of swelling and heave have occurred where sulphates were present in the soil and this swelling has been linked with ettringite formation. Mitchell (2) and Hunter (3) reported very large amounts of heave, in excess of 100%, leading to pavement failure in the Stewart Avenue lime-treated sub-base in Las Vegas, Nevada, USA. Snedker and Temporal (4), on the other hand, reported at least 60% heaving on the Banbury IV contract, part of the M40 motorway between Oxford and Birmingham in the UK. In both cases, the heave-induced failures were shown to be related to sulphate reactions when water gained access to the treated sulphate-bearing clay, leading to the formation of expansive materials - ettringite and thaumasite.

In the case of lime-treated kaolinite, in the presence of gypsum, a swelling mechanism has been proposed by Wild *et al.* (6) which involves an osmotic process associated with initial nucleation and growth of ettringite crystals on the surface of clay particles. Sulphate expansion associated with ettringite formation can also cause problems in Portland cement-based mortar and concrete, where one method widely employed to prevent sulphate expansion is to replace part of the cement by ground granulated blastfurnace slag.

Ground granulated blastfurnace slag

Ggbs on its own has only slight cementitious properties and for most applications activation by alkali is required. Portland cement is the most commonly used activator. The reaction of ggbs with Portland cement and water is a complex process. When Portland cement hydrates, the principal hydration products are $Ca(OH)_2$ and C-S-H gel. The ggbs, due to its higher alumina and silica content, produces slightly different hydrates from normal Portland cement. Precipitates of calcium silicate hydrates and calcium aluminate hydrates predominate, with relatively little $Ca(OH)_2$. The ggbs reactions, which are slower than the hydration of Portland cement, have a 'pore-blocking' effect and lead to higher ultimate strength and lower permeability (7). This together with the reduced $Ca(OH)_2$ and other improved binding and absorptive effects, enhances resistance of ggbs concrete to attack from sulphates.

The formation of ettringite in systems containing ggbs does not necessarily result in expansion and swelling. For example, in supersulphated cement 80-85% of ggbs is blended with 10-15% of calcium sulphate and about 10% Portland cement is included as an activator. Although ettringite is a principal hydration product and a substantial amount of sulphate is present in the system, the cement has no tendency to expand. It is also highly resistant to attack by external sulphates. The well established sulphate-resisting properties imparted to cements by blending them with ggbs suggested that blending lime with ggbs might impart similar sulphate-resisting properties to lime-stabilised clays. In both sulphate-containing lime-stabilised clays and hydrated portland cements, similar phases are present i.e. C-S-H and C-A-S-H gels, $Ca(OH)_2$ and ettringite.

LABORATORY TESTS

Materials

In order to produce a 'soil' with potential for swelling, a porcelain clay consisting of 84% kaolinite 13% mica, 1% feldspar and 2% other minerals, was blended with laboratory-quality gypsum.. The gypsum content of the artificial soil was varied between 0% and 8% (i.e.0% to 3.72% SO_3). This material is referred to as 'kaolinite'. Tests were also carried out with an as-dug Kimmeridge type clay which naturally contained 1.73% SO_3.

The lime and ggbs were typical of materials commercially available in the UK. The lime consisted primarily of calcium hydroxide. The ggbs had a fineness of 450 m^2/kg and its chemical composition was:

43% CaO, 35.5% SiO_2, 8% MgO, 12% Al_2O_3, 0.5% K_2O, 0.2%Na_2O.

A wide range of combinations of clay, gypsum, lime and ggbs was investigated to determine the effect on combating sulphate expansion or enhancing strength

Preparation of Test Samples

The dry constituents were thoroughly mixed in a variable speed mixer for 2 minutes before slowly adding the required amount of water for optimum moisture content. This had been determined as 30.55% for kaolinite mixtures and 24.22% for Kimmeridge clay mixtures. Intermittent hand mixing with palette knives was necessary to achieve a homogeneous mixture. A steel mould and a collar capable of accommodating all the material required for one specimen, was used to compress the sample to maximum dry density. The design of the mould ensured that the material was not over-compressed and produced a compacted cylinder, 50mm in diameter and 100mm in length The cylinders were extruded using a steel plunger, trimmed, cleaned of releasing oil, weighed, measured and wrapped in several layers of cling film.

Strength Testing

The specimens for strength testing were labelled and placed in polythene bags before being placed on a platform in sealed plastic containers. Water was always maintained below the platform to ensure that there was no evaporation from the samples. The plastic containers were then placed in an environmental chamber capable of maintaining ± 0.1°C and ± 2% relative humidity. After moist curing for 7- or 28- days at 30°C and 100% relative humidity, the specimens were removed from the environmental chamber and all wrapping, including the cling film, was removed. Any surface moisture on the cylinders was absorbed in paper tissue, prior to their being weighed. At least two duplicate cylinders were used for unconfined compressive strength (UCS) tests. The end surfaces of the specimens to be tested for UCS 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 and this was applied at 1mm/min.

Swelling Measurements

The specimens to be tested for swelling, had the bottom 10mm of cling film removed to expedite water ingress. Initially (see Fig.1) they were placed on a platform in a glass tank and covered with a lid fitted with dial gauges and containing some water below the platform. This "curing" started immediately after the samples were fabricated.

After the required period of moist curing, the cylinders were partially immersed in water to a depth of 10mm above their base by increasing the water level in the tank, without disturbing the specimens. This process is referred to as "soaking". During both moist curing and soaking, the tank was contained in the environmental chamber where conditions were maintained at 30°C and 100% relative humidity. Linear axial swelling during soaking was monitored on a daily basis, for several weeks. Both the moist curing environment and the soaking environment were closed sealed systems to reduce the availability of carbon dioxide and prevent carbonation of the lime. Excessive carbonation of the lime would have reduced the amount of lime available for pozzolanic reaction which was undesirable.

COMPRESSIVE STRENGTH RESULTS

Kaolinite System

Fig.2 plots the unconfined compressive strength at 7- and 28-days for specimens of kaolinite with and without added gypsum, when stabilised with different ratios of lime / ggbs. In all cases the total ggbs+lime content was 6%. The mixtures which contained ggbs but no lime, achieved insignificant strength, indicating that lime was necessary to activate the ggbs. This was slightly unexpected in view of the reported ability of gypsum to activate ggbs (8).

With lime/ggbs but no gypsum, substitution of ggbs for lime, tended to increase strength at 7-days. By 28-days, this was much more marked showing a distinct peak at a ggbs: lime ratio of 5:1. This would be consistent with the hydration of the ggbs being at a much more advanced state at 28-days in contributing strength, than the pozzolanic reaction between lime and the kaolinite.

The addition of gypsum accentuated the trend for 7-day strength to increase with increasing slag:lime ratio. However at 28-days the effect was different and in the presence of higher levels of gypsum, the lime-only mixtures showed considerable strength with little additional strength resulting from increasing slag:lime ratio. This suggested that the lime-gypsum-kaolinite reaction can develop significant strength on its own by 28-days.

Kimmeridge Clay

Fig.3a plots the 7- and 28-day strength for Kimmeridge clay against slag:lime ratio for 5% stabiliser (i.e. lime + ggbs) content. Subsequent plots are for 6%, 8% and 10% stabiliser content. Unlike the kaolinite system where the SO_3 level was artificially varied, the sulfate level in the Kimmeridge clay was left at its natural content of 1.73% SO_3. In contrast to the kaolinite system, Kimmeridge clay compositions containing ggbs but no lime, achieved measurable strengths. This implies that the Kimmeridge clay contained a component, not present in the kaolinite-gypsum system, which activated the ggbs. To date this component has not been identified.

The Kimmeridge clay mixtures showed similar trends to those with kaolinite, when compared at similar levels of stabiliser and gypsum. Comparable plots are Fig.2b (kaolinite with 1.86% SO_3 and 6%stabiliser) and Fig.3b (Kimmeridge clay with 1.73% SO_3 and 6%stabiliser).

In the Kimmeridge clay series of mixtures (unlike with kaolinite), the stabiliser content was varied. This was found to have a significant effect on the strength trends. For example at 5% stabiliser, the 28-day strength reduced slightly as the ggbs: lime ratio increased (Fig.3a). At 8% and 10% stabiliser the 28-day strength increased markedly with the ggbs: lime ratio, peaking at a ratio of about 1:1 (Figs.3c and 3d). This complex behaviour makes it difficult to provide generalised guidelines for optimising strength.

SWELLING TEST RESULTS

Kaolinite System

Figs. 4, 5, 6 and 7 plot the expansion behaviour of kaolinite-lime-slag mixtures with 0%, 1.86%, 2.79% and 3.72% of SO_3 respectively. In all cases the stabiliser content was 6%. For comparison purposes, approximate UK Dept.of Transport limits for average and maximum swell are indicated (The DofT limit of 5mm on a 127mm specimen equates to 4% expansion, and 10mm to 8% expansion).

During the initial moist cure period of 7-days, specimens without gypsum exhibited shrinkage. Those containing gypsum generally showed slight expansion.During the subsequent soaking, much more water was available and expansions of up to 25% were observed. In all cases the expansion increased with increasing gypsum content and decreased with increasing substitution of ggbs for lime. The effect of substitution of ggbs for lime in suppressing this expansion is consistent and dramatic. The mechanics of this suppression are being investigated further. Initial results indicate an inhibition in the formation of ettringite when ggbs is present.

Kimmeridge Clay

Fig.8 plots the expansion behaviour of Kimmeridge clay stabilised with 4%, 5% and 6% lime- only and compares the behaviour of mixtures stabilised with different lime:ggbs ratios at 5% stabiliser content. Once again the effectiveness of ggbs in suppressing expansion is demonstrated.

FULL SCALE TRIAL

The trial formed part of the construction of a distribution warehouse. Associated with the warehouse were lorry-loading areas and car parking, totalling some 20000m^2. The pavement design for the former called for pavement quality concrete on hard-core, and for the latter, bituminous surfacing on hard-core. In each case, the thickness of the hard-core was specified as 200mm. Following a site investigation and laboratory testing it was decided, for reasons of economy, to carry out cement-stabilisation of the existing subgrade of very silty/clayey sand with flint and chalk gravel. Typically there was about 20% gravel and 35% silt and clay. The specification for the cement stabilisation required a seven day cube strength of 2Mpa and the laboratory testing indicated that a Portland cement content of 9% was necessary to achieve this.

Prompted by the proximity of a source of ggbs, it was decided to incorporate a trial area stabilised with ggbs. An area of 500m^2 in the lorry loading area was set aside for this purpose. From laboratory testing, a combination of 2% lime with 8% ggbs was selected to give comparable 28-day strength to that achieved with 9% cement. A feature of ggbs stabilisation, is slower strength development than with cement and a reduced 7-day cube strength was anticipated.

The cement stabilisation was carried out in the normal manner. Cement was spread on the surface of the prepared subgrade with a powder spreader unit and then mixed to the required depth with a stabiliser-rotovator. Water was added to achieve the optimum moisture content of 10% and mixed in by another pass of the rotovator to complete the mixing operation. After compaction by vibrating roller, the stabilised material was trimmed to level and sealed with emulsion.

For the lime/ggbs stabilisation, lime was first spread over the surface at a rate of 8kg/m^2 and rotovated in. To ensure accuracy of proportioning in the ensuing treatment, the treated layer was then compacted. About two hours later, ggbs was spread at a rate of 32kg/m^2, rotovated in and compacted. Water was added to achieve the optimum moisture content of 12% and mixing completed by another pass of the rotovator. The layer was then compacted before being trimmed to level and sealed.

In this trial, separate application of the lime and the ggbs was chosen to mirror the common practice where lime is added initially to sticky soils to break them down before attempting soil-stabilisation with cement. With highly-sticky soils this two stage application is advantageous. For the soil present in this trial, a single stage application may well have been appropriate with the lime and ggbs being spread together on the surface before being rotovated in.

The trial was a total success. Using standard plant and techniques, the stabilisation contractor experienced no difficulties, and satisfactory density and strengths were achieved. At 7-days, cube strengths for the ggbs area were typically 2Mpa compared with 3Mpa for the cement area. At 28- days, the ggbs strengths exceeded those for cement and by 90- days had attained 6Mpa. The trial area was overlain with the concrete surfacing and has now been in use for three years.

CONCLUSIONS

1) Laboratory investigations and a full-scale trial have demonstrated that lime/ggbs combinations can be successfully used for soil stabilisation.

2) Substitution of ggbs for lime can significantly increase compressive strength, but the effects of changing the total stabiliser content, and proportions of lime, ggbs and gypsum are complex and there are interactive effects between these variables.

3) In the presence of sulphates, substitution of ggbs for lime, consistently and dramatically suppresses soaking expansion. This is potentially very beneficial in view of the problems which have been encountered when stabilising sulphate-bearing soils with lime-only.

REFERENCES

1) Wild. S., Kinuthia J.M., Robinson R.B. and Humphreys I. "Effects of ground granulated blastfurnace slag on the swelling properties of lime-stabilised kaolinite in the presence of sulphates". Clay Minerals, 31, pp423- 433 (1996).

2) Mitchell J.K. "Delayed failure of lime-stabilized pavement bases". J. Geot. Eng. 112, 274-279 (1986).

3) Hunter D. "Lime-induced heave in sulphate-bearing clay soils". ASCE J. Geot. Eng. 114, 150-167 (1988).

4) Snedker E.A. and Temporal J. "M40 motorway Banbury IV contract - Lime Stabilisation". Highways Transportation, Dec 7-8 (1990).

5) Sherwood P. T. "The effect of sulphates on cement-and lime-stabilised soils". Roads and Road Construction, 40 (470), 34-40 (1962).

6) Wild S., Abdi M. R. and Leng Ward G. "Sulphate expansion of lime-stabilised kaolinite: II Reaction products and expansion". Clay Miner 28, 569-583 (1993).

7) Macphee D. E., Atkins M. and Glasser F. P. "Phase development and pore solution chemistry in ageing blastfurnace slag-portland cement blends". Mat.Res. Soc. Sym., 127, 475-480 (1989).

8) Talling B. and Brandstetr J. "Present state and future of alkali-activated slag concretes". ACI, SP-114, 1519-1545 (1989).

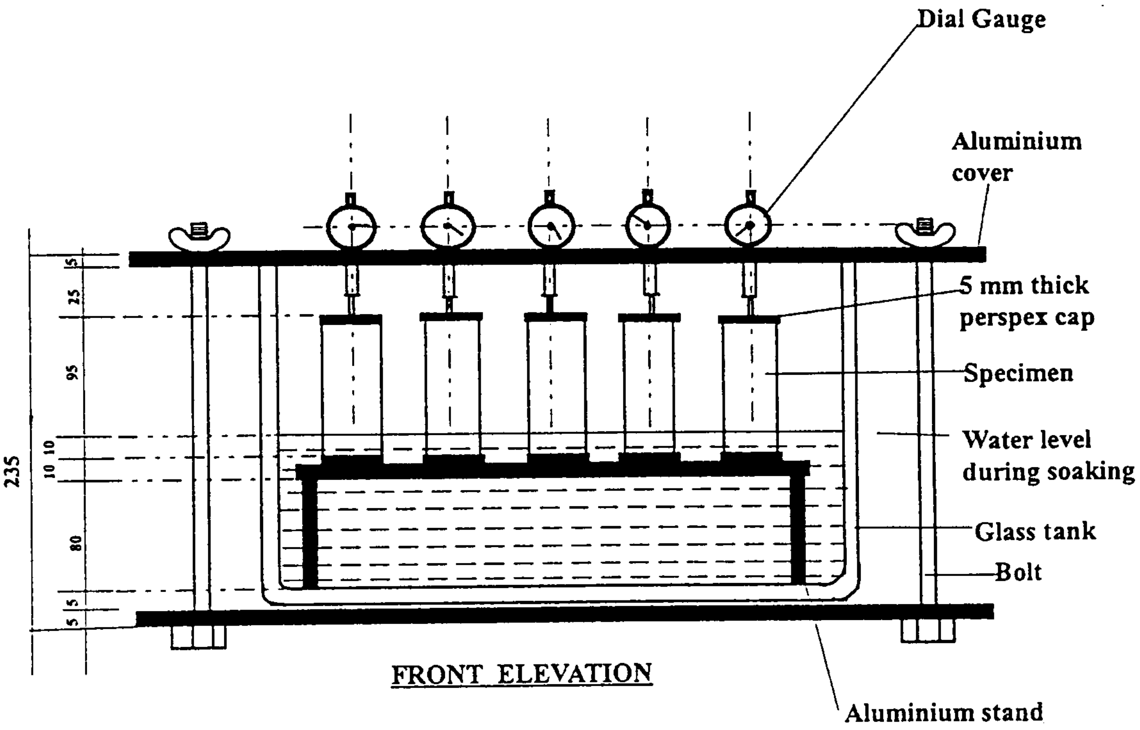


Fig. 1—Chamber employed to moist-cure and monitor expansions of cylinders

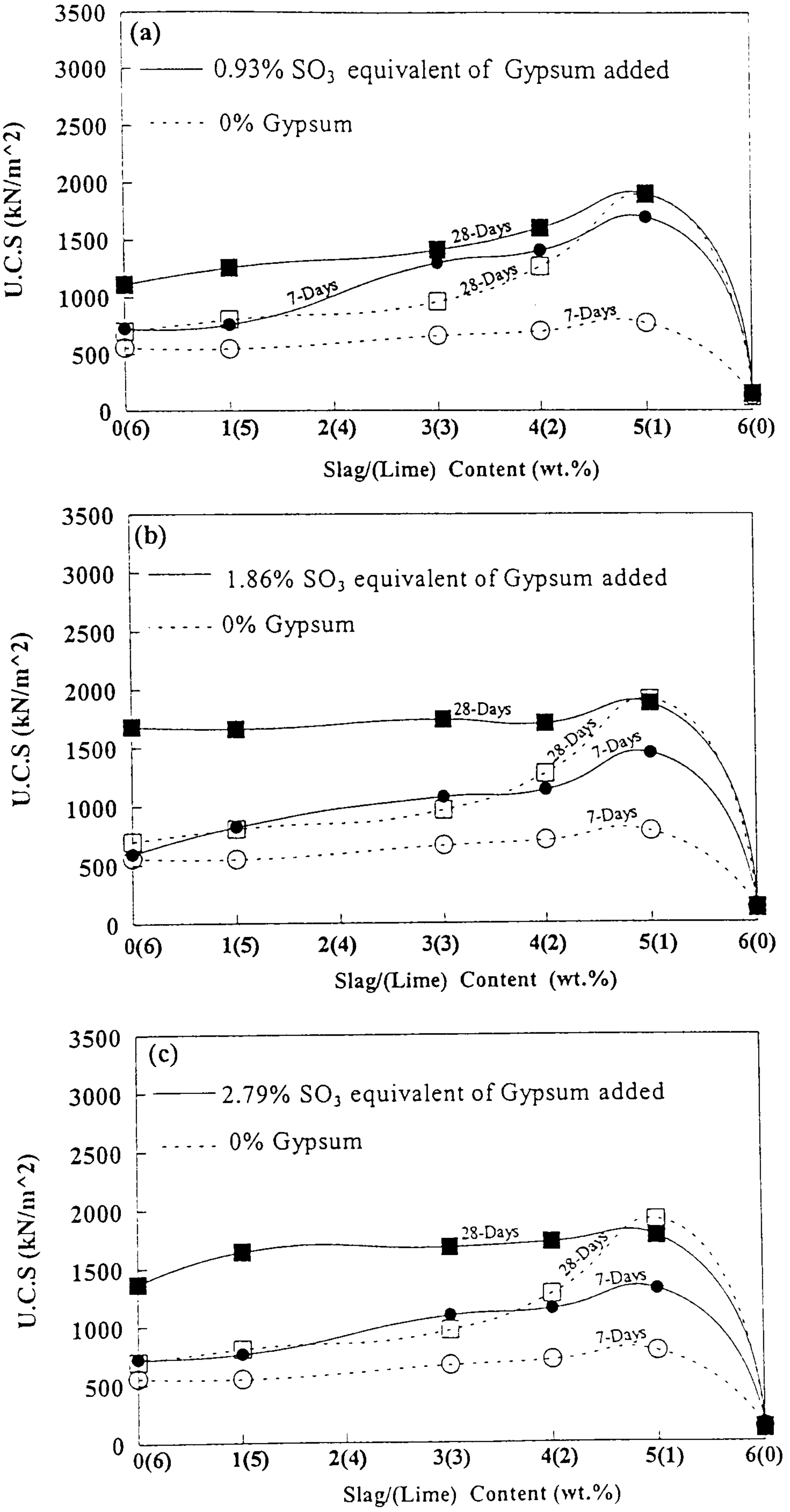


Fig. 2—UCS versus slag/ (lime) content for kaolinite with different proportions of added gypsum

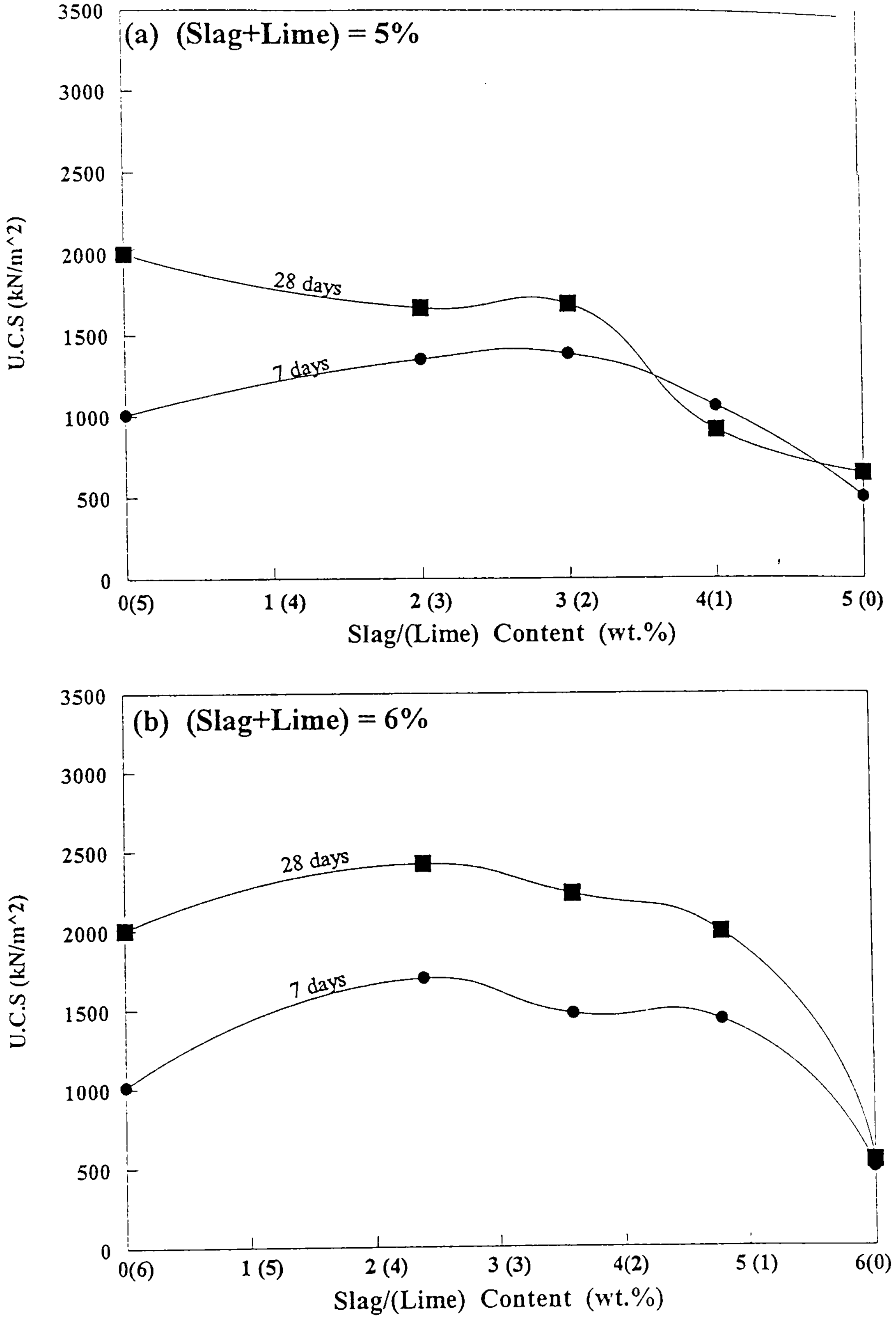
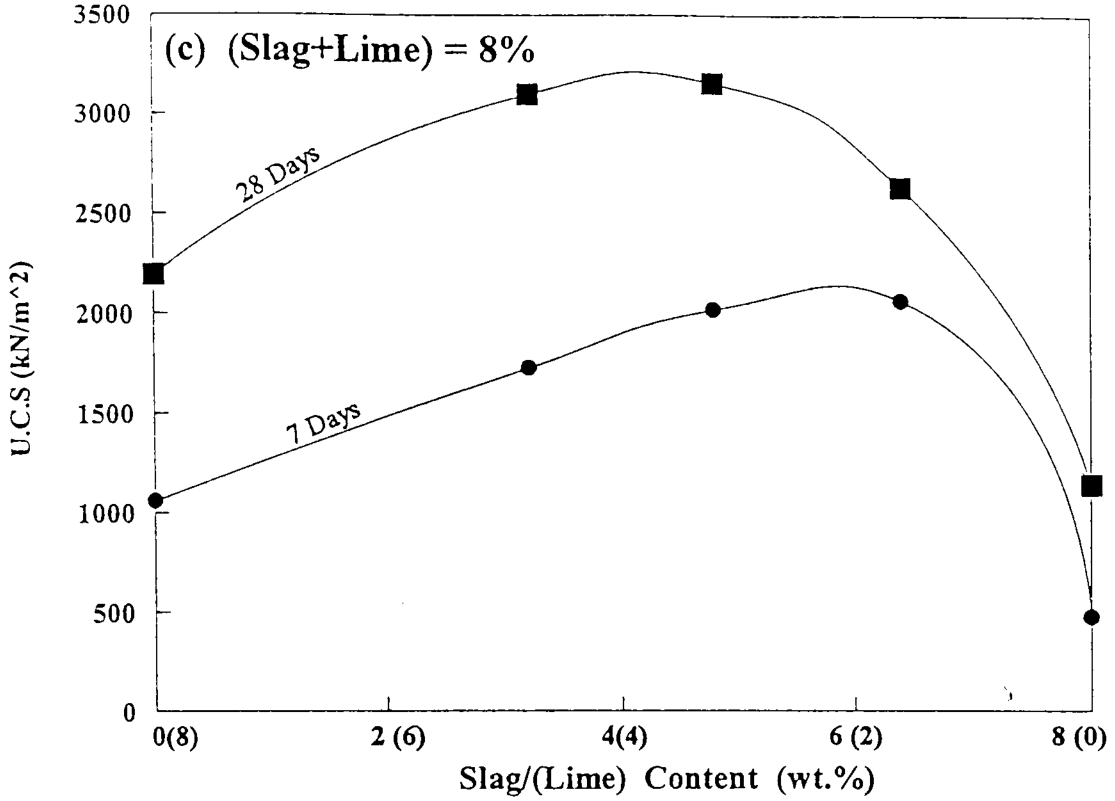


Fig. 3—UCS versus slag/ (lime) content for Kimmeridge clay with different (lime + ggbs) contents



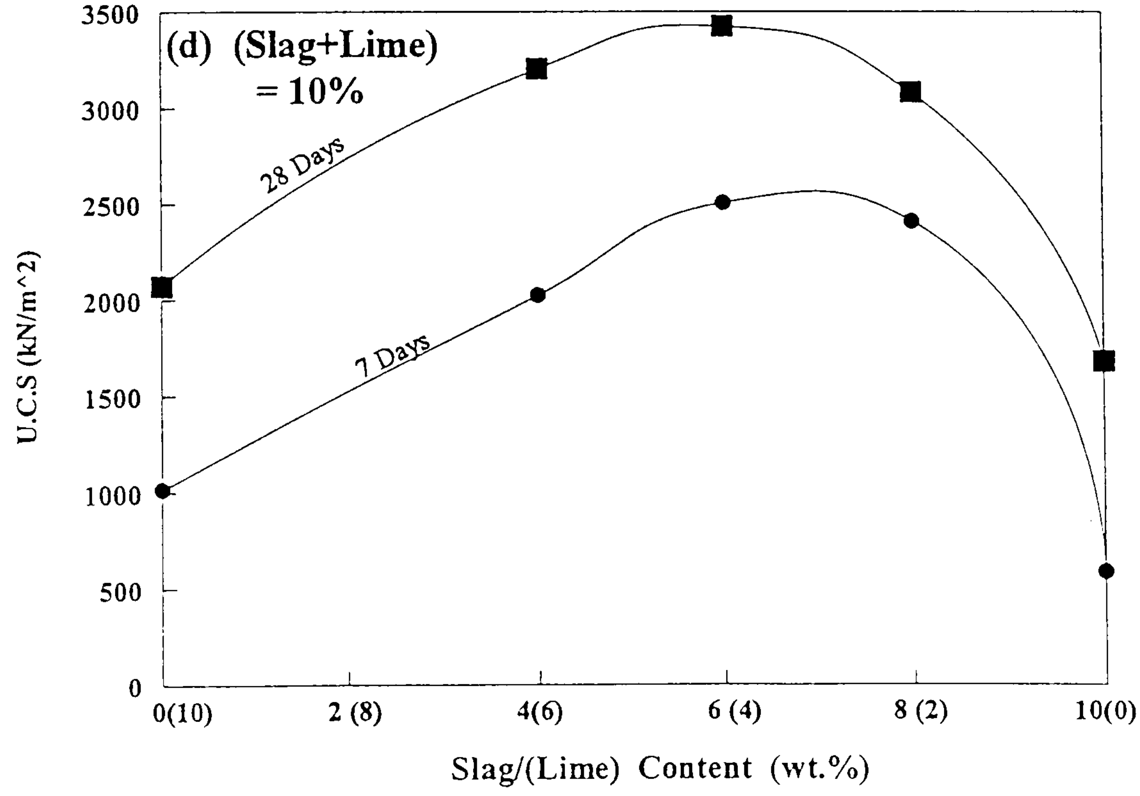


Fig. 3 (continued)—UCS versus slag/ (lime) content for Kimmeridge clay with different (lime + ggbs) contents

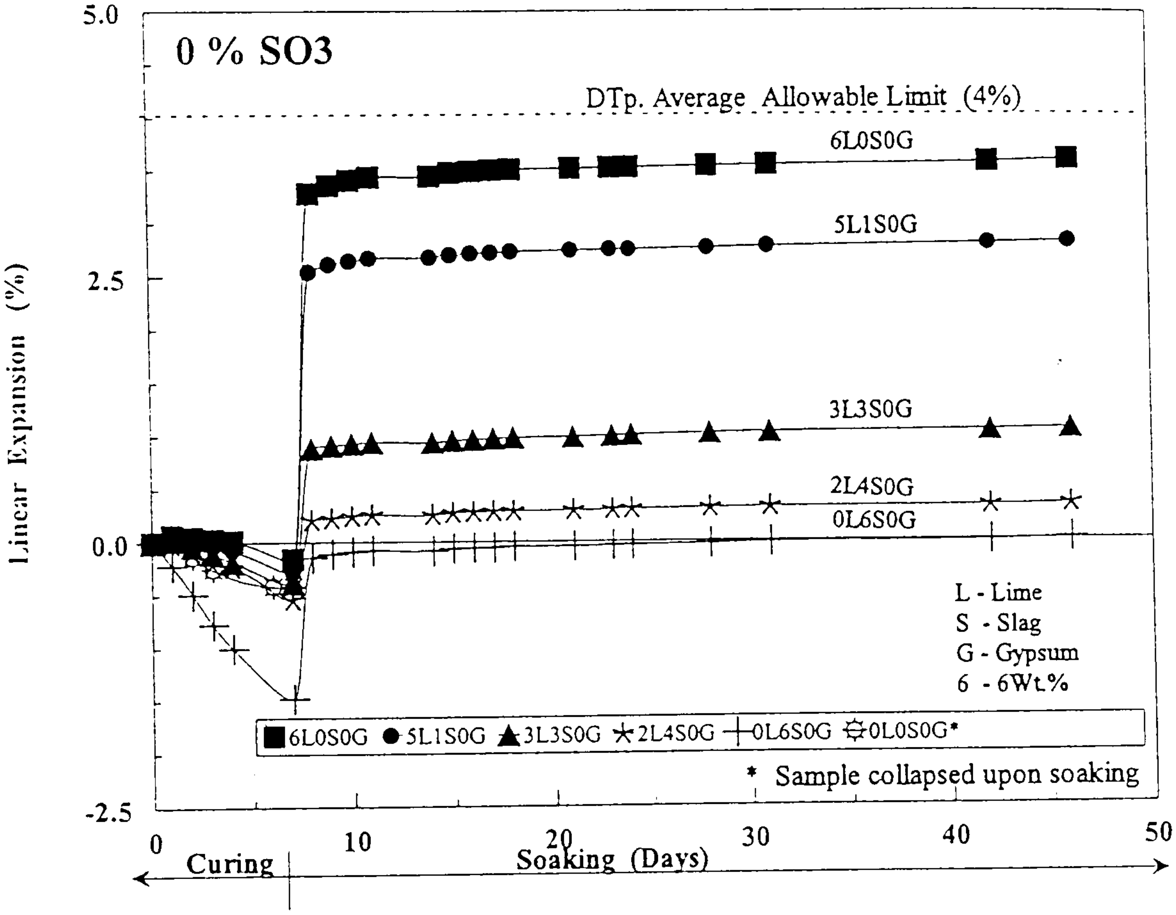


Fig. 4—Expansion of kaolinite-lime-ggbs, without gypsum

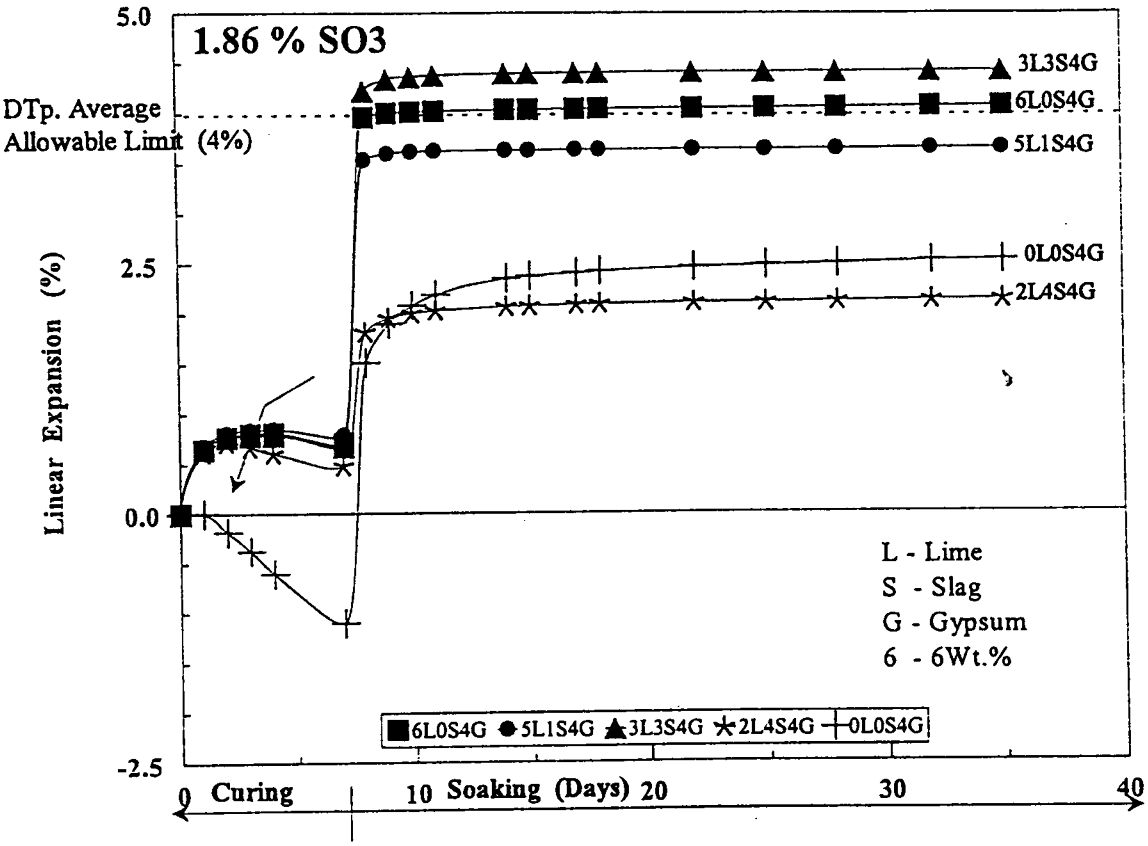


Fig. 5—Expansion of kaolinite-lime-ggbs with 4 wt. % addition of gypsum (1.86%SO_3)

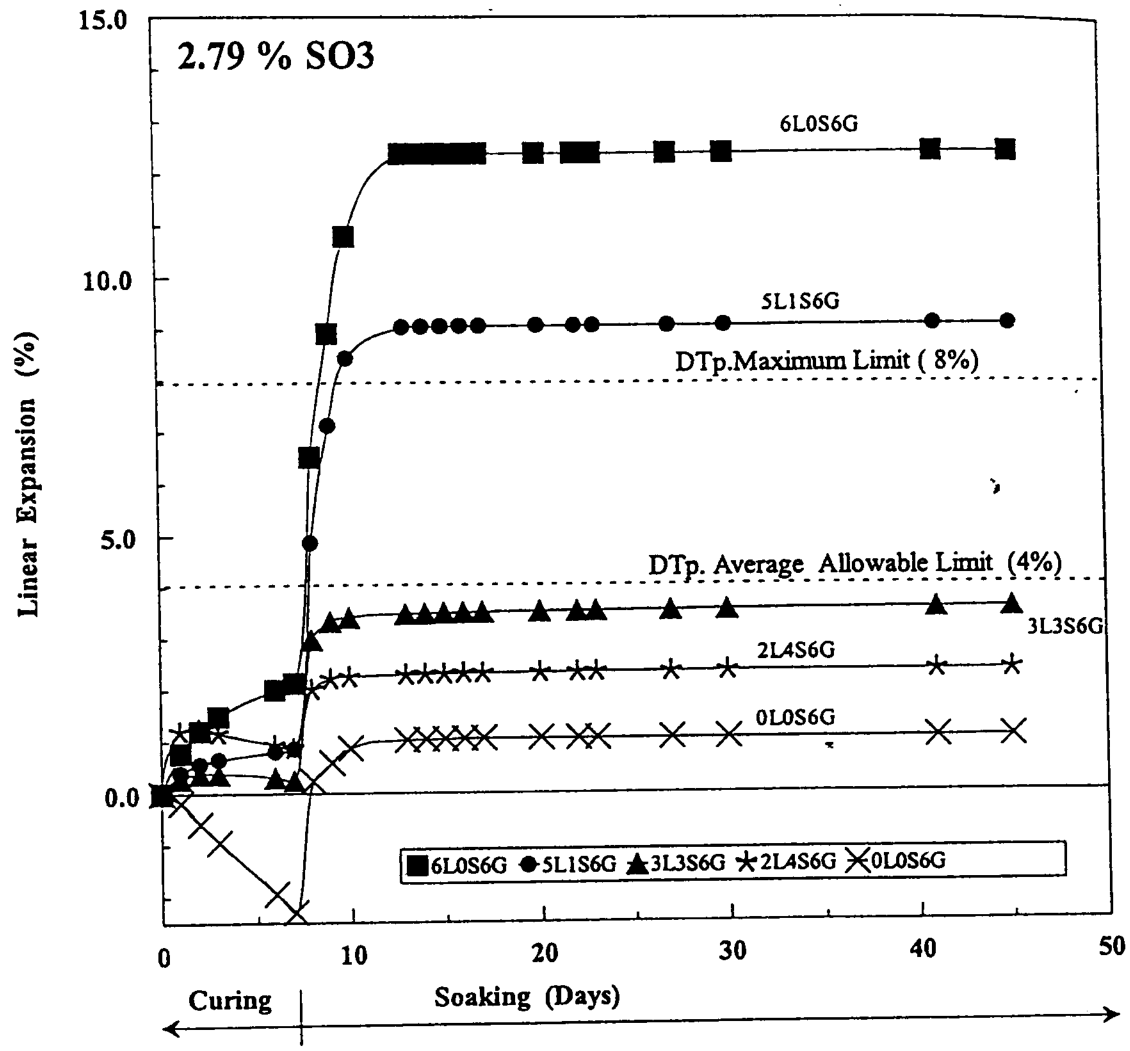


Fig. 6—Expansion of kaolinite-lime-ggbs with 6 wt. % addition of gypsum (2.79%SO_3)

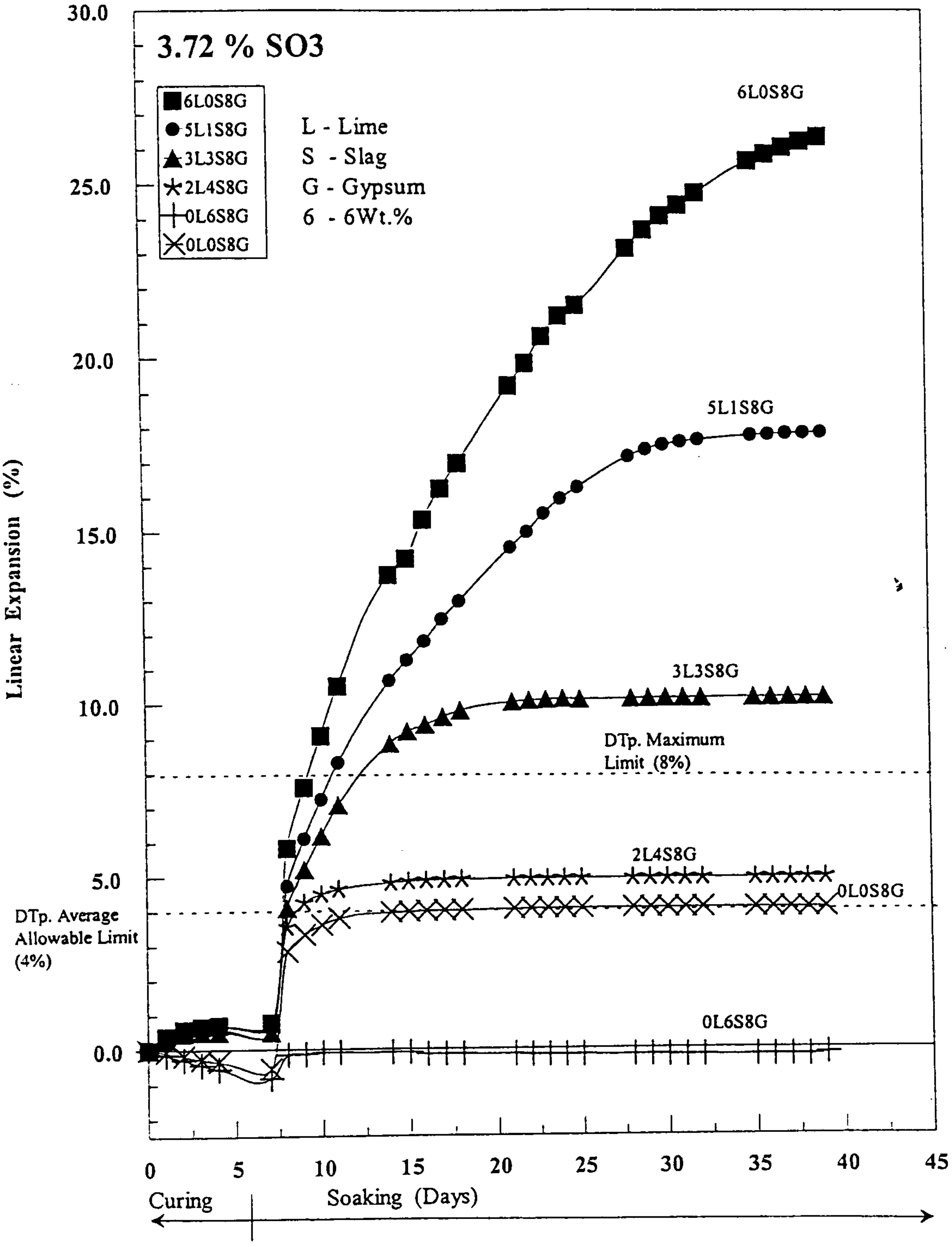


Fig. 7—Expansion of kaolinite-lime-ggbs with 8 wt. % addition of gypsum (3.72%SO_3)

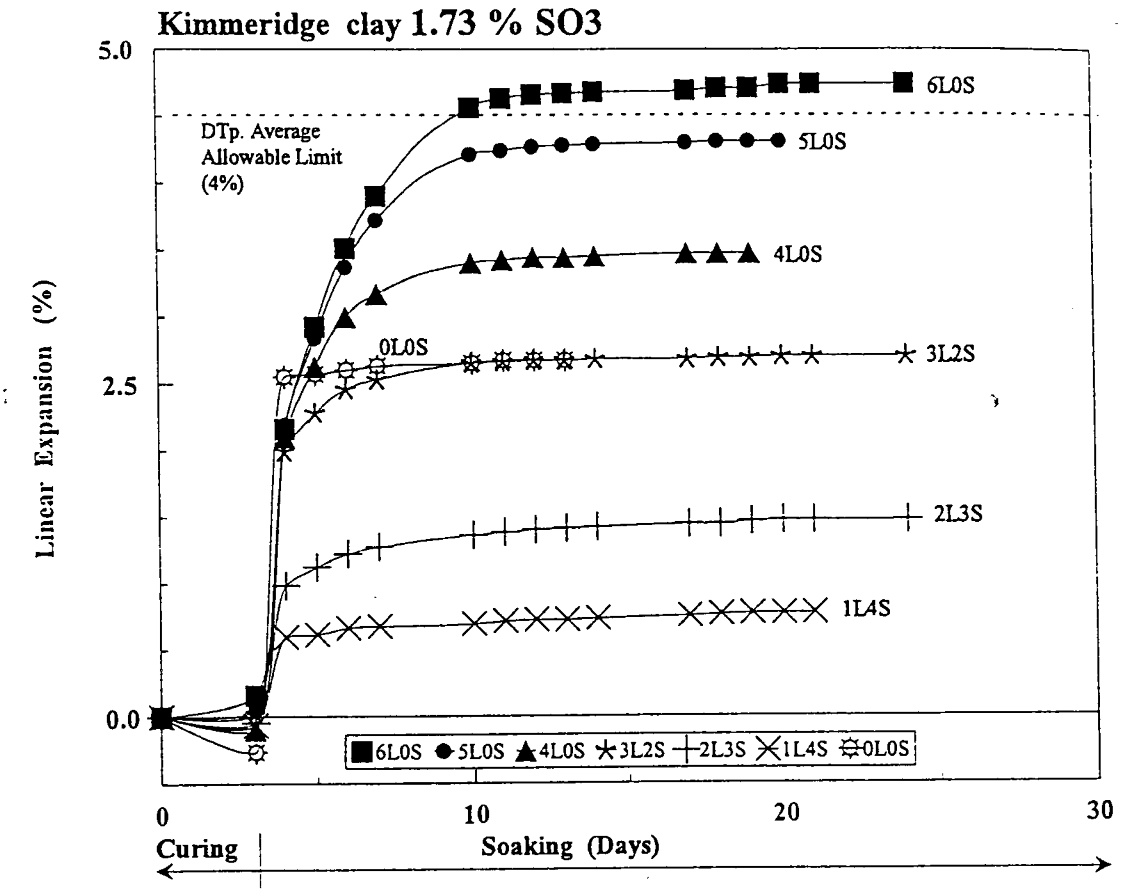


Fig. 8—Expansion of Kimmeridge clay-lime-ggbs