Stabilisation of sulphide rich soil: problems and solutions

Bari Ian Thomas

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Certificate of Research

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

Bari Thomas .... 18th July 2002

Bari I. Thomas (Date)
(Candidate)

S. Wild .... 18' July 2002

Prof Stan Wild (Date)
(Director of Studies)

John Kinuthia .... 18th July 2002

Dr John M. Kinuthia (Date)
(Supervisor)

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Abstract

The research presented in this thesis can be split into two well-defined areas.

Firstly, the effects of the addition of lime (either 2%, 4%, 6% or 8%$Ca(OH)_2$ or 1.5%, 3%, 4.5% or 6%CaO) on various engineering properties of a sulphide (pyrites) rich, naturally occurring clay - Lower Oxford Clay (LOC) - were studied. Experimental tests representing, or relating to, tests outlined in the Design and Construction of Lime Stabilised Capping Specification (DoT, 1995) were utilised and consisted of Atterberg (consistency) tests, compaction tests, unconfined compressive strength tests, linear expansion measurements and durability tests. Also, sulphate (SO_3) analyses, pH measurements, differential thermogravimetric (DTG) analyses and X-ray diffraction (XRD) tests were employed to confirm experimental data. Environmental conditions were chosen to reflect temperatures experienced in the UK - between 5°C, 10°C and 20°C. The majority of samples were mellowed (the time delay between initial mixing and compaction) for 3 days at 20°C prior to testing. The results show that small additions of lime (i.e. 2%$Ca(OH)_2$ or 1.5%CaO) modify the engineering properties of LOC by causing flocculation, and also increase SO_3 levels due to increased gypsum levels via pyrites oxidation. However, strength development is poor as little cementitious bonding is formed. Mellowing further modifies the engineering properties as the increased time allows greater flocculation leading to a less dense, more porous material. Also ettringite forms during mellowing allowing expansive reactions to occur prior to compaction, consuming both calcium and sulphate in the process and leading to slightly reduced pH levels compared to similar unmellowed samples. Further additions of lime give further change to the engineering properties of the LOC, up to an addition of 6%$Ca(OH)_2$ or 4.5%CaO. Further additions result only in supplying an excess of calcium. Strength development is improved with increasing lime additions, especially after 4 weeks of curing at higher curing temperatures (20°C); however linear expansion increases and durability worsens. However, a period of mellowing prior to compaction reduces linear expansion and improves durability. Sulphate (SO_3) levels are also increased with increasing additions of lime due to pyrites oxidation. In samples containing >2%$Ca(OH)_2$ or 1.5%CaO, pH levels are maintained to a level where ettringite formation is sustained rather than gypsum formation.

Secondly, the effects of a secondary stabilising agent (ground granulated blast furnace slag - GGBS - incorporated at various percentage additions (2%, 4%, 6% or 8%)) on the strength development, linear expansion and durability of mellowed, lime-modified LOC is presented. For comparative purposes, Portland cement (PC) is also used. The results show that although LOC-lime-PC samples exhibit greater strengths (especially when cured for long periods at 20°C), linear expansion is lower and durability is higher in similar LOC-lime-GGBS samples. As the hydration process of PC produces lime, and as lime is usually consumed during GGBS hydration, then samples containing the former stabiliser will maintain pH levels well above samples containing the latter. Therefore, on soaking disruption and expansion due to the formation of ettringite (which is unstable at pH levels <10.5) is common to LOC-lime-PC samples but not in similar GGBS samples. In conclusion, the findings from this thesis indicate that soil stabilisation with lime and GGBS is particularly effective for naturally occurring sulphide rich clay soils (such as the LOC) and is an environmentally friendly alternative to PC-stabilised soils.

List of Abbreviations and Symbols

amu	Atomic mass unit
FeS_2	Pyrites
GGBS	Ground Granulated Blast-furnace Slag
MDD	Maximum Dry Density
OMC	Optimum Moisture Content
PC	Portland cement
SEM	Scanning Electron Microscopy
SSC	Super Sulphated Cement
TGA	Thermogravimetric Analysis
TSA	Thaumasite form of Sulphate Attack
UCS	Unconfined Compressive Strength
XRD	X-ray Diffraction
A	Al_2O_3
C	CaO
CH	$Ca(OH)_2$
H	H_2O
$\underline{S}$	SO_3
S	SiO_2

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1 Introduction

1.1 General

Growing environmental concern, initially as a consequence of the publication of the novel "Silent Spring" by Rachel Carson (1962) and more recently as a result of action groups such as Green Peace and the World Wildlife Fund, has led to a number of high-profile meetings involving the most powerful nations on Earth concerning the production of pollutants and their effect on the planet. Scientists are agreed that the production of certain gases - primarily carbon dioxide (CO_2), methane, nitrous oxides as well as industrial chemicals such as chlorofluorocarbons (CFCs), have the ability to absorb the sun's energy that is usually radiated back into space from Earth and as a consequence the temperature on the Earths' surface is steadily increasing. This process is called the greenhouse effect. In fact, the Organisation for Economic Co-operation and Development (OECD) analysis of economic growth scenarios show that by the year 2020, global energy-related emissions, of CO_2 in particular, are likely to be more than double the 1990 levels. Furthermore emissions originating from developing countries are expected to increase even more rapidly, from the present share of roughly 30% of global emissions to just over 50% by the year 2020. Subsequently, World Climate Summits have been held throughout the 1990's with the latest (the 6th at the time of writing) held in The Hague, Netherlands (November 2000). However, due to self-interest and politics no great steps were taken to reduce the amount of pollution greenhouse gases, other than to plant more trees. In fact the USA, among the worlds leading polluters, have expressed a wish to actually purchase emissions quotas from other less polluting countries in order to continue certain industrial processes.

The problem of reducing pollution becomes even more difficult when one realises that the production of essential construction materials, such as cement, produces greenhouse gases. In fact, it is estimated that for one tonne of cement produced, one tonne of CO_2 is emitted into the earth's atmosphere. In an attempt to minimise the impact of production processes on the environment, researchers have experimenting by replacing cement in concrete with recycled or waste materials; thus reducing CO_2 emissions per tonne of concrete utilised. Examples of this include pulverised fuel ash, condensed silica fume or even crushed powder from recycled bricks. In addition to moral considerations the introduction of recycled materials to cement is also of economic concern, as such materials reduce energy consumption, which in turn leads to lower overall production costs.

In the United Kingdom, the landfill tax, which was introduced by the British government on October 1st 1996, is an additional incentive for the promotion of sustainable waste management and has forced civil engineers to utilise sometimes unsuitable materials in the construction process in order to cut costs. Examples of this include the modification or stabilisation of clay soils with lime rather than the importation of costly aggregate. Lime is being used increasingly to modify and stabilise soils for numerous engineering applications such as embankments, road sub-grade and sub-base stabilisation, and foundations for small buildings (Arabi and Wild, 1989). However, although the addition of lime (usually CaO in commercial developments) to clay soils results in immediate flocculation, changes to consistency, moisture content and maximum dry density, and therefore increased workability (Bell, 1988), in the presence of sulphates (such as gypsum) lime addition promotes the formation of deleterious and expansive reaction products which cause disruption and heave in lime-stabilised material (Gouda et al. 1975; Abdi and Wild, 1993). The detailed chemistry of the reactions between the added lime, sulphates (usually expressed as SO_3) and the soil particles is complex and depends greatly on the pH of the soil, the temperature and the water conditions. It is widely accepted that substantial swelling is associated with the formation of the mineral ettringite, the hydration of which is accompanied by large dimensional changes as the water of crystallisation is incorporated into the mineral structure. Also, if the temperature of the system falls below 15°C, and the pH value remains high (above 10.5) then the dissolution of carbonates together with available silica allows a substitution of silica for alumina and carbonate for sulphate leading to a conversion from ettringite to thaumasite - a mineral with similar destructive properties to ettringite (Hunter, 1988). In addition to deterioration due to the presence of sulphates, more recently deterioration in lime-stabilised soils has been attributed directly to sulphide (such as pyrites) oxidation. Snedker (1996) reported heave in lime-stabilised pyritic mudstone pavements along the M40 at Banbury, UK. Although the unstabilised material was deemed suitable for stabilisation as the SO_3 content was found to be in agreement with Department of Transport Guidelines (DoT, 1995) (i.e. <1% SO_3), site investigations carried out after deterioration reported that the SO_3 content had increased and was as high as 4% in the disrupted layer. It was concluded that the increased SO_3 levels and subsequent deterioration of the stabilised layer was due to pyrites oxidation, ultimately producing sulphuric acid and gypsum (Hawkins and Pinches, 1987), and as a consequence developing ettringite. Even the mixing of a secondary stabilising additive to the soil, such as Portland cement, may not suppress expansion due to ettringite formation in pyrites rich material (Thomas et al, 1981). However, the addition ground granulated blastfurnace slag (GGBS), a by-product of the pig-iron industry, with lime to a soil is not only an environmentally friendly stabilisation method (as no further pollution is emitted during production), stabilised GGBS-lime-clay mixes also show improved strengths compared to lime-only stabilised material. Of most consequence, deterioration due to expansion and heave is significantly reduced when GGBS is incorporated into a lime-stabilised, sulphate-rich clay soil as sulphates (such as gypsum) accelerate slag hydration (Wild et al. 1998; Wild and Tasong, 1999; Veith, 2000).

1.2 Structure of Thesis

The current work is laboratory based and examines the effects of lime addition (either $Ca(OH)_2$ or CaO) and stabiliser addition (PC or GGBS) to a sulphide-rich clay soil (the Lower Oxford Clay) - specifically to monitor the effects of pyrites oxidation and the process of mellowing (a process briefly outlined in DoT Guidelines (1995) describing the delay between initial mixing and subsequent compaction of clay-lime). Various experimental tests, many chosen as they represent or relate to tests outlined in the Design and Construction of Lime Stabilised Capping specifications (DoT, 1995), were carried out under environmental conditions similar to those experienced by engineers in the United Kingdom.

This introduction is followed by a critical review of relevant literature, consisting of 3 chapters. Chapter 2 looks at the clay mineralogy of the Lower Oxford Clay (LOC) and describes the clay minerals' structure and other characteristics, whilst chapter 3 illustrates the effects of lime addition to a clay soil, focusing specifically on the effects of sulphates, pyrites and ettringite formation on stabilised materials. Finally, chapter 4 examines the hydration processes of both Portland cement (PC) and slag (GGBS) and debates the relative advantages of either material when incorporated into a stabilised soil. Chapter 5 describes the mineralogy and chemistry of the subject material (LOC) in detail along with the other materials used in the current work - lime (hydrated lime and quicklime), PC and GGBS. The main focus of the thesis begins chapter 6, which describes in detail the experimental procedures carried out on the modified/stabilised LOC, including consistency limits, compaction tests, strength tests, expansion measurements and durability tests, in order to monitor the changes in the engineering properties of the LOC under various environmental conditions. Additionally, SO_3 analyses and other analytical techniques (thermogravimetric (TGA) and X-ray diffraction (XRD) analysis) are described. The results of the experimental work are presented in chapters 7 and 8 focusing on LOC-lime systems and LOC-lime-PC or GGBS systems respectively. Chapter 9 of this thesis is a critical discussion of the results attained, including the practical implications of the results. Finally, the salient conclusions of the current work are presented together with recommendations for further work in chapter 10. The progress of this research was presented regularly to a steering group of industrial partners, including Buxton Lime Industries, Cementitious Slag Makers Association, RMS Industrial Materials Ltd. and Singleton Birch Ltd., to ensure the relevance of the current work for practical application.

1.3 Research Objectives and Contribution to Knowledge

Although much work has been carried out on the effects of lime addition to clay soils, few researchers have looked specifically at the stabilisation of a naturally occurring, sulphide-rich clay soil with both quicklime and hydrated lime, especially when a period of mellowing is employed prior to testing or compaction and when curing is carried out at temperatures reflecting conditions in the UK. Also, although much laboratory-based work has been published on the engineering properties of GGBS-stabilised soils the author could not locate published work directly comparing the engineering properties of GGBS and PC stabilised naturally occurring soils. Thus the salient aims of the current project are:

- To examine the effectiveness of lime-addition (either $Ca(OH)_2$ or CaO), for modification and/or stabilisation purposes, on a naturally occurring, sulphide rich clay soil (the Lower Oxford Clay (LOC)) and to assess the differences in engineering properties (such as consistency limits, compaction, strength expansion and durability), if any, between hydrated lime and quicklime addition.
- To monitor the rate and effect of pyrites oxidation (using SO_3 tests and pH measurements) in a lime-modified/stabilised naturally occurring sulphide-rich clay soil.
- To assess the impact of mellowing lime-modified/stabilised soils prior to testing or final compaction, and also to consider the influence of testing under environmental conditions experienced in the UK.

- To compare and contrast the engineering properties (strength, expansion and durability) of lime-modified LOC-lime stabilised with various percentage additions of either PC or GGBS, again under low temperature conditions.

2. Clay Mineralogy

This chapter briefly describes the clay minerals present in the Lower Oxford Clay (LOC) - namely kaolinite, illite and chlorite - and gives details of their respective structures, characteristics and swelling capabilities and suitability for stabilisation.

2.1 Introduction.

The term "clay" is used in various contexts, and can be used as a rock term or as a particle-size term in the mechanical analysis of sedimentary rocks, soils, etc. In general the term clay implies a natural, earthy, fine-grained material which develops plasticity when mixed with a limited amount of water (Grim, 1968). Chemical analyses of clays show them to be composed essentially of silica, alumina and water, commonly with appreciable amounts of iron, alkalis and alkaline earths. There are several factors affecting the properties of a clay soil or clay material, including: clay mineral composition, non-clay mineral composition, organic material, exchangeable ions and soluble salts (Grim, 1968).

2.2 Clay Mineral Composition.

This refers to the identity and relative abundance of *all* clay-mineral components. Certain clay minerals can have a tremendous influence on clay soils, even if present in only small amounts. (e.g. the presence of smectite or montmorillonite (≈5%) is likely to provide a material very different from another clay with the same composition in all ways except for the absence of smectite/montmorillonite.) In the same way crystallinity and variability in clay minerals affect such properties as plasticity (Grim, 1968).

- **Non-clay Minerals.**

Minerals such as calcite, dolomite, mica, quartz, pyrite, feldspar, gibbsite and other minerals are abundant in clay soils, and the effects of these minerals on the properties of a clay soil can influence the potential uses of the clay soil. For example, a material with a high pyrites content may, under certain conditions, prove problematic in the construction industry, as pyrites has been known to oxidise, and, under the right conditions produce gypsum, the precipitation of which may cause significant heave (Thomas et al., 1981; Cripps and Edwards, 1992).

- **Organic material.**

Organic material can be present in clay soils as discrete particles of wood, leaf matter, spores etc, as molecules adsorbed on the surface of the clay mineral particles or even intercalated between the silicate layers of clay minerals (Grim, 1968). Organic material usually acts as a pigment in clay soil giving the material a dark-grey or black colour, though there is no direct relationship between colour and organic content.

- **Exchangeable ions and soluble salts.**

At the time of deposition, or as a result of weathering, water-soluble salts may be entrained in the clay. Common salts found in clay materials are chlorides, sulphates, and carbonates of alkalis, alkaline earths, aluminium and iron. Clay minerals and some organic material that can be found in clay soils have significant ion-exchange capacities and can affect stabilisation.

2.3 Clay Mineral Structure

Two structural units are involved in the atomic lattices of most clay minerals. One unit consists of two sheets of closely packed oxygens and hydroxyls in which atoms of aluminium, iron or magnesium are embedded in octahedral co-ordination (Figure 2.1.1). If aluminium is present only two-thirds of the possible positions are filled to balance the structure, which is the Gibbsite structure ($Al_2(OH)_6$). If magnesium is present all the positions are filled and the structure is balanced; this is called the Brucite structure ($Mg_3(OH)_6$). The second unit is built of tetrahedra in which a silicon atom is equidistant (assuming no distortions) from four oxygens (or possibly hydroxyls, depending on structural balance), arranged in the form of a tetrahedron with a silicon atom at the centre (Figure 2.1.2). These tetrahedra are arranged so that their tips all point in the same direction and the bases are in the same plane to form a hexagonal network, which is repeated indefinitely to form a sheet of composition $Si_4O_6(OH)_4$. The structure can be considered to be made of a perforated plane of oxygens (which is the plane formed from the base of the tetrahedral groups); a plane of silicon atoms with each silicon in the cavity at the junction of three oxygen atoms and therefore forming a hexagonal network; and a plane of hydroxyl atoms with each hydroxyl directly above the silicon at the tip of the tetrahedrons.

2.4 Clay Mineral Types.

The clay minerals are usually divided into 7 main groups, with the texture or lattice structures of the minerals serving as the basis for their classification. These groups are the kaolinites, the montmorillonites, the illites, the chlorites, the vermiculites, the mixed-layer clay minerals, and the attapulgites, sepiolites and palygorskites (Millot, 1970). The scope of the current work is such that it would be impractical to examine all the groups in detail, and as the Lower Oxford Clay (LOC) contains only kaolinite, illite and chlorite (Smith, 1999) then no other clay mineral types will be described.

2.4.1 The Kaolinite Group.

Kaolinite minerals are formed of units consisting of a single tetrahedral silica and a single octahedral alumina sheet – these units may repeat themselves indefinitely to form a lattice of the mineral (Figure 2.2). The chemical composition is expressed by the general formula $(OH)_8Al_4Si_4O_{10}$. As the charges within the structural lattice are balanced there is very little substitution within the lattice, although limited substitution is possible in poorly crystalline kaolinites. The tetrahedral and octahedral sheets are combined so that the tips of the tetrahedra of each silica sheet and one of the hydroxyl layers of the octahedral sheet form a common layer. The atoms common to both the tetrahedral and octahedral layer become O instead of OH (Grim, 1968). A relative of kaolinite is halloysite which differs from kaolinite by having one additional water molecule to the basic kaolinite unit (i.e. $(OH)_8Al_4Si_4O_{10}.4H_2O$). When wet, halloysite masses have a tendency to creep or flow horizontally and may be viewed as unstable and undesirable as materials for embankments and related structures (Cernica, 1995).

2.4.2 The Illite Group.

The basic structure of illite consists of a gibbsite octahedral layer between two silica tetrahedral sheets (Figure 2.3). The unit is the same as that for montmorillonite except that aluminiums always replace some of the silicons and the resultant charge deficiency is balanced by potassium ions. However, illites differ from montmorillonites in that charge deficiency due to substitutions per unit-cell is about 1.30 to 1.50 for illite and 0.65 for montmorillonite. The seat of this charge deficiency in illite is largely in the silica sheet and therefore close to the surface of the unit layer, whereas in montmorillonite it is frequently, perhaps chiefly, in the octahedral sheet at the center of the unit layer. Also in the case of illite the balancing cations between the unit layers are chiefly, or entirely, potassium. Because of these differences the illite structural unit layers are relatively fixed in position so that polar ions cannot readily enter between them and cause expansion (Grim, 1968). The inner layer bonding by the K ions is sufficiently strong so that the basal spacing of illite remains fixed at 1μm in the presence of polar liquids (Cernica, 1995). The structural formula of illite is $(OH)_4K_2(Si_6.Al_2)Al_4O_{20}$ and its theoretical composition is $K_2O = 11.8\%$, $SiO_2 = 45.2\%$, $Al_2O_3 = 38.5\%$, $H_2O = 4.5\%$ (Grim, 1968). Other close relations of illite include glauconite which is a dioctahedral illite with considerable replacement of Al^{3+} by Fe^{3+}, Fe^{2+} and Mg^{2+} and has a distinctive green hue. Since illite is always found mixed with other clay and non-clay minerals, it is, on its own, of little significance to engineers.

2.4.3 The Chlorite Group

The word chlorite comes from the Greek meaning "green minerals" (Kostov, 1968). The presence of chlorites has been well known for a long time in crystalline schists, in hydrothermal rocks and in the alteration products of many silicates. Morphologically the chlorites correspond with illite as the structure consists of alternate sheets of trioctahedral mica bounded by sheets with a brucite structure (Figure 2.4). The basal spacing is about 1.4μm but in contrast to the montmorillonites is fixed (Millot, 1970). The ideal composition of a pure magnesium chlorite should be $Mg_3SiO_4O_{10}(OH)_2.Mg_3(OH)_6$. (Kostov, 1968). Grim (1968) describes chlorites as being of the composition $(OH)_4(SiAl)_8(Mg.Fe)_6O_{20}.(Mg.Al)_6(OH)_{12}$, whilst Barth (1962) comments that the chemical variation of chlorite is very great, but describes talc-chlorite as being of the composition $Mg_6Si_4O_{10}(OH)_8$.

2.5 Characteristics of Clay Minerals

Many of the characteristics of the clay minerals (such as ion exchange and sorption, swelling and reactions with organic material) depend to a great extent on their crystal structure. The use of X-ray methods in the identification of mineral structures (i.e. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS)), pioneered by Pauling in the early 1930s has enabled scientists to study, in great detail, the shape and size of crystal particles. If a crystal particle has 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 identification cannot be based solely on diffraction data. Therefore diffraction and hence clay mineral characteristics mainly depend on a) layering of the tetrahedral and octahedral units, b) types of interlayer ion exchange (if any) and, c) substitution within the crystal lattice. As the layering and structure of the relevant clay minerals have been dealt with, it is important to address ion exchange and substitution in the crystal lattice in order to fully understand the characteristics of the clay minerals.

2.5.1 Ion Exchange.

Clay minerals have the property of sorbing certain anions and cations and retaining them in an exchangeable state; i.e. these ions are exchangeable for other anions or cations by treatment with such ions in a water solution (although the exchange reaction also takes place sometimes in a nonaqueous environment). The property of exchange capacity is measured in terms of milliequivalents per gram, or 100g. In clay materials the commonest exchangeable cations are Na^+ Li^+, H^+, K^+, Ba^{2+}, Ca^{2+}, Mg^{2+}, and Al^{3+}. Some common anions are SO_4^{2-}, Cl^-, PO_4^{3-} and NO_3^- (Grim, 1968). Construction engineers may inadvertently cause ion-exchange reaction by a shift of the water table or emplacement of a large mass etc. with an unexpected change in soil properties such as changes in plasticity, compaction and shrinkage.

2.5.1.1 Cation Exchange

2.5.1.1.1 Cation Exchange Capacity

The range of cation exchange capacity of the clay minerals is given in Table 2.1. The cation exchange capacities in Table 2.1 were taken at pH 7 (neutral). A range of capacities must be shown for each group as there is no single capacity that is characteristic of a given group of clay minerals (Grim, 1968). Mukherjee et al. (1943) (from Grim, 1968) also found that exchange capacity might also vary with the nature of the cation. They found, using titration methods for kaolinite and montmorillonite, that exchange capacity was found to be considerably larger with divalent cations, such as Ca^{2+}, than with monovalent cations (e.g. Na^{+}). Other factors such as particle size, lattice distortion, clogging of exchange position etc., may also affect the cation-exchange capacity (Grim, 1968). There are 3 main causes of cation exchange:

- Broken Bonds,
- Substitution within the Lattice Structure,
- Hydrogen (Exposed Hydroxyls).

2.5.1.1.2 Replaceability of Exchangeable Cations.

Early studies have shown (e.g., Way, (1850), Gedroiz, (1922) (both from Grim, 1968)) that under a given set of conditions, various cations were not equally replaceable and did not have the same replacing power. It was concluded that replacing power of the common ions was:

$$\mathbf{Na<K<Ca<Mg<NH_4}$$

Simply, this means that in general, Ca^{2+} will more easily replace Na^+ than Na^+ will replace Ca^{2+}. However, over time it became obvious that the series varied depending on the conditions of exchange. For example, work by Cobbe (1988) and Arabi, (1987) in lime stabilised soils quoted the series to be:

$$Li^+ < Na^+ < K^+ < Mg^{2+} < Ca^{2+} < Ba^{2+} < Al^{3+} < H^+$$

Suffice to say that whichever series is appropriate for the appropriate conditions, the ions on the left are usually replaced by the ions on the right. Cation replacement is of great importance, especially in the field of lime-stabilised soils. Allaway (1945) investigated the replaceability of Ca^{2+} in various clay minerals by determining its availability to plants. He found that for Ca^{2+} the availability is peat>kaolinite>illite>montmorillonite and that the availability increases as the saturation increases. In other words, Ca^{2+} would be more available (i.e. not taken into the clay structure) in a lime treated kaolinite clay soil compared to a lime treated montmorillonite soil.

2.6 Swelling

Terzaghi and Peck (1967) state that mechanical effects, such as particle arrangement, have been found to be important in soil swelling behaviour. They also observed that two samples of the same clay could be at the same pore fluid concentration, with one exerting a large swelling pressure and the other almost none. Therefore, it can be said that swelling is a phenomenon that involves both the solid and liquid phases, induced by negative pore pressures which are created by the strong surface tension forces of the pore water meniscus and/or by osmotic effects. In both cases, the result is water being pulled into the air voids. Barshad (1955) states that water adsorption in clays starts with the hydration of the external clay particle surface by a unimolecular layer of water. This layer then builds up with time to form multimolecular water layers at a rate dependent on the clay type. These multilayers then find a way into the interior surfaces of the clay particles themselves, probably through diffusion of water vapour through the clay particle and/or seepage at the clay particle edges (Barshard, 1955). The interlayer cations are still in position at this stage attached as they are to the oxygen sheets. As more molecular water finds its way into the interlayer spaces the cations get detached creating an external surface. However, if water is in vapour form (as during curing of stabilised soils), then expansion is minimal. Swelling results from an increase in the basal spacing as water is adsorbed between the layers. The extent of clay water adsorption is very much a function of the particle size, particle pore size and void ratio (density). For example, montmorillonitic clays have external adsorption surfaces of the order of 22-90m^2/g depending on the method of measurement, which is far higher than for kaolinitic and illitic clays, as reflected in typical swelling magnitudes shown in Table 2.2.

Clay Minerals	**Milliequivalents per 100g**
Kaolinite	3-15
Illite	10-40
Chlorite	10-40
Montmorillonite*	80-150
Vermiculite*	100-150

Table 2.1 Cation exchange capacity of clay minerals, in milliequivalents per 100g at pH = 7. (after Grim, 1968)

(not present in Lower Oxford Clay used in the current work)*

% SWELL	0 - 100	1000	2000
Kaolinite	5 70		
Illite	15 120		
Ca Montmorillonite *	95 145		
Na Montmorillonite *		1400	2000

Table 2.2 Typical free swell figures of common clays. (Krahn and Fredlund, 1972)

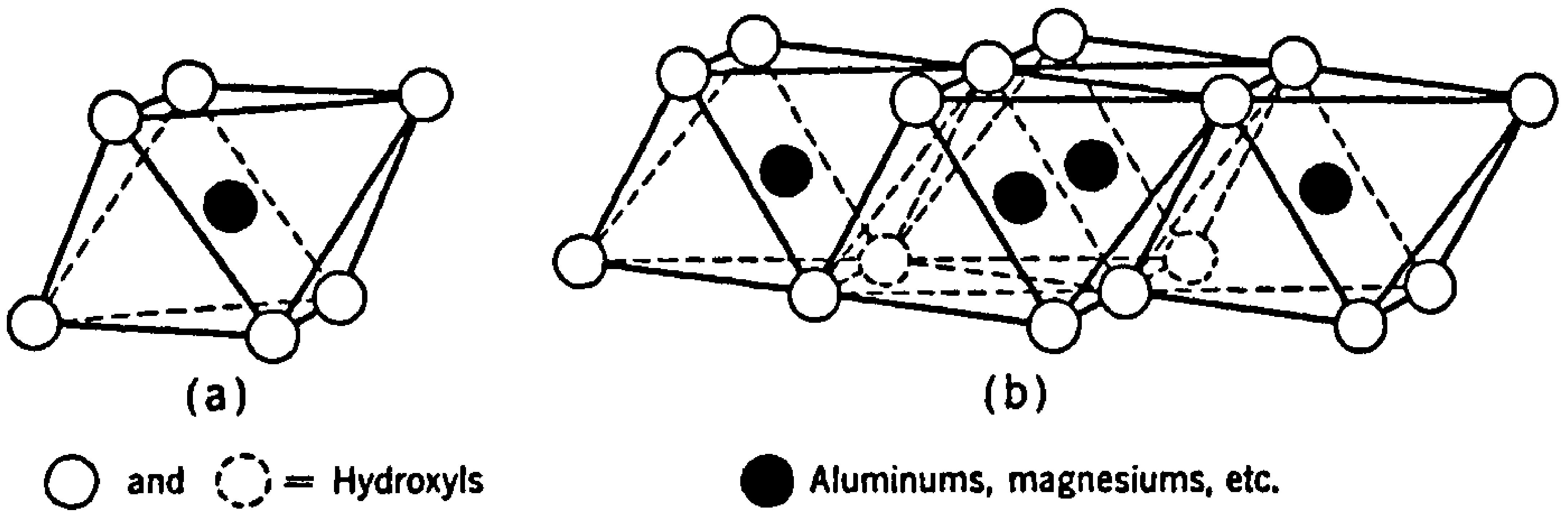


Figure 2.1.1 Diagrammatic sketch showing (a) a single octahedral unit and (b) the sheet structure of the octahedral units (Grim, 1968).

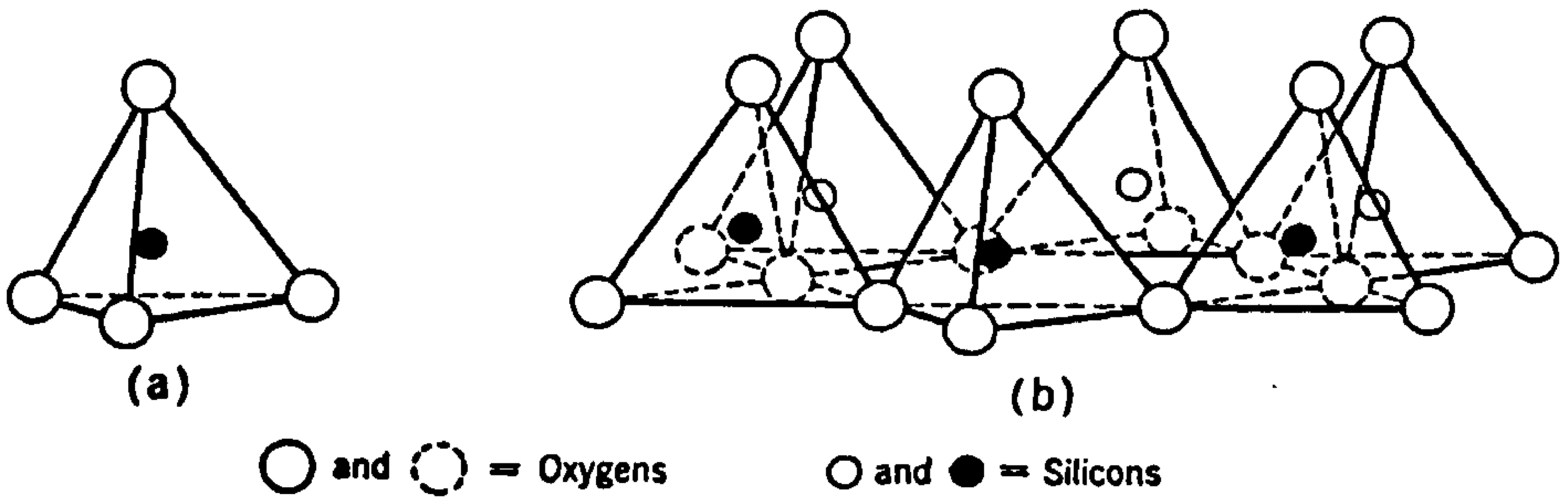


Figure 2.1.2 Diagrammatic sketch showing (a) a single silica tetrahedron and (b) the sheet structure of silica tetrahedrons arranged in a hexagonal network (Grim, 1968).

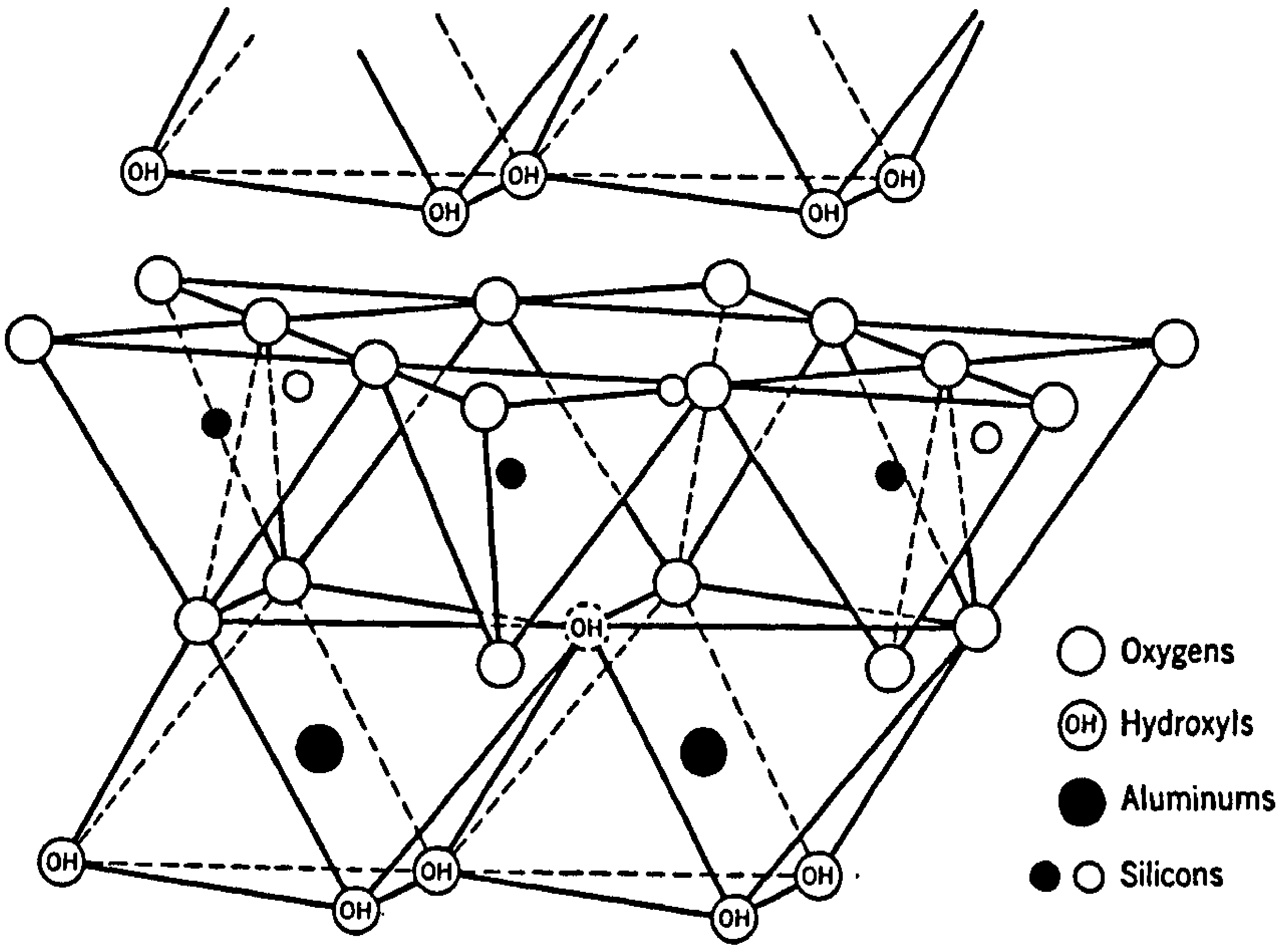


Figure 2.2 A diagrammatic sketch of the structure of the kaolinite layer (from Grim, 1968).

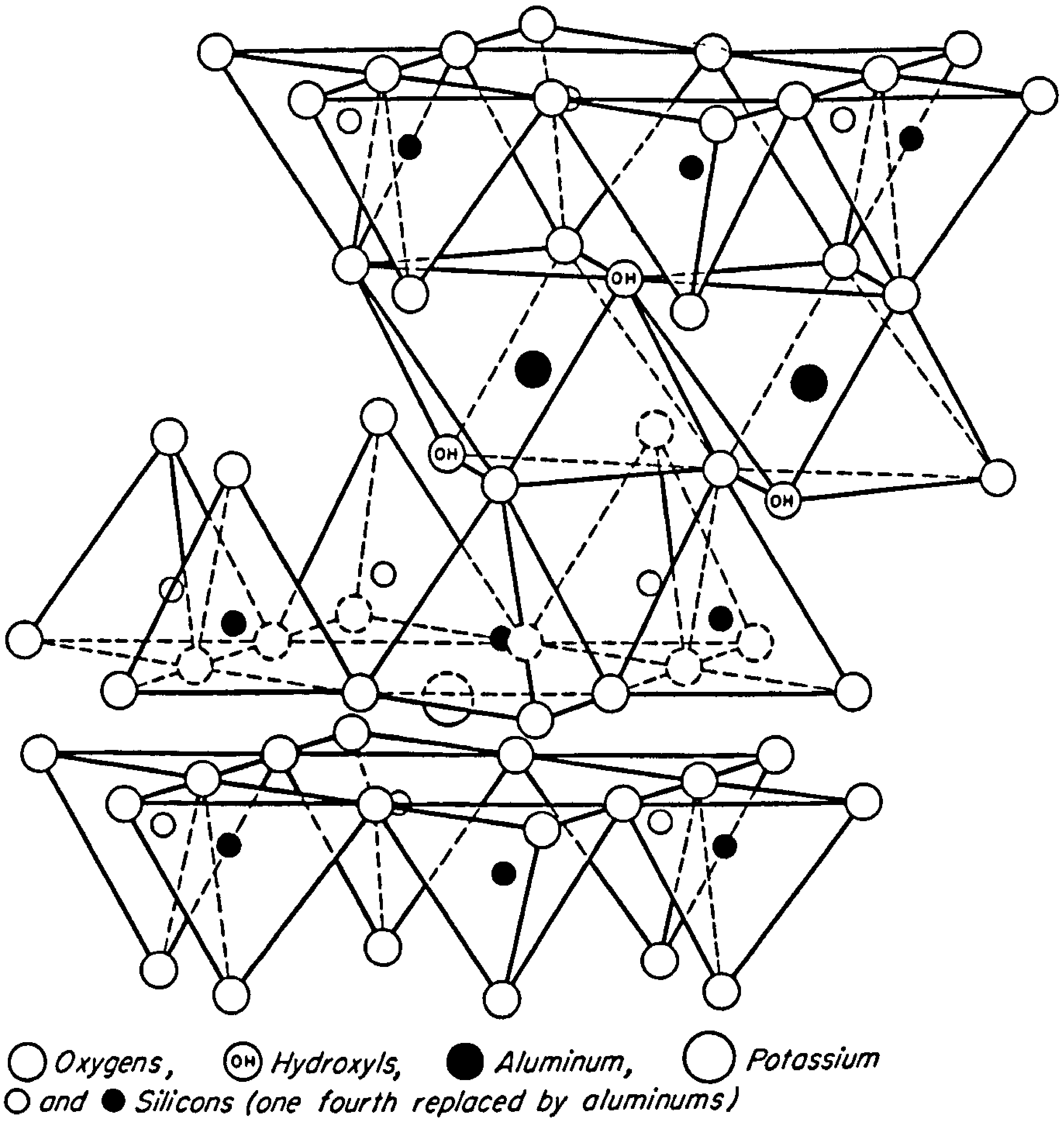


Figure 2.3 A diagrammatic sketch of the structure of muscovite (illite) (after Grim, 1968).

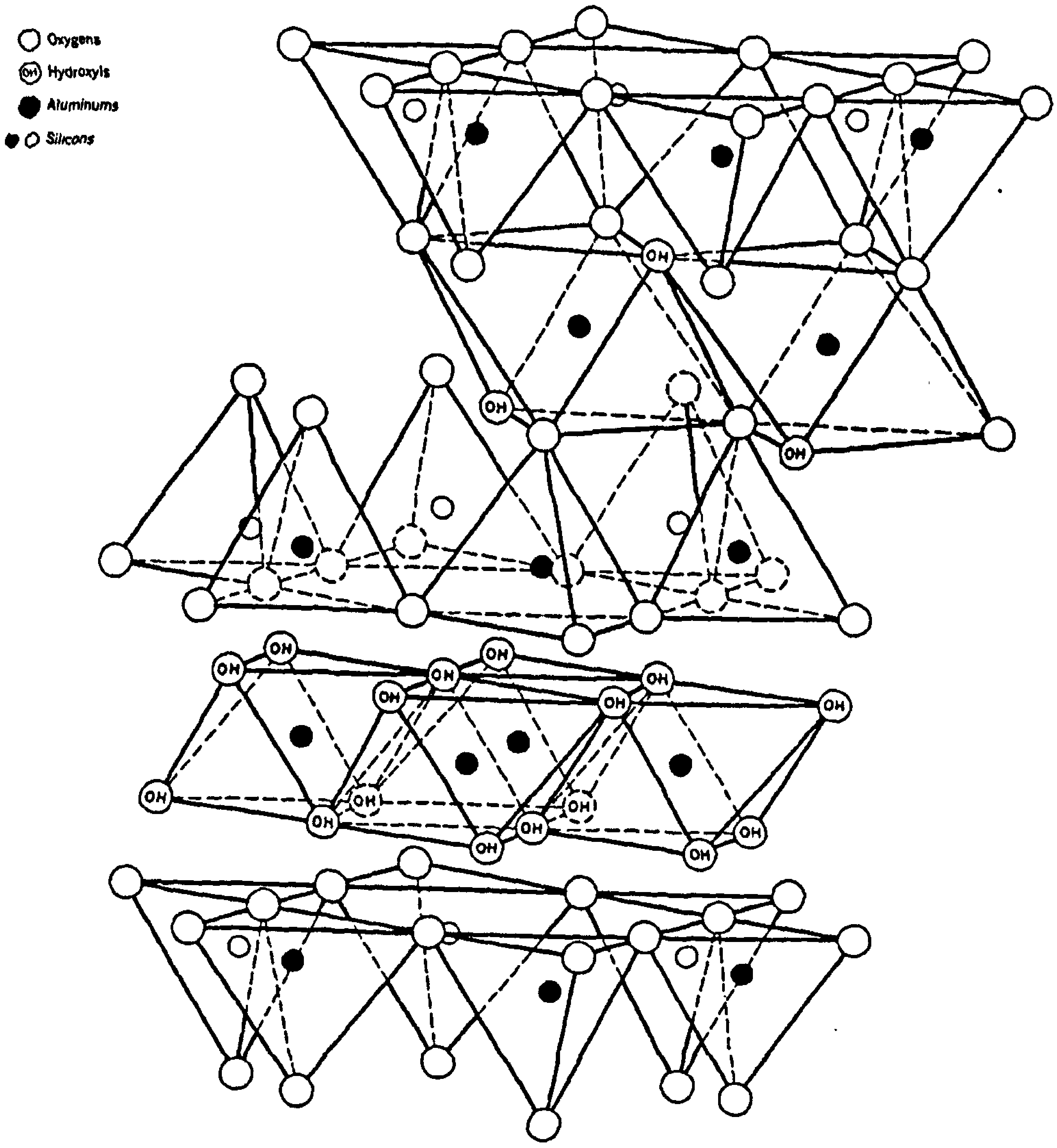


Figure 2.4 A diagrammatic sketch of the structure of the chlorite layer (after Grim, 1968).

3. Lime-Soil Stabilisation.

This chapter examines the effects of lime addition to a clay soil and describes, in detail, the reactions and mechanisms that occur when modification or stabilisation is carried out in the presence of sulphides and / or sulphates

3.1 Introduction

The term "soil stabilisation" may be defined as the alteration of the properties of an existing soil to meet specified engineering requirements (Sherwood, 1993). The main properties that require alteration by stabilisation, with specific regard to road pavements, are:

- ***Strength*** – to increase strength and thus stability and bearing capacity;
- ***Volume Stability*** – to control the swell-shrink characteristics caused by moisture changes;
- ***Durability*** – to increase the resistance to erosion, weathering or traffic usage, and
- ***Permeability*** – to reduce permeability and hence the passage of water through the stabilised soil. (Sherwood, 1993)

The three main techniques for stabilisation are: stabilisation by compaction, stabilisation by mechanical means and stabilisation using a stabilising agent.

3.1.1 Stabilisation by Compaction

The fact that a loose material may be made more stable simply by compacting it is so obvious that compaction is not normally considered to be a stabilisation process. However, compaction is the cheapest and most widely used method for improving the character of a soil on site (Cernica, 1995). Benefits from compaction include increased soil strength and improved bearing capacity, reduction in the voids (reduced void ratio and increased density), reduction of settlement and permeability and reduced shrinkage. These benefits are usually greatest on granular materials compacted in thin layers (0.3-0.5m deep), such as soil used to backfill a trench or behind a retaining wall. Specification for the satisfactory compaction of backfill material used in highway works are issued by the UK Department of Transport (DoT, 1995). Clay is sometimes used as a backfill as it is less expensive and/or more readily available than granular material, though generally clay is more difficult to compact unless it contains sufficient air voids.

3.1.2 Stabilisation by Mechanical Means

Mechanical stabilisation is the process whereby the grading of a soil is improved by the incorporation of another material that affects only the physical properties of the soil. Unlike stabilisation by the incorporation of stabilising agents, the proportion of material added usually exceeds 10% and may be as high as 50% (Sherwood, 1993). With well graded materials nearly all the air can be removed by compaction. However this cannot happen with poorly graded materials but their stability may be improved by adding another material to fill the voids between the particles. The granular materials specified by the UK Department of Transport for sub-base construction are examples of mechanically stable materials. The materials are manufactured to have gradings which give the required stability, but the same end result can be achieved by blending naturally occurring soils to produce the required particle size (Sherwood, 1993). Mechanical stabilisation has drawbacks particularly in those countries that have heavy rainfall or where frost is a problem. Although mechanical stability is highly desirable, it cannot always be achieved and even when it can it is often necessary to add a stabilising agent to bring about a further improvement in the properties of the material (Sherwood, 1993).

3.1.3 Soil Stabilisation by the Addition of Stabilising Agents.

It is this method that will be dealt with in the current work and encompasses lime modification/stabilisation of clay soils, and lime-modified, Portland cement (PC)-stabilised clay soils, and lime activated, ground granulated blastfurnace slag (GGBS)-stabilised clay soils.

3.2 Lime Stabilisation of Clay Soils

It has long been understood that the engineering properties of clay soils can be modified by the addition of small percentages (1% to 3% by weight) of lime. It is also widely accepted that larger additions of lime (between 2% and 8% by weight) can stabilise soil. The properties of lime-soil mixtures are dependent on a number of variables including:

- Percentage of clay minerals in the soil,
- The mineralogy of the clay,
- The moisture content of the clay,
- The quantity of lime added,

- The climate,
- The length and temperature of the curing period.

When added to a clay soil, lime chemically attacks the clay mineral fraction (Bell, 1988; Cobbe, 1988; Arabi and Wild, 1989).

3.3 Lime

Lime used for stabilisation or modification has many guises including quicklime (CaO), slaked or hydrated lime ($Ca(OH)_2$), dolomitic lime and agricultural lime (though this is usually calcium carbonate ($CaCO_3$) and is unsuitable for soil improvement). Either quicklime or hydrated lime is used for soil stabilisation or modification. In the UK quicklime has several advantages over hydrated lime:

- Quicklime has a higher available lime content per unit mass than hydrated lime (3% quicklime is normally equivalent to 4% hydrated lime).
- Quicklime is denser than hydrated lime requiring less storage and transport space.
- Quicklime is considerably less dusty than hydrated lime.
- Quicklime produces a large reduction in moisture content due to hydration and evaporation (up to 32% of its own mass of water from the surrounding soil). It is therefore particularly beneficial with wet soils.
- Quicklime generates heat which accelerates strength gain as the slaking reaction of quicklime is highly exothermic (approximately 0.882kJ/g are expelled (see Appendix A)). This is of benefit in a temperate climate such as that found in the UK (Greaves, 1996).

When lime is exposed to carbon dioxide (CO_2) it undergoes carbonation which in turn leads to a decrease in the availability of Ca^{2+} ions, and if carbonation of lime in lime-soil mixes occurs, a reduction in pH value also occurs. Matsushita et al. (1993) analysed the carbonation process of a $Ca(OH)_2$ slurry using X-ray photoelectron spectroscopy (XPS) techniques. They postulated that the reaction shown in Equation 3.1 is due to the decrease in ion concentration in the early period of the carbonation process.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \qquad \textbf{Eq.3.1}$$

In practice carbonation has not been reported as a significant problem in the UK as lime stabilised soils are almost invariably compacted to a low air content soon after mixing (Sherwood, 1992). In hotter climes however, a number of failures have been attributed to carbonation of lime causing reversion of the stabilised layer.

3.4 "Lime Modification" and "Lime Stabilisation"

When lime is mixed with a cohesive material, the material is first modified before further chemical reactions occur, which in most soils lead to stabilisation. (Perry et al. 1996). Lime modification (or lime improvement) usually requires between 1-3% lime (as $Ca(OH)_2$) and is a rapid process resulting in increased permeability, changes in plasticity and increased workability of the modified material (Arabi and Wild, 1989). The immediate response of clay soil to the addition of lime is that it generally becomes apparently drier, more friable and more easily trafficked and compacted by construction plant (Cobbe, 1988). These aspects of the lime-soil reaction are generally termed "modification". Over time as the lime soil mix is allowed to cure, pozzolanic reactions occur which are time and temperature dependent resulting in the growth of cementitous products increasing strength, volume stability, decreasing permeability and improving frost resistance (Arabi and Wild, 1989). These combined aspects are termed "stabilisation".

3.5 Material Suitability for Lime Modification or Stabilisation

- ***Type and Percentage of clay minerals in the soil***

As stated in Chapter 2, clay minerals are generally composed of two basic units, these being the silicon tetrahedron and the aluminium or magnesium octahedron. All clay minerals are attacked when lime is added to a clay soil, although those possessing the highest available silica normally react most strongly (Bell, 1987; Cobbe, 1988).

- ***Organic Matter***

Organic matter can preferentially adsorb calcium ions particularly affecting the strength development of lime treated clay soils. (Bell and Coulthard, 1990). The same applies to soils treated with cement as cement hydration can also be retarded or completely prevented (Sherwood, 1992). The retardation is caused by organic compounds that combine with the lime liberated during cement hydration, which reduces the pH below the value required for hydration. It is the type rather than the amount of organic matter that is the critical factor, and therefore a simple determination of total organic content is a poor guide to the presence of deleterious compounds.

- ***Sulphates***

Sulphates occur in most of the major clay formations in the UK and are usually low in the surface layers and increase progressively with increasing depth. Therefore the absence of sulphates in the surface layers of a clay soil is no indication of true sulphate content. Sulphate may be present as a component of the soil, may be produced by the oxidation of sulphides (e.g. pyrites) in the soil, or may be introduced into the soil by groundwater (Perry et al. 1996). Swelling can either be caused by the formation of gypsum when sulphates (e.g. sodium sulphate or sulphuric acid from pyrites oxidation) react with lime, which can be detrimental to the treated materials strength and cause deformation, or more commonly by the formation of deleterious phases containing sulphates, such as ettringite or thaumasite (Sherwood, 1993).

3.6 Lime-Clay Reactions

3.6.1 Introduction

There are basically three types of reaction (both physical and chemical) between soil and lime. They are: cation exchange, flocculation (or agglomeration), and pozzolanic reactions (Bell, 1987; Cobbe, 1988). In addition lime carbonates by reacting with CO_2 in the air. If quicklime (CaO) in used in lime stabilisation, it immediately reacts with water on mixing to form slaked or hydrated lime ($Ca(OH)_2$) thus:

$$\mathbf{CaO + H_2O \rightarrow Ca(OH)_2 + Heat \uparrow} \qquad \textbf{Eq.3.2}$$

The advantages of the exothermic reaction (Eq.3.2) are twofold. Firstly the heat raises the temperature, encouraging more effective cementation, and secondly the heat helps the evaporation of water in heavy, waterlogged clay soils. The slaked lime raises the pH of the mix to around 12.4.

$$\mathbf{Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^- + \uparrow pH} \qquad \textbf{Eq.3.3}$$

Alumina and silica from the clay dissolve at a pH of at least 10.5 and go into solution (Snedker and Temporal, 1990), as do (depending on their solubility) any existing sulphate minerals in the clay soil. The reactions that follow are complex and depend on other variables such as clay mineralogy, temperature and sulphate type and content.

3.6.2 Flocculation.

Lime addition immediately transforms a clay soil that would otherwise soften, collapse and disperse in water into a firm water-resistant material. Cation exchange may be triggered by: a) broken Si-Al bonds at the particle edges and cleavages, such as those created during compaction and/or grinding (Sloane, 1965), or b) cation substitution within the lattice structure. Depending on the unit structure, Si^{4+} may be replaced by Al^{3+} in the tetrahedral structure, while in the octahedral unit Mg^{2+} may replace Al^{3+}. This is termed isomorphous substitution. When the substituted element has the same valency as the substituting element this is of little consequence, but when the valency of the latter is of lower valency the crystal then carries a net negative charge and an equivalent number of positively charged ions (cations) are attracted to the crystal surface from the soil water and in addition the clay crystal is slightly deformed. If a soil is already saturated with, calcium, magnesium, ferrous or ferric cations, exchange will not occur when lime is added, but the increased concentration of cations is thought to cause a "crowding" of cations around the particles. This crowding leads to a reduction in the thickness of the double diffuse layer allowing closer approach of particles and hence increased attraction due to increased Van der Waals forces (the forces of attraction that occur between particles of matter), causing flocculation (Cobbe, 1988).

Flocculation results in the formation of irregular aggregates of particles and hence lower packing density, less regular particle packing and thus increasing permeability and reducing density. The rate and effectiveness of flocculation due to lime stabilisation relies heavily on the type of clay minerals present in soil. Isomorphous substitutions (and therefore crystal imperfections) are few in kaolinite and so, despite the relative weakness of the hydrogen bond, the particles tend to be large and have a low net negative charge resulting in adsorption of cations to crystal surfaces (Cobbe, 1988). Cation exchange occurs principally around broken edges and corners in kaolin clay minerals, with the number of sites increasing as the particle size decreases and also where the occasional exposed hydroxyl ions disassociate with the hydrogen ion being replaced by a cation. Poorly crystalline clay minerals with a 2:1 structure such as illite experience frequent isomorphous substitutions of aluminium (Al^{3+}) for silicon (Si^{4+}) in the tetrahedral layers. This results in a net negative charge, which is balanced by the adsorption of cations between the crystal sheets. Adsorbed cations result in variably shaped and sized illite crystals, other than when the adsorbed cation is potassium as a perfect fit is then achieved.

3.6.3 Pozzolanic Reactions

A pozzolan is a material that is capable of reacting with lime in the presence of water, at ordinary temperatures, to produce cementitious compounds. Clay minerals are natural pozzolans and have the ability to react with lime to produce cementitious products (Sherwood, 1993). Pozzolanic reactions give rise to the formation of various types of hydrated calcium silicate and calcium aluminate cementing agents and are time dependent, with strength developing gradually over a long period of time (in some instances taking several years) (Bell and Coulthard, 1990). The actual reaction products formed vary depending on clay type, temperature, lime content and curing time, though it is generally recognised that the principal cementitious product is a calcium silicate hydrate (C-S-H) gel (Bell 1987; Cobbe, 1988; Arabi and Wild; 1989). Work by Al-Rawi (1981) highlighted the importance of temperature, especially during the curing period, of lime stabilised clay soils. He noted that increased curing temperature (50°C, compared with similar tests at 20°C) resulted in large increases in unconfined compressive strength even when the stabilised material was soaked. Bell (1988) hypothesised that the long-term strength development of lime-clay material may be attributed to the gradual crystallisation of C-S-H gel forming an interlocking structure, although this is disputed by Wild et al. (1989) who argued that an impermeable pore-filling gel is formed rather than a crystalline material. Small amounts of crystalline calcium aluminate hydrate (such as C_4AH_{13} and C_3AH_6) and calcium aluminate silicate hydrate phases (C_2ASH_8) form in some circumstances, particularly in lime-stabilised kaolinite, which has a high alumina content (Arabi and Wild, 1989).

3.7 Property Changes

3.7.1 Introduction

It is the clay fraction and content of the soil that the construction engineer must pay attention to when considering stabilisation. Changes in material property include changes to consistency limits (i.e. liquid limit (LL), plastic limit (PL) and plasticity index (PI)) and changes to compaction parameters (i.e. optimum moisture content (OMC) and maximum dry density (MDD)). Other changes include unconfined compressive strength (UCS), California bearing ratio (CBR), expansion and volume stability and where applicable changes in freeze thaw properties.

3.7.2 Consistency Limits

Calcium ions from the lime cause a reduction in the plasticity of cohesive soils, so they become more friable and have greater workability. The changes in plasticity is caused by the flocculation of the clay particles from the addition of lime (due to cation exchange or the crowding of additional cations onto the surfaces of particles of clay, hence clay particles become electrically attracted to one another (Bell and Coulthard, 1990)). In calcareous soils the clay may be saturated with calcium ions before the addition of lime but cation exchange may still occur. (Calcareous soils may have a pH value up to 8.5 but the addition of lime potentially raises the pH to 12.4) (Sherwood, 1993). Although bonding between the clay particles within the floc or aggregate is increased, the bonding between clay aggregates is relatively weak and they behave like particles of silt. Very small quantities of lime are required to bring about these changes, the amount being around 1-3% depending on the type of clay minerals present in the soil (Bell, 1987). The liquid limit (LL) is generally lowered by the addition of lime. However the liquid limit of kaolinitic clay may remain unchanged after lime treatment, or even increase (Bell, 1988; Arabi and Wild, 1989). According to Croft (1964) the increase in LL 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. Polarised water molecules are therefore attracted and bound to the clay layer surfaces by the formation of hydrogen bonding (Arabi and Wild, 1989). The rate of increase in plasticity index (PI) with lime addition increases in a similar order to cation exchange capacity i.e. kaolinitic clays – illitic clays – montmorillonitic clays (Bell, 1987; Sherwood, 1993). Researchers have noticed that lime treated kaolinitic clays are rather variable in terms of consistency limits. Abdi (1992) reported a decrease in LL and PI in kaolinitic clays with additions beyond 6% $Ca(OH)_2$, though he reasoned that the use of clay with a very high kaolinite content (84% by weight) could be the cause of the erratic behaviour.

3.7.3 Dry Density and Moisture Content

Compaction of lime-stabilised soil is more tolerant than cement-stabilised soils. Not only is delay less critical, but so also is compaction moisture content. In other words, lime flattens the compaction curve ensuring a given percentage of the prescribed density can be achieved over a much wider range of moisture contents, so that relaxed moisture control specifications are possible (Ingles and Metcalfe, 1972; Bell, 1988). The addition of lime to all clay increases the optimum moisture content (OMC) and reduces the maximum dry density (MDD) for the same compactive effort. The decrease in density is not only dependent on lime percentage, but also on the amount and type of clay minerals present. Croft (1964) reported that higher compaction densities were obtained in lime treated clays with low cation exchange capacities (i.e. kaolinite) than in clays with higher cation exchange capacities (i.e. montmorillonites). A pronounced decrease in compactive density occurs with increasing time intervals between mixing and compaction and so maximum density occurs at somewhat higher optimum moisture content. Moreover if a lime-soil mixture remains uncompacted it undergoes carbonation, the cemented particles then behave like sand grains and any subsequent compaction is not as easy (Bell, 1988).

3.7.4 Strength Development

The strength development of a lime stabilised soil is primarily dependent on the pozzolans present, but is also influenced by other factors such as soil type, type and amount of added lime, curing time and condition (temperature and water availability), moisture content, unit weight and compaction moisture content (Ingles and Metcalfe, 1972; Bell, 1988). These are outlined below.

- *Amount and Type of Lime:*

Ingles and Metcalfe (1972) noted that montmorillonitic clays give lower strengths with dolomitic limes than high calcium or semi-hydraulic limes. Kaolinitic clays on the other hand yield the highest strengths when mixed with semi-hydraulic lime and the lowest strengths are obtained with high calcium limes (Bell, 1988).

- *Clay Type:*

Stabilised kaolinite achieves higher strengths than illite, chlorite or halloysite, though it is generally the expansive clays that show more rapid rates of increase in strength than other clays (Bell, 1988). The amount of the clay minerals has little effect on strength development. Soils with high clay contents are not more responsive to lime than are soils of low clay contents. Hence it would appear that the absolute amount of silica or alumina required to sustain pozzolanic reaction in soils is relatively small (Bell and Coulthard, 1990).

- ***Curing Time and Compaction:***

Curing is one of the major variables influencing the strength development of lime stabilised soil and its effect on strength is a function of time, temperature and relative humidity. Al Rawi, (1981) found that increased temperature resulted in a large increase in the unconfined compressive strength (UCS) of lime-stabilised clays. It is widely observed amongst researchers that strength first increases rapidly, notably during the first seven days of curing, then increases more slowly at an approximately constant rate for about 15 weeks. This supports the view that cementitious products due to lime-clay reactions begin to form at an early stage (as soon as flocculation is completed). Workers such as Mateous (1964) and Arabi and Wild (1989) found that specimens cured at 35°C developed more than twice the strength of those specimens cured at 25°C. In fact, temperatures less than 4°C retard or may even terminate the lime-soil pozzolanic reaction (Thompson, 1968).

- ***Moisture Content:***

The strength of lime stabilised clay soils decreases with increasing natural moisture content (Bell, 1988). Even three months after lime stabilisation the strength of the clays with high natural-moisture contents remains low. Conversely, lime-soil mixtures compacted at moisture contents above optimum attain, after brief periods of curing, achieve higher strengths than those compacted with moisture contents less than optimum (Bell, 1987) as 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).

- ***Unit Weight and Compaction Moisture Content:***

Wild et al (1999) reported that compacting soil-lime mixes either wet or dry of optimum moisture content minimises the potential for future expansion. Inter particle void space is greater both wet or dry of MC than at OMC and therefore there is more space available to contain developing expansive products, such as ettringite.

The compactive effort significantly influences strength as shown by Mateous (1964), (as reported from Bell (1987)). He showed that when the compactive effort was increased from standard, the compressive strength of lime-soil mixtures increased by 50-250% for both 1 and 28 day curing periods. Mitchell and Hooper (1961) showed that samples of clay and lime, compacted within one hour of mixing, attained a higher strength than those that were compacted after 24 hours had elapsed.

3.8 Swelling in Lime-Stabilised Soils.

Swelling of clay soils (discussed in chapter 2) is mainly caused by an increase in the basal spacings due to water adsorption between layers and is generally confined to clay soils containing significant levels of montmorillonitic clay minerals. In the presence of lime and/or salts such as sulphates, osmotic suction (i.e. the negative gauge pressure to which a pool of pure water must be subjected in order to be in equilibrium through a semi-permeable membrane with a pool containing a solution identical in composition with the soil water) must also be considered (Krahn and Fredlund, 1972).

The addition of lime to clay soils will affect the engineering properties of the material and, in time will result in the formation of cementitious products that cement the clay plates together. Cation exchange (mainly involving Ca^{2+} ions introduced by lime) and cementation can reduce water adsorption properties at clay particle surfaces, reducing the potential of the clays to swell (Bell, 1988; Arabi and Wild, 1989). The Department of Transport (DoT) allows an average swell for lime-stabilised material of <5mm measured on the standard 127mm high CBR mould – i.e. 4% linear expansion after not more than 72 hours mellowing, followed by 3 days of curing and 4 days of soaking. A test specimen swelling to more than 10mm (around 8% linear expansion) renders the soil unsuitable for stabilisation. These limits are rarely exceeded unless the presence of sulphates is confirmed.

3.9 Effects of Sulphates on Lime Stabilisation

3.9.1 Occurrence of Sulphates.

Sulphates are found in natural ground in solid form as crystals or nodules within the soil matrix or within open soil discontinuities such as joints, faults and fissures. They are also found as dissolved ions in groundwater occupying the pore spaces within the soils and filling joints and fissures below the groundwater table. Within the soil, sulphate most commonly occurs as calcium sulphate in the form of selenite or gypsum ($CaSO_4.2H_2O$), but also as magnesium sulphate in the form of epsomite ($MgSO_4.7H_2O$), as potassium sulphate in the form of arcanite (K_2SO_4) and as sodium sulphate in the form of thernadite ($Na_2SO_4.10H_2O$) or Glaubers salt (Kinuthia, 1997; Thaumasite Expert Group, 1999). Sulphates generally tend to occur naturally in regions of limited rainfall as primary constituents of Sabkha-like deposits and evaporite cycles in such places as Australia and certain areas of the USA, though significant amounts are found today in more temperate regions. However, sulphates tend to show a non-uniform distribution in many clay soils in the UK. Work by Bessey and Lea (1953) suggests sulphate concentration may vary widely due to wide seasonal variations with rainfall. Certain salts such as $MgSO_4$ and Na_2SO_4 can also be contained in industrial waste that may be used in pavement and/or other construction (Li et al. 1996). Calcium sulphate is commonly found in the UK, especially in Triassic and Jurassic soils such as the Mercia Mudstone Group and Lower Oxford Clay.

Reports of problems of heave in lime stabilised soils, due to sulphate attack and ettringite (and/or thaumasite) formation have previously attributed the problem solely to the presence of sulphates in the soil (normally selenite or gypsum).

3.9.2 Pyrites

Many soils contain iron pyrites (FeS_2) which, when exposed to a moist atmosphere, oxidises to produce sulphates and oxides or hydrated oxides of iron (Robbins, 1990a/b; Hawkins, 1992). In fact sulphate, in the form of gypsum present in soils, normally derives from the reaction of weak sulphuric acid (originating from sulphide oxidation) with calcite. Therefore even if a soil is sulphate free, it is possible that over time oxidation of pyrites may greatly increase its sulphate content. The likelihood of heave in lime-stabilised material containing pyrites will depend upon the rate and degree of oxidation of the pyrite after its exposure to the atmosphere and within the stabilised layer. According to Midgely (1978), pyrites can occur in two forms, reactive and nonreactive. When immersed in limewater the reactive form produces, rapidly, a blue-green precipitate of ferrous hydroxide, which is further oxidised to brown ferric oxide. An example of a source of such reactive pyrites is in Thames River gravel. The degree and rate of pyrites oxidation depends greatly on the surrounding chemical environment. Marsh waters sometimes contain pyrites, which oxidises under suitable conditions to produce free sulphuric acid, which is then neutralised by bases present in the soil to give sulphate salts. If however the pyrites remains below the water table no oxidation takes place due to oxygen starvation. Oxidation is most rapid in regions of fluctuating water level. The oxidation of pyrites during weathering proceeds chemically in moist air to produce sulphuric acid and ferrous sulphate and particularly in an acid environment this process may be assisted by autotropic bacteria, such as *Thiobacillus Ferrooxidans* (Backes et al. 1986; Komnitsas et al. 1995), which further oxidises the ferrous sulphate to ferric sulphate. The oxidation rate is greater for fine-grained amorphous and impure forms of pyrites, and where bacteria are involved optimum conditions are an acidic environment and a temperature of about 35°C. If calcite is present then gypsum will be produced (Eq.3.4 and 3.5) and this in itself can involve volume increases and heave (Hawkins and Pinches, 1987).

$$FeS_2 + 7/2O_2 + 8H_2O \rightarrow FeSO_4.7H_2O + H_2SO_4 \qquad \textbf{Eq.3.4}$$

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4.2H_2O + CO_2\uparrow \qquad \textbf{Eq.3.5}$$

Normally in mudrock formations, such as Oxford Clay, the deepest and least weathered deposits contain calcite and pyrites with no gypsum and these become successively replaced by gypsum in the upper levels. The pyrites often occurs as disseminated grains of 0.1-0.5μm diameter or as framboids (pyrite clusters 2-40μm in size). Although many reports of heave, due to pyrites oxidation, have focused on acidic environments (Thomas et al. 1981; Cripps et al. 1994), work by Cassanova et al. (1996, 1997) has considered pyrite oxidation over a wide pH range. They report earlier work by Singer and Stumm (1970) and Nicolson et al. (1988) that indicate that the rate of sulphide oxidation is pH dependent between 4.5 and 6, and pH independent below 3.5, and between 7.5 and 8.5. They demonstrated, from thermodynamic considerations, that no iron sulphide would be stable above a pH of 10. Cassanova et al. (1996, 1997) also refer to experimental evidence from Hawkins (1992), that the speed of oxidation is greatly enhanced under strongly alkaline conditions ($12.5<pH<13.7$), the rate increasing 50 times for every 1.2 increase in pH. They also establish that ferrihydrite ($Fe(OH)_3$) is the predominant sulphide oxidation product under alkaline conditions (Eq.3.6).

$$FeS_2 + 4.5O_2 + 2H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + H^+ \qquad \textbf{Eq.3.6}$$

In concrete in which pyrites is present in the aggregate, the rate of oxidation is slow and depends strongly on the alkalinity of the pore solution, the availability of molecular oxygen and the grain size (Cassanova et al. 1997). Also the volume increase associated with the formation of ferrihydrite is small compared to that of monosulphate or ettringite formation (from the reaction of sulphate ions with Portlandite and/or C_3A). Cassanova et al. (1997) establish, from observations of the sulphoaluminate phases formed in a concrete containing pyrites, that sulphate attack can be induced by the oxidation of sulphides. This therefore suggests that sulphate attack and swelling could also be induced in lime-stabilised soil by oxidation of pyrites. An example of such a case was seen at the Banbury IV section of the M40 in the UK. It was found that lime-stabilised material (a pyrite-rich Lower Liassic mudrock) had swollen and heaved due to sulphate attack, even though the material was initially found to have a sulphate content (expressed as SO_3) of less than 1%. Snedker and Temporal (1990) reported that in places the stabilised material had heaved up to 150mm. From field studies they deduced the following:

- There was a strong relationship between moisture content (and related swell) and the total sulphate content in the lime stabilised material.
- The total sulphate content of the stabilised material was generally greater than that of the underlying sub-formation suggesting a contribution from external sources possibly through groundwater, (Robbins (1990b) reported that the sulphate levels were as high as 4% in and below the stabilised layer).
- The total sulphate content of the unstabilised sub-formation material was generally higher than the values recorded in the same material in the ground investigation prior to stabilisation.

Snedker and Temporal postulated that the disruption of the stabilised material was caused by the formation of ettringite and/or thaumasite in the presence of water due to rising sulphate levels caused by the oxidation of pyrites in the disturbed Lower Lias. Robbins (1990b) also reported that the use of lime stabilisation methods on a pyritic mudstone probably inadvertently oxidised the pyrites and formed gypsum.

If lime were added to a soil containing metal sulphates, such as Na^+ or K^+, the pH of the system would increase above that of a saturated lime solution (i.e. 12.4 pH).

$$Ca(OH)_2 + Na_2SO_4 + 2H_2O \rightarrow 2NaOH + CaSO_4.2H_2O \qquad \textbf{Eq.3.7}$$

$$\textbf{pH 12.4} \quad \rightarrow \quad \textbf{pH 13.8}$$

However, it is thought that the addition of lime to soils containing pyrites reduces the pH of the system by precipitation of gypsum and geothite, thus:

$$2Ca(OH)_2 + 7.5/2O_2 + FeS_2 + 2.5H_2O \rightarrow 2CaSO_4.2H_2O + FeOHO \quad \textbf{Eq.3.8}$$

$$\textbf{pH 12.4} \quad \rightarrow \quad \textbf{pH} \downarrow$$

3.9.3 Lime-Clay-Sulphate Reactions

At high pH values of at least 12.4 provided by lime in solution, the clay fraction of the soil reacts with sulphates (Snedker and Temporal, 1990). Also the more Ca^{2+} ions introduced to a clay soil, the more sulphate ions are adsorbed, especially in soils rich in iron and alumina (Bolan et al. 1993). At high concentrations, alkali metal sulphates can increase the pH of the pore solution to such a high level that lime ($Ca(OH)_2$) becomes almost insoluble (Li et al. 1996) (Eq.3.7). The effects of sulphates on lime treated soils differ from the effects of sulphates on untreated clays (Bell, 1988). In lime-treated soil, the unconfined compressive strength (UCS) increases with a low sulphate content (around 1%), especially when the water content of the soil exceeds optimum moisture content (OMC) or compaction moisture content (Bell, 1988). In contrast the UCS of untreated clay (i.e. without stabiliser) is reduced by the presence of sulphates regardless of moisture conditions (Stevens and Littleton, 1989). Kinuthia et al. (1999) also found that added sulphates lowered the liquid limit of lime-stabilised kaolinite, though the magnitude of lowering depends on the nature of the sulphate cation(s). He also points out that the changes in Atterberg limits and in compaction characteristics result mainly from cation exchange processes that affect the viscosity of the clay-water mix. There is evidence that early formation of ettringite and gypsum may also influence these material properties.

The presence of sulphates influence the engineering properties of lime-stabilised clay soils and can influence both the reaction mechanism and the reaction products. The increased pH due to lime addition allows the release of both alumina and silica from clay minerals. Normally the calcium sulpho-aluminate phase ettringite ($C_3A.3C\underline{S}.H_{32}$) is formed first and at low sulphate concentrations the metastable phase ($C_3A.C\underline{S}.H_{12}$) may also be observed (Abdi and Wild, 1993; Waswa et al. 1993; Kinuthia et al. 1999). Additionally, at low temperatures where carbonate is present thaumasite ($Ca_2[Si(OH)_6]_2.(SO_4)_2(CO_3)_2 24H_2O$) can occur. It is well documented that ettringite and thaumasite can, under certain conditions cause severe damage to concrete structures and stabilised soil pavements independently or together (Hunter, 1988; Snedker and Temporal, 1990; Bickley et al. 1995; Thaumasite Expert Group, 1999).

As previously mentioned, pozzolanic reactions involving calcium ions and liberated silica from the clay minerals produce the strength-forming calcium silicate hydrate (C-S-H) gel, which is also the principal long-term cementing component of the lime-clay reaction. However C-S-H gel requires a pH of about 12.5 in order to remain stable and breaks down as pH drops towards 10.5 (Gaze and Crammond, 2000). Once the C-S-H starts to decompose it releases lime into the system and, depending on the system, brucite, ettringite or thaumasite may be precipitated. A continuous reduction in pH ultimately results in complete C-S-H breakdown as the pH drops towards 10.5. As demonstrated in Eq.3.8 it is possible that the oxidation of pyrites in a stabilised clay soil may reduce the pH of the system, resulting in the breakdown of the strength-giving C-S-

H gel and a subsequent reduction in strength (under these low pH conditions ettringite would also be unstable). Under conditions where ettringite is stable, in addition to being incorporated in the ettringite, some of the liberated alumina can combine with other ions in the system and be incorporated in the cementitious products, whilst some silicon may also be taken up in the formation of ettringite. For example Wild et al. (1993), working with near pure kaolinite mixed with lime (6%wt) and various percentage additions of gypsum, found two principal reaction products of the hydrating system using TEM (transmission electron microscopy). The first was a fibrous amorphous calcium aluminate silicate hydrate (C-A-S-H) gel containing small amounts of sulphur, and the second were rods or needles of a calcium sulpho-aluminate hydrate of composition similar to that of ettringite, but which also contained significant amounts of silicon.

3.10 Ettringite Formation

Lime-clay reactions provide further complications in the presence of sulphates in that they produce expansion principally as a result of ettringite formation (Abdi and Wild, 1993). The use of the term ettringite without qualification normally refers to “sulphate ettringite”, which has the formula $C_6A\underline{S}_3H_{32}$. Ettringite can be represented either in cement chemistry notation as $C_3A3C\underline{S}H_{32}$ or $C_6A\underline{S}_3H_{32}$ (i.e. $3CaO.Al_2O_3.3CaSO_4.32H_2O$) or in the structural chemistry notation as $Ca[Al(OH)_6]_2(SO_4)_326H_2O$). However, it should be noted that ettringite is in fact a general term used to denote a group of minerals, all with very similar crystal structures (Day, 1992) and in the current work the term "ettringite" refers to both amorphous and crystalline ettringite.

After the dissolution of alumina and silica at high pH from the clay and of the sulphate minerals, Wild et al. (1993) theorised that a colloidal product forms on the clay particle surfaces consisting of a complex calcium-silicate-sulphate-aluminate-hydrate (C-A-S-$\underline{S}$-H). The $\underline{S}$/S ratio of the colloidal product increases progressively with curing/soaking time due to its property of attracting sulphate ions and rejecting the silicate ones, due to the differing solubilities. Eventually, within this colloidal product a compound with little or no silica in it is precipitated as ettringite. Ettringite precipitation is a direct 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 mainly on pH, temperature and sulphate ion concentration. Above 50°C ettringite is not generally formed at sulphate concentrations below $5\text{x}10^{-4}$ mole/litre sulphate, while at 5°C only $2\text{x}10^{-7}$ mole/litre would be required (Glasser, 1996).

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

Eq.3.9

The formation of ettringite, sometimes accompanied with the formation of gypsum (Eq.3.10), lowers the concentration of Ca^{2+} and $[SO_4]^{2-}$ in the pore solution.

$$Ca^{2+} + [SO_4]^{2} + 2H_2O \Leftrightarrow CaSO_4.2H_2O$$ **Eq.3.10**

Assuming that the chemical environment during the cement hydration process is similar to that during the hydration process in lime-stabilised clay soils, a pore solution of high alkalinity would lead to the formation of fine ettringite crystals which form close to the clay particle surfaces, and if water is available this ettringite formation would be accompanied by large expansions. However, at lower pH, $Al(OH)_4^-$ ions would move into the bulk pore solution and ettringite may precipitate in voids giving rise to little or no expansion (Glasser, 1996). Also ettringite is not stable in low-lime environments when the pH falls below approximately 10.5 (Gaze and Crammond, 2000; Santhanam et al. 2001). In Portland cement (PC), sulphate (usually in the form of gypsum) is intentionally added during manufacture to the cement clinker to form ettringite and inhibit "flash setting" of the C_3A component of the cement during hydration (Day, 1992; Neville, 1995). (The hydration of PC will be discussed in Chapter 4). Day (1992) demonstrates in cement related cases that ettringite withdraws water from the pore solution, increasing the concentration of OH^- ions and therefore increasing the pH of the pore solution. This helps in maintaining the pH for further ettringite formation until all the reactants are depleted.

3.10.1 Nature of Ettringite

The nature and form of ettringite differs under differing chemical environments, making the understanding of the influence of ettringite on the expansive behaviour of stabilised clay soils very complex. Ettringite and its characteristics and stability are strongly dependent on pH, sulphate activity and temperature.

- *Influence of pH.* Above a pH$\approx$10 calcium sulpho-aluminate hydrates precipitate from solution in ordinary Portland cement systems (Mehta, 1983). Below this level only gypsum and aluminium sulphate are stable phases. Calcium sulpho-aluminate (ettringite ($C_3A3C\underline{S}H_{32}$)) appears at a pH$\approx$10.5-10.7 and on further increase in pH monosulphate ($C_3AC\underline{S}H_{12}$) appears, at pH$\approx$11.6. Mehta (1983) observed that ettringite formed in the presence of lime (high pH) consists of small, needle-like crystals and that ettringite formed in the absence of lime (lower pH) consisted of much larger lath-like crystals (six times as big), though the latter is almost colloidal in texture and is not formed of prismatic crystals. The exact pH value at which ettringite decomposes is unclear, though it is generally thought to be around 10.5 pH. According to Santhanam et al. (2001) ettringite is not stable at a pH as high as 11.5 and could decompose to form gypsum. However Gaze and Crammond (2000) suggest that ettringite found in crushed mortar tablets, which had been soaked in potassium sulphate solutions and exposed to the atmosphere for 53 days, had decomposed at a pH of 10.5.

- *Influence of Sulphate Ion Concentration:* Almost all ettringite is eventually transformed to monosulphate at low sulphate concentrations (Neville, 1995). When sulphate is low in a system, for example in the hydration of Portland cement, little or no ettringite is present after 24 hours (Mehta, 1983). 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 (<0.5%) (Kuzel, 1996). In a moist, CO_2 containing environment, ettringite carbonates to give calcite and alumina gel (Eq.3.11).

$$3CaO.Al_2O_3.3CaSO_4.32H_2O + 3CO_2 \rightarrow$$

$$3CaCO_3 + 3(CaSO_4.2H_2O) + Al_2O_3.xH_2O + (26-x)H_2O \qquad \textbf{Eq.3.11}$$

Nishikawa et al. (1992), working on synthesised ettringite, reported two different carbonation mechanisms under dry and wet conditions. Under dry conditions, gypsum, calcium carbonate and ettringite were identified using XRD techniques, though only needle-like alumina deficient crystals were observed. Under wet conditions however, decomposition of ettringite to gypsum, calcium carbonate and alumina gels were evidently observed by XRD and SEM techniques. The differences in the carbonation mechanisms can be attributed to the excess or lack of water in or around ettringite. Carbonation of ettringite has also been observed in lime treated clay soils. Waswa et al. (1993), working on murram soil with additions of 5, 10 or 15wt.% lime, attributed cracking and reduced strength of the stabilised material to a loss of integrity due to surface carbonation and decomposition of ettringite, resulting in enhanced swelling and softening of the outer layer of samples. More recently Gaze and Crammond (2000) reported that ettringite, formed in mortar tablets which were crushed, totally immersed in 200mls of dilute sulphate solution (0.42%SO_4) and exposed to the atmosphere, was found to decompose at pH levels of around 10.5. However, ettringite was found to be abundant in similar samples that were not exposed to the atmosphere, as the pH remained relatively high (at around 13). It was concluded that the exposed samples (which exhibited a pH of between 7.7 and 6.5 after 63 days) were dominated by the effects of carbonation or "alkali carbonation" due to the generation of alkalise in the lime/sulphate reaction. As alkali metal hydroxides readily absorb CO_2, the presence of a carbonate (in this case K_2CO_3) also allowed the carbonation of lime and the removal of calcium sulphate and regeneration of the original alkali sulphate (Eq.3.12). (Interestingly it is known that K_2CO_3 solutions remove gypsum crystals from limestone statues damaged by acid rain (Gaze and Crammond, 2000)).

$K_2CO_3 + CaSO_4 = CaCO_3 + K_2SO_4$ **Eq.3.12**

Furthermore Gaze and Crammond suggest that sulphate attack by alkali metal sulphates in the field may well be accompanied by an accelerated rate of carbonation. Normally carbonation (via the dissolution of CO_2 in water) is inhibited by very dry or very wet conditions where the pores become filled with water. However, in the case of alkali carbonation, since (a) alkali metal hydroxides are hygroscopic and (b) their solutions have a strong affinity for CO_2 it seems unlikely that inhibition would apply to the same extent. Additionally, if ettringite forms and is then partially removed, it may appear that a great deal of damage has been caused by only a small amount of ettringite. Complete carbonation combined with wash-out of the regenerated alkali sulphate could lead to what might be termed "fossilised sulphate attack", where only the physical effects are preserved.

- *Influence of Temperature:* Ettringite remains stable until 50°C when its solubility increases and at 100°C it becomes unstable and disappears (Glasser, 1996). Mitchell (1986) reported that at temperatures below 15°C ettringite can (under the right circumstances) undergo carbonation to form thaumasite. However more recent work using photo-micrographs concludes that in hardened cement pastes thaumasite formation is the result of the attack and transformation, under moist conditions and low temperatures, of C-S-H gel. (Crammond and Halliwell, 1995).

3.10.2 Ettringite and Swelling

Expansive behaviour due to ettringite formation has been reported in numerous cementitious systems. Examples of these include expansive cements, lime-pfa (fly ash) systems, Portland cement-stabilised colliery shale (Thomas et al. 1981) and delayed ettringite formation in steam cured concrete (Brown, 1965). There are also numerous examples of expansion due to ettringite formation in lime-stabilised soils. Mitchell (1986) drew attention to this phenomenon in a study of the failure of lime-stabilised pavement bases in Las Vegas, (USA). Distress to the pavement occurred two and a half years after completion. He also noted that in the failed areas the material had a much lower density and a much higher moisture content than in the unfailed areas. Significant amounts of ettringite and thaumasite were observed in both failed and unfailed zones. (Interestingly samples of the unfailed material were found to swell when placed in water.) Failure was attributed to the expansive nature of ettringite. Later, Hunter (1988) reported on the heave of a lime-treated soil sub-base, also in Las Vegas (USA) and came to conclusions similar to those of Mitchell. The areas of major damage were found adjacent to a source of water and it was concluded that the availability of pore-water is the single most important factor controlling sulphate-induced heave.

Expansion mechanisms resulting from ettringite formation have been explained by two theories: *Crystal Growth* theory and the *Swelling* theory. Mitchell (1986) believed expansion in lime-stabilised clay in the presence of sulphates to be partly caused by the growth of ettringite crystals formed on the clay particle surfaces. Others have suggested that it may be concentration gradients and osmosis that induce water intake. In this model osmotic pressure arises from concentration differences of dissolved ions between the solid particles and the surrounding liquid phase, separated by a colloidal gel from which ettringite crystallises (Krahn and Fredlund, 1972). Mehta (1983) found that ettringite formed in the presence of lime was gel-like, with a large surface area and unsatisfied negative charge. He concluded from observations of swelling in a Portland cement system 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. Similarly, Wild et al. (1993), testing kaolinite with various lime and gypsum contents, agreed that osmotic swelling will take place within the colloidal layer in regions of high sulphate concentration in close proximity to the developing ettringite rods at the clay particle surfaces. However, it may not be appropriate to classify this product as ettringite because by definition ettringite is a crystalline mineral of fixed composition. Wild and co-workers go on to say that if moist curing of the lime-stabilised material is carried out where there is no continuous supply of water, then crystalline ettringite continues to develop along with the fibrous C-A-S-H gel until reaction is complete. At this stage the material becomes dimensionally stable and contact with water no longer produces large increases in volume.

3.11 Thaumasite Formation

Thaumasite is a heavily hydrated triple compound of calcium silicate, calcium sulphate and calcium carbonate in the ratio 1:1:1 (Varma and Bensted, 1973) that occurs: i) naturally as a rare mineral in metamorphosed rocks that have undergone hydrothermal changes with time (Bensted, 1999); ii) as a weathering product (Wilson, 1978); iii) as a consequence of sulphate attack on concrete (Crammond and Nixon, 1993; Collepardi, 1999; Gaze and Crammond, 2000), and iv) as a consequence of sulphate attack of soil cements (Gouda et al. 1975). The thaumasite form of sulphate attack (TSA) differs from conventional sulphate attack because it is calcium silicate hydrate (C-S-H) (the main binding agent in all Portland cements), which is targeted for reaction as opposed to the calcium aluminate hydrates (C-A-H) attacked in ettringite formation. The formation of thaumasite is therefore accompanied by a reduction in the binding ability of affected cement in hardened concrete, resulting in a loss of strength and transformation into a mushy, un-cohesive mass (Thaumasite Expert Group, 1999). The expansive disruption, which is normally associated with sulphate attack, sometimes accompanies the formation of thaumasite, but is not a characteristic feature. However, Gaze (1997) states that although thaumasite formation implies some C-S-H breakdown, usually occurring at around 10.5 pH, it is possible that calcium sulphate can attack the C-S-H implying that thaumasite may form at high pH where free lime is present. The formation of thaumasite requires the following conditions:

- A source of calcium silicate (usually derived from cementitious calcium silicate phases present in Portland cements, but can be obtained from some clays);
- A source of sulphate ions (derived from a variety of sources including surrounding soils and ground water, sulphate bearing clays, gypsum plaster; historical mortars containing gypsum and aggregates contaminated with sulphates/sulphides);
- A source of carbonate (derived either from carbonate sources within the building component itself or less commonly, from CO_2 dissolved in surrounding groundwater);
- Very wet, cold (<15°C) environment (Thaumasite Expert Group, 1999)

In other words, thaumasite is formed by a general reaction involving calcium ions, silicate, sulphate, carbonate and sufficient water to permit both transport of the potentially reactive species and interaction of these species under the low temperature conditions prevailing to form thaumasite. Its chemical formula is $CaSiO_3.CaCO_3.CaSO_4.15H_2O$ and has been successfully synthesised in the laboratory using the ingredients calcium sulphate, calcium carbonate and both hydrated and un-hydrated calcium silicates with excess quantities of water (Bensted and Varma, 1974).

3.12 Effects of Thaumasite Formation

Sulphate attack on cement-based construction materials has been recognised in the UK for some time. Since 1990 however, a few cases of TSA have been discovered in good quality buried concrete. In the light of this discovery an expert group on thaumasite was set up by the British Government with the remit to produce interim advice and guidance on the implications for existing buildings and structures and for the design and specification of new construction in the UK. The report outlines several cases of TSA and delivers guidance and recommendations for new works. Although much of this is beyond the scope of this work, it is important to outline particular case studies and explain how TSA occurred.

Macneil (1998) and Thaumasite Expert Group (1999) reported that bridges on the M5 motorway in Gloucester, UK had decayed due to TSA in a way similar to corroding steel. It was discovered that sulphide bearing unweathered Lias clay was used as backfill around the concrete sub-structures. Disturbance and aeration of this clay resulted in oxidation of pyrite leading to a substantial increase in the sulphate content.

Sulphuric acid, the initial oxidation product, reacted with calcium carbonate in the Lias clay to form gypsum. These factors coupled with a cold environment resulted in the formation of thaumasite.

Collepardi (1999) found that some historic buildings may contain gypsum or other sulphate salts. If they need to be repaired, C-S-H and C-A-H formed by the hydration of hydraulic binders used for restoration can react with water and gypsum and produce thaumasite and/or ettringite. Due to the formation of these products, degradation of the repaired structures can occur causing expansion cracking, spalling and strength loss. Gouda et al. (1975) reported that thaumasite and ettringite or possibly a solid solution between the two, had affected and deteriorated a seven-year-old soil-cement with an SO_3 content of between 3.3 and 4.9%. The material had also been in contact with ground water containing about 2000ppm SO_3, was in a "cold" environment and was contaminated with calcium carbonate. Lime stabilised clay soil pavements are also susceptible to TSA. Within a period of two years following lime stabilisation, adverse chemical reactions between lime and salts in the native soils caused heave at Stewart Avenue and Owens Street in Las Vegas, USA (Hunter, 1988). It was thought that TSA followed ettringite formation at temperatures <15°C in the presence of silicic and carbonic acid (Eq.3.13).

$$Ca_6(Al(OH)_6)_2.(SO_4)_3.26H_2O + 2H_2SiO_4^{2-} + 2CO_3^{2-} + O_2 \rightarrow$$
$$Ca_6(Si(OH)_6)_2.(SO_4)_2.(CO_3)_2.24H_2O + 2Al(OH)_4^- + SO_4^{2-} + 4OH^- + 2H_2O \quad \textbf{Eq.3.13}$$

Hunter also noted the formation of secondary gypsum (Eq.3.14).

$Ca^{2+} + SO_4^{2-} + 2H_2O \rightarrow CaSO_4.2H_2O$ **Eq.3.14**

TSA transforms C-S-H gel into a white, pulpy mass and although associated with heave, is not thought to be directly responsible for it. Hunter describes the mechanism of heave as a complex function of available water, the percentage of soil clay and ion mobility. The release of sulphate and aluminate involved in Eq.3.13 would allow the formation of a swelling colloidal gel at advanced stages of curing. It is also possible that the formation of secondary gypsum assisted the heave of the stabilised material.

4 Other Methods of Soil Stabilisation

This chapter deals with methods of soil stabilisation where a stabilising agent is added to a clay soil in addition to lime, which is usually employed as a soil modifier and/or activator prior to stabilisation. That is, the addition of a second material in order to achieve long-term strength, durability and dimensional stability. The two materials considered in the current work are Portland cement (PC) and ground granulated blastfurnace slag (GGBS).

4.1 Portland Cement Stabilisation

4.1.1 Introduction

Cement is an essential component of the construction industry. It binds together various raw materials, producing strong and durable products such as mortar and concrete. Cement has also been used effectively in the strengthening of granular materials such as soils (Herzog and Mitchell, 1963; Croft, 1967; Sherwood, 1992 among others). The most common cement is Portland cement (PC) - a name given to it due to the similarities in appearance of its hardened state with that of Portland stone (a limestone building material found in Portland, Dorset, UK). Portland cement is defined in BS12: 1978 as "a product mostly of calcium silicate obtained by heating to partial fusion a pre-determined and homogenous mixture of materials containing lime and silica, with small proportions of alumina and iron oxide."

In cement chemistry it is usual to abbreviate chemical formulae to a shorthand notation. In this notation a single letter is used to represent the oxide of a metal or non-metal enabling the quick notation of complex compounds or compounds that have no mineral name. The abbreviations used can be found in Table 4.1. There are four compounds that are usually regarded as the major constituents of cement: tricalcium silicate (alite), dicalcium silicate (belite), tricalcium aluminate and tetracalcium aluminoferrite. These are listed together with their abbreviated symbols in Table 4.2. Cement is principally formed from four components; lime (C), silica (S), alumina (A), and iron oxide (F). The raw materials selected for cement manufacture reflect these requirements and are normally limestone or chalk (C), shale or clay (S and A) and hematite (F).

Before discussing the role of PC in soil stabilisation, it is important to understand the hydration of standard Portland cement.

Table 4.1 Oxide and abbreviated notations used in cement chemistry.

Oxide	**Abbreviated Notation**
CaO	C
SiO_2	S
Al_2O_3	A
Fe_2O_3	F
SO_3	$\underline{S}$
H_2O	H

Table 4.2 Main compounds of Portland cement.

Compound Name	**Oxide Composition**	**Abbreviation**
Tricalcium silicate *(alite)*	$3CaO.SiO_2$	C_3S
Dicalcium silicate *(belite)*	$2CaO.SiO_2$	C_2S
Tricalcium aluminate	$3CaO.Al_2O_3$	C_3A
Tetracalcium aluminoferrite	$4CaO.Al_2O_3.Fe_2O_3$	C_4AF

4.2 Hydration of Portland Cement

The hydration of standard PC is a chemical reaction between the phases present in the cement powder and water. As stated earlier, cement is composed of four phases, alite (C_3S), belite (C_2S), tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF). During production around 4-7% gypsum ($C\underline{S}H_2$) is added (the reason for which will be explained later). As water is introduced to the cement it reacts with the aforementioned phases. Hydration then commences resulting in the formation of a number of hydration products. It is these hydration products that contribute to the properties of the hardened cementitious material. As the alite and belite phases come into contact with water a calcium silicate gel (C-S-H), the primary binding component of the hardened PC paste, is formed (the reactions are shown in equation 4.1 and 4.2).

$$2C_3S + 6H_2O \rightarrow C_3S_2H_3 + 3CH \qquad \textbf{Eq.4.1}$$

$$2C_2S + 4H_2O \rightarrow C_3S_2H_3 + CH \qquad \textbf{Eq.4.2}$$

Alite reacts faster with water than belite and produces over twice as much portlandite (calcium hydroxide or hydrated lime – CH) than belite. Portlandite or lime is a by-product of the hydration process that is partially soluble, but has little or no cementitious value. As C_3A comes into contact with water immediate stiffening of the cement paste (known as "flash set") occurs. To overcome this the added gypsum reacts with C_3A in the presence of water to form the calcium sulphoaluminate ettringite ($C_6A\underline{S}_3H_{32}$). This is then followed by further reactions between the C_3A and the hydration products already formed to produce monosulphoaluminate ($C_4A\underline{S}H_{12}$) and a calcium aluminate hydrate (C-A-H) phase. These reactions are shown in equations 4.3 to 4.5.

$$C_3A + 3C\underline{S}H_2 + 26H_2O \rightarrow C_6A\underline{S}_3H_{32} \qquad \textbf{Eq.4.3}$$

$$2C_3A + C_6A\underline{S}_3H_{32} + 4H_2O \rightarrow 3C_4A\underline{S}H_{12} \qquad \textbf{Eq.4.4}$$

$$C_3A + CH + 12H_2O \rightarrow C_4AH_{13} \qquad \textbf{Eq.5.5}$$

It is the calcium sulphoaluminates that are the first hydration products to form and it is these that contribute to the early strength of cement. The C-A-H forms later in the hydration process, as it requires the presence of CH (derived from the alite and belite hydration).

The C_4AF phase follows a similar hydration process to that of C_3A producing the iron equivalent of ettringite ($C_6F\underline{S}_3H_{32}$), monosulphoferrite ($C_4F\underline{S}H_{12}$) and calcium ferrite hydrate (C-F-H).

Ettringite dominates the hydration products in the early stages due to the abundance of sulphate ions from gypsum. As the sulphate ion concentration decreases with progressive hydration, ettringite becomes unstable and converts to monosulphoaluminate. The formation of ettringite (Eq.4.3) involves a volume change with ettringite occupying a slightly smaller volume than the sum of its constituent parts. The volume-change from Eq. 4.3 results in a decrease of 8.59%. However, if the water consumed in this reaction is drawn from outside its volume would not be included with other reactants. Therefore, the change in volume on reaction would give an increase of 128.2% (see Appendix A). This increase is accommodated without disruption when the cement is still in a plastic state but not after it has set and hardened. Ettringite formation reduces the sulphate concentration in the pore solution to such a level that monosulphate then becomes the more stable sulpho-aluminate phase (Eq.4.4). However, if the concentration of sulphate ions in the pore solution should subsequently increase gypsum forms, causing the monosulphoaluminate to become unstable therefore converting it back to ettringite (Eq.4.6).

$$CH + \underline{S} + H \rightarrow C\underline{S}H_2 \qquad \textbf{Eq.4.6}$$

$$C_4A\underline{S}H_{12} + 2C\underline{S}H_2 + 26H_2O \rightarrow C_6A\underline{S}_3H_{32} \qquad \textbf{Eq.4.7}$$

If the reaction in Eq.4.7 occurs in hardened cement then the formation of ettringite will lead to expansion and an increase in internal stress within the cementitious product and if unchecked will, in a similar way to lime stabilised soils (Chapter 3), cause damage.

4.3 Soil Stabilisation with Portland Cement

Portland cement is a primary stabilising agent, which can be used alone to bring about a stabilising action (Sherwood, 1993). As mentioned earlier C-S-H gel and C-A-H phases form during hydration, which in time produce a strong, hard matrix in which a granular material, like clay soil is embedded. As the hydration reaction proceeds from the surface of the cement grains the reaction is slow and the centre of the cement grains will normally remain unhydrated. There is a further reaction that takes place in most cement-stabilised soils. When lime ($Ca(OH)_2$) is liberated from hydrating Portland cement it can combine with clay minerals in the soil. Over time this reaction may form C-S-H, C-A-H and C-A-S-H strength-promoting phases in a similar way to lime-stabilisation. Herzog and Mitchell (1963) substantiated this theory by testing cement stabilised kaolinitic and montmorillonitic clays. Using X-ray diffraction techniques, they found that the clay-cement specimens contained only a fraction of the free lime that would be present if normal hydration of the cement took place without interaction between the cement and the clay. It was concluded that the missing calcium hydroxide had participated in pozzolanic reactions with the clay minerals. More work by Herzog (1963) described cement stabilisation as the development of a strong, semi-continuous skeleton consisting of a hardened cement core and clay particles bonded by primary and secondary cementitious material. He divided the cement-clay reaction into two parts:

The primary reaction: where Portland cement hydrates and immediately produces cementitious gels subsequently producing a modification of the clay structure to a skeletal matrix-type system. The secondary reaction: where the lime originating from the cement reacts with the clay minerals to form strength giving phases over time.

Unlike lime, cement can therefore, in principle, be used to stabilise any type of soil. However, in practice the difficulty of mixing cement with heavy clays means that lime is usually preferred as the stabiliser for such soils. Whether or not a bond forms between the hardened cement matrix and the particles of the stabilised material depends on the chemical composition of the material. Soil mineralogy, sulphide and sulphate content and type and amount of organic material are all factors that affect stabilisation of clay soils by Portland cement.

4.3.1 Soil Mineralogy

Croft (1967) studied the mechanisms of soil-cement stabilisation and the influence of the common clay minerals on this process. He found that the weakly active clay minerals, such as kaolinite and illite had little effect on hydration and hardening of cement. He postulated that with ageing the increases noticed in unconfined compressive strength were attributed to the desiccation of gelatinous hydration products, the crystallisation of new minerals and to the reactions between lime and the clay minerals to produce secondary cementitious products, with the behaviour of illite similar to kaolinite. Montmorillonite is little affected by small additions of PC. The pH of the montmorillonite-cement aqueous phase dropped from 12.2 to around 10 in less than one week in mixes containing up to 10% cement. In the absence of a strongly alkaline environment hardening of montmorillonite-cement mixtures was inhibited and the strength development retarded. Similarly, Akpokodje (1985) stabilised a series of clays and soils from arid areas with cement and concluded that the high smectite (montmorillonite) and gypsum contents of soils resulted in a large strength reduction on soaking. He also found that the abundance of illite and carbonate in other soils tended to show less strength loss on soaking.

4.3.2 Sulphide and Sulphate Content

The presence of sulphates may have a detrimental effect on cement stabilised clay soils. In the presence of water, sulphates may cause problems by reacting with hydrated cement to form products that occupy a greater volume than the combined volume of reactants (Sherwood, 1992). Calcium hydroxide, a product of cement hydration, may react with sulphates and alumina (released from the clay) to form ettringite. Also it is possible that hydrated calcium aluminates (C-A-H phase) may react with calcium sulphate, again to form ettringite (Eq. 4.7) (Sherwood, 1992).

$$4CaO.Al_2O_3.19H_2O+3(CaSO_4.2H_2O)+7H_2O \rightarrow 3CaO.Al_2O_3.3CaSO_4.32H_2O \quad \textbf{Eq.4.7}$$

Akpokodje (1985), found that the high content of gypsum and bassanite in soils tested from arid zones render them unamenable to cement stabilisation due to high swelling and shrinkage. However it is not solely the presence of sulphates in the soil that can affect the quality of the stabilised material. Equally important is the presence of groundwater containing soluble sulphates.

Laboratory work by Barker and Hobbs (1999) proved that Portland limestone cement is susceptible to the thaumasite form of sulphate attack (TSA) from sulphate solutions. Similarly, Crammond and Nixon (1993) commented on the deterioration of concrete foundation piles from TSA due in part to the sulphate bearing groundwater. Gouda et al. (1975) reported that a seven-year-old soil-cement pavement had been attacked by TSA. It was found that the material had been in contact with ground water containing about 2000ppm SO_3. The presence of sulphides in the cement-bound material may also prove problematic as it is known that sulphide oxidation can lead to increased sulphate levels, which in turn increases the potential for the formation of deleterious phases such as ettringite and/or thaumasite (Thomas et al. 1981; Sherwood, 1992 and1993; Thaumasite Expert Group, 1999; Hobbs and Taylor, 2000).

4.3.3 Organic Material

The effect of organic matter is known to be closely associated with its ability to combine with calcium ions liberated by the hydrating cement. Maclean and Sherwood (1961) reported that the depth of soil containing “active” organic matter (or organic matter that may interfere with the hardening of cement stabilised soil) ranges from 0 to 5 feet (0m to 1.52m) in the UK depending on which major soil group the soil profile belongs. Sherwood (1992, 1993) briefly mentions the potential effects of organic material on soils and agrees with Maclean and Sherwood (1961) that the effect of organic matter is mainly of significance in the case of the stabilisation of the surface layers of natural soils. As with lime, certain organic compounds may retard or even inhibit the hardening of stabilised soils making them impossible to stabilise with cement (Sherwood, 1993). Similarly as with lime stabilisation it is the type of organic compound rather than the total amount that is important. The organic compounds able to interfere with the hydration of cement do so by virtue of their ability to react with calcium ions at the high pH values existing in cement-stabilised soils. Also water containing organic material can induce acid attack on concrete. Peaty water with CO_2 is known to be particularly aggressive as it can have a pH value as low as 4.4 (Neville, 1995). The ingress of water with such a low pH can lead to the decomposition of the products of hydration and formation of new compounds which, if soluble, may be leached out and, if not soluble may be disruptive in situ. The most vulnerable cement hydrate is $Ca(OH)_2$, but C-S-H, the main cementing product, can also be attacked. Cowie and Glasser (1991) also commented on the reaction between cement and natural waters containing dissolved CO_2. Their results showed the formation of passivating layers of $CaCO_3$ formed due to $Ca(OH)_2$ carbonation, and residual SiO_2 (gel) at the cement-water interface. The formation of these products results in strength loss in cements and if residual SiO_2 gel is present that means that the C-S-H has carbonated.

4.4 Soil Stabilisation with Lime and Portland Cement

It is known that cement can be used to stabilise most soils. The principal exceptions are those soils containing expandable clay minerals, clays with an appreciable level of sulphate or sulphide minerals, and soils containing organic matter in a form that retards the hydration of cement. In comparison with cement, the potential use for lime in soil stabilisation is more restricted. When used in equivalent amounts it generally produces lower strengths than does cement (Sherwood, 1993). The main application of lime is the modification of the engineering properties of the potentially stabilised material, and for use with clay soils that are difficult to stabilise with cement alone. Therefore it is attractive to use a two-stage lime/cement stabilisation process whereby lime is added initially to modify the soil properties followed by the addition of cement to bring about a long-term increase in strength. Even where cement alone is effective the use of both lime and PC may prove advantageous. Tresoriere et al. (from Sherwood, 1993) found that a heavy clay soil of high pozzolanic activity, attained higher strengths when stabilised with lime and cement than it did with equivalent amounts of lime or cement used alone. Economic reasons dictate however, that this two-fold modification and cementation stabilisation process will be restricted to soils that are difficult to mix with cement only, due to their high plasticity.

Two-stage stabilisation is becoming increasingly common in the UK as contractors realise the economic benefits of improving in situ material rather than removal and replacement with costly imported materials. For example, in 1999 Tarmac Special Projects Ltd. stabilised a soft, sandy clay with 2% cement and 2.5% lime at the site of the New Acute and General Hospital, Dartford, UK (DoETR, Digest 058, 1999). Laboratory testing established that stabilisation had resulted in improved California bearing ratio (CBR) values in excess of 30%. However, lime (1.5%CaO) and cement (8.5% PC) stabilisation of a stretch of boulder clay at the A421 Tingewick bypass, UK, resulted in the heave of the stabilised material due to the oxidation of sulphides present in the material to sulphates causing sulphate attack (Higgins and Kennedy 1999). A further stretch of the same road stabilised using lime and ground granulated blastfurnace slag (GGBS) showed no signs of significant heave.

4.5 Lime-Activated Ground Granulated Blastfurnace Slag (GGBS) Clay Soil Stabilisation.

4.5.1 Introduction

Although itself not cementitious, GGBS (a by-product of pig-iron manufacture) possesses latent hydraulic properties which can be developed by the addition of an activator such as lime or another alkaline material. GGBS has been used with cement pastes and concrete as a partial replacement for PC (called "slag cement" where the slag is activated by lime during C_2S and C_3S hydration) and in super sulphated cements (SSC), which contains around 70-85% GGBS together with a small amount of clinker and around 10-15% sulphate (usually gypsum or anhydrite). Slag has also been used in alkali-activated slag cement (AASC), which is a mixture of GGBS and alkaline additive. Much laboratory work has been carried out on lime-activated GGBS stabilised-clay soils (Wild et al, 1996 and 1998; Kinuthia, 1997; Higgins, 1998; Higgins and Kennedy, 1999; Tasong et al, 1999; Wild and Tasong, 1999). As GGBS hydration is a complex process, it is important to discuss the hydration process and cementing properties of GGBS.

4.6 GGBS Hydration

There are several factors influencing slag hydration, including the chemical composition of the GGBS, the alkali concentration of the reacting system, the glass content of the GGBS; the fineness of the GGBS and the temperature during the early phases of the hydration process. In the presence of water only, slag produces a low permeability coating low in calcium on the grain surface. The Si-O, Al-O, Ca-O and Mg-O bonds on the surface of slag break under the polarisation effect of OH^- ions from water. As the Ca-O and Mg-O bonds are weaker than Si-O and Al-O bonds, more Ca and Mg enter into solution than Si and Al, and a Si-Al rich layer forms quickly on the surface of the slag grains. This "pseudomorphic" layer may absorb some H^+ ions from the water, resulting in an increased pH of the solution. However, this increase in alkalinity still cannot break enough Si-O and Al-O bonds for the formation of the C-S-H, C-A-H or C-A-S-H cementing phases. Therefore in order to produce cementing products from GGBS the pH of the pore solution must increase further in order to penetrate the pseudomorphic layer and activate the GGBS. Examples of activators are lime or calcium hydroxide ($Ca(OH)_2$), sodium sulphate (Na_2SO_4), potassium aluminium sulphate ($KAlSO_4.H_2O$), gypsum ($CaSO_4.2H_2O$), hemi-hydrate ($CaSO_4.0.5H_2O$), anhydrite ($CaSO_4$) and phosphogypsum. Many of these activators are used in conjunction with lime to bring about increased strength development in blended cements (Shi and Day, 1993). The principal GGBS activator in the current work will be lime.

4.6.1 GGBS Activation by Lime

GGBS has, in the past, been blended with Portland cements to produce a durable, sulphate resistant material, termed supersulphated cement (BFSC) (Neville, 1995). In these cements the hydration of GGBS is mainly activated by the hydration product $Ca(OH)_2$. Thus lime may be added either as an additive or released from PC hydration in order to activate GGBS and produce cementing hydration products. According to

Wu, et al (1990), Na_2SO_4, as opposed to lime, shows the best effects at an early stage whilst alum is the best at later stages. Daimon (1980) states that calcium sulphate, despite being used to accelerate the reaction of slag hydration, is not an activator but plays a special role as a powerful reactant. The accelerated hydration of GGBS 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.

The hydration of slag under the activation of alkali is generally described as a complex process of structural disruption of slag and polycondensation of hydrate products. It is thought that the chemical activation process of slag can be divided into 5 stages, namely: *Initial reaction; Induction; Acceleration of reaction; Deceleration of reaction* and *Final* (Zhou et al. 1993). As previously mentioned, slag activation is initiated in an alkaline environment in which the water-impermeable pseudomorphic layer is broken down, attacking the chain structure of SiO_4 and Al_2O_3 and subsequently leaving behind a negative charge. Neutrality is achieved by absorption from Ca^{2+} ions (from the solution or from the slag itself) which react with silica and alumina dissolved from the slag in the presence of an increased concentration of OH^- ions. Up to this point the degree of hydration of the slag is only around 2% (Uchikawa, 1986). At the end of the dormant period aluminate and silicate groups dissolved from the slag precipitate as low-solubility C-S-H, C-A-H and C-A-S-H or other hydrates. The acceleration period is characterised by slight exothermic hydration reactions, which are assumed to be most effective at a pH of around 12 (Wu et al. 1990). During the deceleration and the final hydration phase, the free water in the microstructure is consumed and hydration products precipitate in thick layers on the slag grains.

4.6.2 Hydration Products of Lime-GGBS Stabilised Soils

As stated earlier, in supersulphated cement the hydration of slag is activated by $Ca(OH)_2$ and minor amounts of alkalis released during the hydration of the cement clinker. By adding slag to PC, the formation of $Ca(OH)_2$ is reduced when the slag has a low calcium content and a higher proportion of the main insoluble cementitious phase C-S-H is formed due to the reaction of slag with the pore solution from the cement paste (Smolczyk, 1980). Meanwhile, since the water-cement ratio (W/C) increases as the slag content increases, the hydration of the clinker is also accelerated. According to the principle of close packing, for very fine slags finer particles of slag may pack within the interstices of the larger particles of cement and aggregates. This results in a densified microstructure in both the matrix of the cement paste as well as the interfacial zone between paste and aggregates (Wu et al. 1990).

The utilisation of GGBS in soil stabilisation is a relatively new phenomenon in the UK. The introduction of GGBS into the clay-lime hydration system modifies the clay lime reaction products (Wild et al. 1998) (see Chapter 3). An indication of the manner in which the products of clay-lime reactions may be modified by slag are obtained from previous findings on activated slag systems as previous work has been carried out in clay-lime-GGBS systems. The slag provides additional alumina, calcia, silica and magnesia to the system, depending on the type and amount of slag (Smolczyk, 1980). Since the principal reactants introduced by slag are also present in the clay-lime system as well as in PC-GGBS blends, the strength of hydrated clay-lime GGBS mixtures is likely to be governed by the same factors observed in hydrated PC-GGBS blends. These factors include the properties of the C-S-H gel, such as its amount, porosity and permeability, the fineness and composition of all reactants involved, the efficiency of mixing, the temperature and the curing time. Also as slag introduces extra and more freely available alumina and silica compared to the clay-lime system alone (due to its high reactivity in the presence of lime), the formation of the strength–contributing silicates and aluminates is enhanced. The lime in the clay-lime mix will provide the required alkaline environment for slag activation and hydration, whilst also modifying the clay (Wild et al. 1998).

4.7 The Presence of Sulphates

As mentioned in Chapter 3, expansive reactions can occur in lime-stabilised soil in the presence of sulphates. Mehta (1973) observed that the presence of sulphate ions in either PC, GGBS or PC-GGBS blends results in the formation of a potentially expansive system mainly through the formation and subsequent growth of ettringite. Kinuthia et al. (1999) and Wild and Tasong (1999) observed that the addition of GGBS to a lime-stabilised kaolinite soil dramatically improved the resistance to sulphate attack and swelling. In particular, percentages of replacement of lime with GGBS, with just enough lime to activate the slag, were the most effective in preventing sulphate attack (i.e. a lime to GGBS ratio of 1:5). They hypothesised that due to its high alumina and silica content, the hydration of GGBS produces C-A-S-H gel and hydrotalcite-type phases containing Mg. In contrast to the pozzolanic reaction of lime with clay, which is very slow, the lime-activated slag hydration is much more rapid and (depending on slag composition) is known to consume lime. Hence there will be competing reactions (i.e. slag hydration activated by lime to give C-A-S-H gel and hydrotalcite, and the much slower pozzolanic kaolinite-lime aqueous reaction to give a colloidal C-A-S-H product) and also competing nucleation sites on the kaolinite particle surfaces and on the slag particle surfaces. Therefore an explanation of the reduction in expansion of soils in the presence of lime, GGBS and sulphates, is that most of the lime is consumed during a period of curing (in Wild and Tasong's (1999) work, 28 days). In addition, the slag hydration reaction is known to reduce porosity resulting in increased long-term hardening. The blocking of pores leads to higher strength and lower permeability. Veith (2000), when testing a highly kaolinitic clay mixed with 2%$Ca(OH)_2$ and 6%$CaSO_42H_2O$ and various additions of GGBS, found similar results. It was found that increasing GGBS additions resulted in substantial shear strength increases and a reduction in linear expansion on soaking. It was also found that if the addition of gypsum was increased, the compressive strength and also indirect tensile strength underwent significant improvement with increases in the addition of GGBS, whereas specimens to which no gypsum had been added showed an overall inferior strength development after curing periods of up to 24 weeks. However after 1 year's curing at high temperatures (30°C) specimens without gypsum exhibited superior strengths.

4.8 Advantages of Lime-GGBS Soil Stabilisation

The addition of lime to clay soils raises the pH of the system allowing silica and alumina from clay minerals to react with calcium ions forming, over time, C-S-H, C-A-H and C-A-S-H phases. However, the abundance of calcium ions coupled with sulphates that occur naturally in some soils will lead to ettringite formation, which although contributing to strength development, is known to be destructive in the presence of excess moisture. The addition of Portland cement (PC) to soil-lime systems greatly enhances the strength of the material by forming much the same strength-giving phases as soil and lime alone, but at a much faster rate. Again, sulphate attack (ettringite or TSA) is well documented in this system, the sulphates arising as soil minerals or in ground water. If GGBS is added to the soil-lime mix in place of PC it will also hydrate and give similar cementing phases to the soil-lime or soil-lime-PC mixes. The rate of hydration is much faster than the pozzolanic lime-clay mineral reaction, but slower than the hydration of PC. Slag is associated with the provision of additional freely available alumina and silica to the system in the presence of lime, the latter increasing pH within the pore solution of the system and thus the solubility of these components, driving the slag hydration reaction forward. The principal difference between the three systems discussed (i.e. lime-stabilisation, lime-PC-stabilisation and lime-GGBS-stabilisation) is that the presence of sulphates (notably gypsum) actually *enhances* the intensity of the hydration reaction in the lime-activated GGBS system. Veith (2000) has shown that in the absence of gypsum, lime-activated GGBS stabilised kaolinite shows markedly reduced strengths relative to those achieved in the presence of gypsum (other than at very extended curing times in excess of 24 weeks). Also, as GGBS hydration is known, in the case of most slags, to consume more lime than it produces, the potential threat of sulphate attack from ettringite and TSA is greatly reduced because of the reduced availability of calcium. The hydration products of GGBS produce a denser microstructure than that of PC, which imparts higher strength. This change in pore structure also affects the development of shear strength parameters as pore blocking gels affect the cohesion of the material due to a reduction in pore space resulting in an increase in the attraction between adjacent particles (Veith, 2000).

4.9 Examples of Lime-Activated GGBS Soil Stabilisation

In South Africa GGBS activated by lime to stabilise soils has a long history, and recently (late 1990's) this combination has also become popular in Australia where the slower initial set and increased time for finishing compared with using PC is preferred by many of the stabilisation contractors (Higgins, 1998). In the UK, work by Kinuthia (1997), Wild et al. (1996, 1998, 1999), Tasong et al. (1999) and Veith et al. (1999, 2000) has proven through laboratory work that lime–activated GGBS is an effective stabiliser of clay soils. A full-scale trial of this method was undertaken by John Mowlem and Co. plc on a temporary diversion at the site of the A421 Tingewick Bypass, Bucks, UK (Higgins, 1998; Higgins and Kennedy, 1999). Two methods were used; lime (quicklime (CaO)) and PC, or quicklime and GGBS in chainages of 50m. The stabilised layers (350 mm in depth) comprised both base and sub-base to the road. The bitumen wearing-surface (130 mm) was placed directly over the compacted stabilised layer. The stabilised material (a boulder-clay) was found to contain around 0.1 % SO_3 and sulphides prior to stabilisation. Due to delays with the main contract, the diversion carried the full flow of the A421 traffic for just over a year, rather than the 6 months originally intended, providing an extended performance test.

After the trial, it was concluded:

- 2-shot stabilisation (lime followed by GGBS) of a plastic clay can readily be carried out using standard plant and techniques.
- A 350mm sub-base of boulder clay stabilised with lime and GGBS and overlaid with 130mm of bituminous surfacing showed no significant visible evidence of distress after carrying A-road traffic for a year.

- Falling weight deflectometer measurements on the stabilised pavement confirmed its good condition at the end of this period.
- Chemical analysis indicated that a large proportion of the sulphide present in the clay had oxidised to sulphate after a year.
- Despite the presence of 1% sulphate in the sub-base at the end of the trial, the lime and GGBS sections exhibited no visible evidence of significant heave (Higgins and Kennedy, 1999). There were however indications of heave at the end of the lime and cement section.

At chainage 210 there were signs of deformation due to improper mixing between the 6.5% GGBS and 8.5% GGBS sections where a strip of poorly mixed material appeared to be behaving in a plastic fashion and moving under load. Analysis indicated that GGBS was lacking in this deformed strip and it appears that in trying to avoid overlap of the 6.5% and 8.5%GGBS section, the contractor had left a strip unstabilised with GGBS. This omission was a consequence of the unique requirements of the trial and should not occur in practice under normal conditions (Higgins and Kennedy, 1999).

5. Materials

This chapter describes the materials used in the current work and includes the mineralogical and chemical breakdown of the subject material (Lower Oxford Clay), and also contains detailed analytical data on all four added materials (i.e. quicklime, hydrated lime, GGBS and PC).

5.1 Lower Oxford Clay

The Oxford Clay is a sedimentary lithology of marine origin deposited in Upper Jurassic times, the outcrop of which follows a diagonal course stretching from Scarborough in Yorkshire to Weymouth in Dorset with an overall dip of a few degrees to the South East (Freeman, 1956). The Oxford Clay is not homogenous throughout. Freeman (1956) describes Oxford Clay as consisting of a thick sequence of bituminous clays, shaley clays and calcareous clay with frequent concretionary limestone doggers concentrated in definite bands throughout the succession. The British Geological Survey (Chatwin, 1961) describes the formation as clay with periodic "limy" material which gives rise to bands of limestone of varying thickness, while some beds include a proportion of sand. Concretionary nodules of calcareous stone, pyrites and water-clear selenite are also of frequent occurrence. In colour the main mass of the clay is greenish or bluish-grey, becoming brown on weathering and in consistency it is tenacious, but shaly and laminated in places. The Oxford Clay Formation was traditionally subdivided into three parts; the Lower, Middle and Upper divisions, which are now formalised as the Peterborough, Stewartby and Weymouth Members respectively (Cox et al. 1992).

For simplicity the material used in the current work (from the Stewartby area) will be referred to only as Lower Oxford Clay (LOC). More recently the LOC has been described by Cox et al (1992) as a predominantly brownish-grey, fissile, organic rich (bituminous) mudstone; shelly with fauna dominated by crushed aragonitic ammonites and bivalves, the latter including *Nuculacean* and *Meleagrinella* shell-beds. Cripps et al. (1994) constructed a table (Table 5.1) for a wide range of geological deposits showing, at various locations, typical concentrations of the mineral pyrites (FeS_2), which is thought, when oxidised, to contribute to the formation of deleterious minerals, such as thaumasite and ettringite (Thomas et al. 1981; Thaumasite Expert Group, 1999).

Perrin (1971), using X-ray diffraction (XRD), differential thermal analysis (DTA) and exchange capacity measurements (Ex), found Lower Oxford Clay to contain 65% mica and 35% kaolinite with traces of chlorite, quartz and vermiculite. Later investigations established that Lower Oxford Clay consisted predominantly of chlorite, kaolinite, mica, feldspar (sanidine and anorthite), quartzite, calcite with minor quantities of gibbsite, goethite (a hydrated iron oxide) and anatase (titanium oxide) (Wild et al. 1996). There was no evidence of gypsum or pyrite in XRD traces probably because the quantity present was rather variable or too small to be detected.

Table 5.1 Typical concentrations of pyrites at various locations in the U.K. (Cripps, et al. 1994).

Formation	Geological Age	Location	% Pyrite
Bembridge Beds	Oligocene	Isle of Wight	?
Barton Clay		Fawley, Hants.	?
London Clay	Palaocene	London Basin	3.3
		Herne Bay	0 - 4
Gault Clay	Cretaceous	Bucks.	1.0
Speeton Clay		Yorks.	?
Fullers Earth		Redhill, Surrey	0.5
Weald Clay		Horsham, Sussex	?
Kimmeridge Clay	Jurassic	Kimmeridge Bay	4.0
Oxford Clay		Oxfords.	3 – 5
Oxford Clay		E & S England	5 – 15
Lower Oxford Clay		E & S England	0 – 17
Fullers Earth		Somerset	3.0
Whitby Shale		N.Yorks.	3 – 9
Upper Lias Clay		Northants.	3 – 5
Lower & Middle Lias Clay		Lincs. & Glos.	?
Stonesfield Clay		Hampden, Glos.	?
Marl Slate	Permian	County Durham	0 – 4
Coal Measures Shale	Carboniferous	England	0.7 – 1.4
Edale Shale		Derbyshire	?
Calciferous Sandstone		Midlowthian	1.1
Carboniferous Limestone		Derbyshire	5 – 10
Colliery Spoil (fine)		U.K	0 – 12
Colliery Spoil (coarse)		U.K	0 – 1
Tansley Shale		Derbyshire	0.1 – 4.9

? = Unknown

Recent mineralogical studies by Hanson Brick Ltd. found the Lower Oxford Clay used in their brick-making process to contain illite (23%), kaolinite (10%), chlorite (7%), calcite (10%), quartz (29%), gypsum (2%), pyrite (4%), feldspar (8%) and organics (7%) (Smith 1999). The clay contains high levels of SiO_2 and is rich in CaO, alkalis, ferromagnesian and Al minerals as would be expected from a shaly, calcareous soil. The high loss on ignition (15.79%) probably reflects the high $CaCO_3$ and organic content of this soil since most of those compounds will decompose or be lost, as volatile hydrocarbons and carbon dioxide (CO_2).

Table 5.2 compares the oxide content and mineralogy of a typical LOC (Wild et al. 1996) with the oxide content and mineralogy of LOC from the suppliers of the material (Hanson Brick Ltd.) used in the current work (Smith, 1999). The mineralogy of the LOC used in the current work was established at the University of Glamorgan using XRD traces. The traces and the mineralogy of the LOC are presented in Chapter 7.

Certain compounds in the clay have different solubilities at various temperatures. The solubilities of calcite and gypsum, in water, are given in Table 5.3.

Table 5.2. Chemical and mineral analyses of the Lower Oxford Clay

Oxide	Wild et al. (1996) (wt.%)	Hanson Brick Ltd. (Smith, 1999) (wt.%)
SiO_2	55.42	46.73
TiO_2	0.86	1.13
Al_2O_3	19.88	18.51
Fe_2O_3	6.21	6.21
FeO	0.68	0.80
Mn_2O	0.07	0.07
CaO	8.56	6.15
MgO	1.83	1.13
K_2O	3.22	4.06
SO_3	-	-
P_2O_5	-	0.17
Na_2O_3	-	0.52
LI	-	15.79
Mineral		
Chlorite	6.47	7%
Illite	22.02	23
Gypsum	1.3	2
Kaolinite	7.62	10
Quartz	28.5	29
K-feldspar	2.37	8
Plagioclase	4.15	-
Calcite	10.44	10
Siderite	4.14	-
Anatase	0.82	-
Pyrite	3.25	4
Apatite	0.41	-
Organics	-	7

LI = Loss on ignition at 1000°C

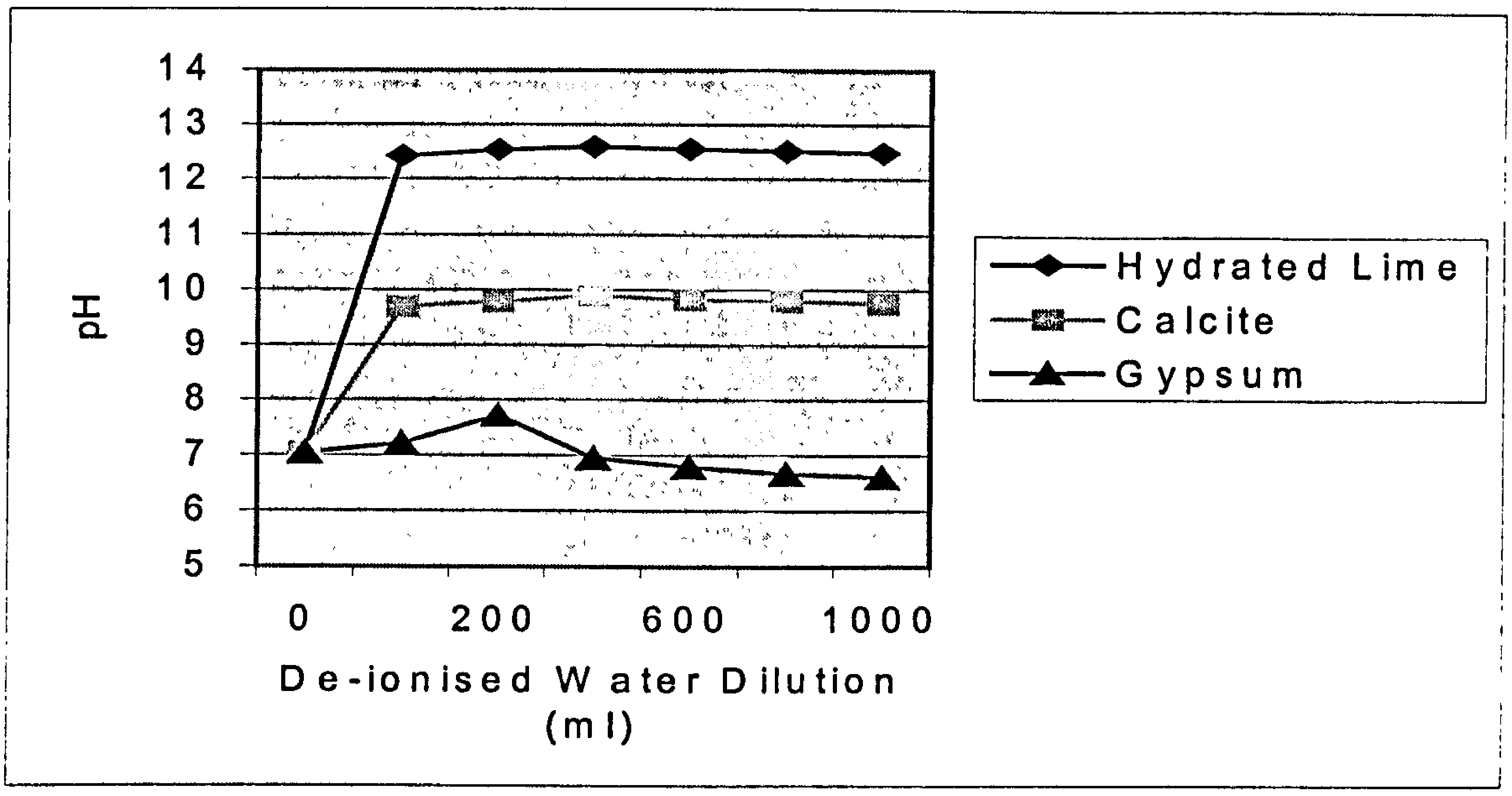
\- = Not Determined

Table 5.3 Solubility (in grams per 100 cc) of calcite and gypsum in water at various temperatures (Seidell, 1940)

Compound	**Temp. (°C)**	**Grams Per Compound Per 100 cc**
Calcite ($CaCO_3$)	18	0.0128
	95-100	0.0207
Gypsum ($CaSO_42H_2O$)	0	0.1759
	10	0.1928
	18	0.2016
	25	0.2080
	30	0.2090
	35	0.2096
	40	0.2097
	75	0.1847
	100	0.1619

Also, certain compounds present either naturally or as additions in the clay exhibit differing pH values in solution. Figure 5.1 shows the pH values of individual solutions of 1g of calcite, 1g of gypsum and 1g of lime (which will be discussed in Section 5.2) with increased water dilution.

Figure 5.1 pH values of solutions of 1g of hydrated lime, 1g of calcite and 1g of gypsum in increasing dilutions with de-ionised water.



From the mineralogical and chemical analysis it can be deduced that the Lower Oxford Clay has many of the ingredients, such as pyrites and gypsum, which form deleterious minerals such as ettringite and thaumasite on stabilisation with lime. It is therefore thought to be an excellent choice for investigative work, as the clay should, when stabilised with lime or Portland cement and subsequently subjected to oxidation, be highly susceptible to expansion and heave.

5.2 Lime

Lime is a generic term, but by strict definition it only embraces manufactured forms of lime – quicklime and hydrated lime. It does not include limestone or other carbonates which are often erroneously referred to as "lime".

5.2.1. Quicklime (CaO)

On the basis of chemical analyses, quicklime may be divided into 3 broad types:

- *High-Calcium quicklime* containing principally calcium oxide (CaO) and <5% magnesium oxide (MgO).

$$CaCO_3 + \text{Heat} \quad \rightarrow \quad CaO + CO_2 \uparrow \text{(gas)}$$

- *Dolomitic quicklime* containing 35 to 40% MgO.

$$CaCO_3.MgCO_3 + \text{Heat} \quad \rightarrow \quad CaO.MgO + 2CO_2\uparrow \text{(gas)}$$

- *Magnesian quicklime* containing 5 to 35% MgO

As it is high-calcium quicklime that is commonly employed throughout the soil stabilisation industry, similar material is used in the current work. Quicklime is produced in a number of particle sizes ranging from lumps and pebbles to pellets and granular lime. The quicklime used in the current work is a fine powder of cement size particles. Quicklime (CaO) in the current work was supplied by Buxton Lime Industries Ltd., as white to off-white solid of angular particle shape with a faint "earthy odour". The material's chemical data are given in Table 5.4

Table 5.4 Chemical Composition of Quicklime (CaO) (Buxton Lime Industries Ltd.)

Chemical Composition	Weight (%)
CaO	95.9
Neutralising Value	96.9
$CaCO_3$	2.2
SiO_2	0.9
Fe_2O_3	0.07
Al_2O_3	0.15
$CaSO_4$	0.16
MgO	0.46
H_2O	0.6
Pb	1.8
Mn	189ppm
As	0.5
F	83ppm

5.2.2 Hydrated Lime ($Ca(OH)_2$)

The chemical composition of hydrated lime generally reflects the composition of the quicklime from which it is derived as well as the method of hydration. There are 3 types of hydrated lime:

- *High calcium hydrate.* A high calcium quicklime will produce a high calcium hydrated lime containing 68% to 74% CaO with 23% to 24% water in chemical combination with the CaO, properly called calcium hydroxide.

$$CaO + H_2O \rightarrow Ca(OH)_2 + \text{Heat}$$

- *Type N dolomitic hydrate.* Dolomitic quicklime will produce a dolomitic hydrate under normal atmospheric hydrate. Under normal atmospheric hydrating conditions, the calcium oxide fraction of the dolomitic quicklime completely hydrates, but generally only a small portion of the MgO hydrates (about 5 to 20%). The composition of a normal or type N dolomitic hydrate will be 46 to 48% calcium oxide, 33 to 34% MgO and 15 to 17% water in chemical combination with the CaO.

$$CaO.MgO + H_2O \text{ at atmospheric pressure} \rightarrow Ca(OH)_2.MgO + \text{Heat}$$

- *Type S dolomitic hydrate.* A pressure hydrated dolomitic lime is also available called Type S. This lime has almost all (>92%) of the oxides hydrated; hence, its water content is higher and its oxide content lower than the Type N dolomitic hydrate.

$$CaO.MgO + 2H_2O \quad \rightarrow \quad Ca(OH)_2.Mg(OH)_2 + \text{Heat}$$

The hydrated lime ($Ca(OH)_2$) used in the current work was supplied by Buxton Lime Industries Ltd., Buxton, Derbyshire, U.K. under the trade name "Limbux". Table 5.5 shows its physical properties, whilst Table 5.6 shows its chemical composition.

Table 5.5 Physical Properties of Hydrated Lime (Buxton Lime Industries)

Properties	**Description**
Chemical Name	Hydrated Lime Calcium Hydroxide
Physical Form	Dry White Powder
Decomposition Temperature	580°C
Bulk Density	480 kg/m^3
Specific Gravity	2.3
Specific Surface	300 –1500 m^2/kg
Solubility in Water	1.76 g/l sat. sol at 10°C
pH Value	12.4

Table 5.6 Chemical Composition of Hydrated Lime (Buxton Lime Industries Ltd.)

Compound	Chemical Formula	Composition (%)
Hydrated Lime	$Ca(OH)_2$	96.76
Calcium Carbonate	$CaCO_3$	1.36
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

The pH value of a saturated calcium hydroxide solution increases with decreasing temperature (see Figure 5.2). Also, unlike calcite and gypsum the solubility of calcium hydroxide increases with decreasing temperature (see Table 5.7)

Table 5.7 Solubility of calcium hydroxide in water at differing temperatures (Seidell, 1940)

Temperature (°C)	Grams CaO per 100 gms solution saturated with fine $Ca(OH)_2$
0	0.143
5	0.142
10	0.138
15	0.133
25	0.129
30	0.121
40	0.107
50	0.0968
60.8	0.0917
70	0.0800

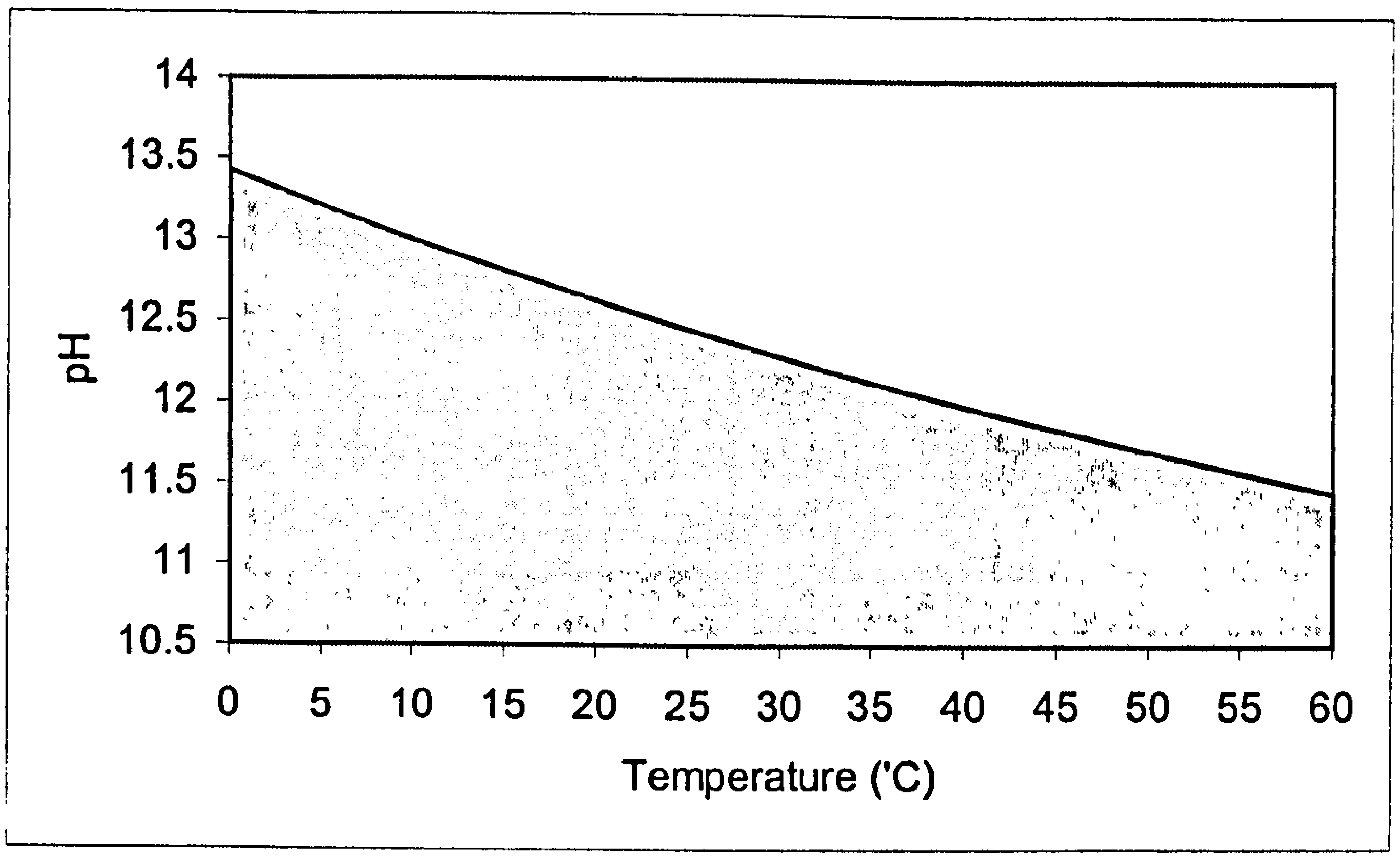


Figure 5.2 Temperature versus pH of saturated calcium hydroxide solutions (NLA, 1995).

5.3 Ground Granulated Blastfurnace Slag (GGBS)

Civil and Marine Cement Ltd., Llanwern, Newport, UK supplied the GGBS used in this work. Its chemical composition and physical properties are shown in Tables 5.8 and 5.9 respectively.

Table 5.8 Chemical Composition of GGBS (Civil and Marine Slag Cement Ltd. UK)

Oxide	**Composition**
CaO	41.99
SiO_2	35.34
Al_2O_3	11.59
MgO	8.04
Fe_2O_3	1.18
MnO	0.45
S_2	1.18
SO_3	0.23

Table 5.9 Physical Properties of GGBS (Civil and Marine Slag Cement Ltd., UK)

Insoluble Residue	0.3%
Relative Density	2.9 t/m^3
Bulk Density	1.2 t/m^3
Colour	off-white
Glass Content	≈ 90%

5.4 Portland Cement (PC)

The Portland cement used in this investigation was supplied by Rugby Cement, a division of Rugby Group Plc., Crown House, UK. The oxide and compound composition of the PC can be seen in Table 5.10.

Table 5.10 Oxide and Compound Composition of Rugby PC used in this investigation (Rugby Group Plc.).

Oxide Composition per cent		**Calculated Compound Composition**	
CaO	65.6	C_3A	8.20
SiO_2	21.00	C_3S	64.00
Al_2O_3	4.63	C_2S	11.00
Fe_2O_3	2.26	C_4AF	6.70
MgO	1.18		
SO_3	2.69		
K_2O	0.78		
Na_2O	0.16		
Loss On Ignition	0.99		

6 Experimental Method

This chapter outlines the experimental methods and analytical techniques used in the current work, namely:
- *Consistency (Atterberg) limits,*
- *Proctor Compaction tests,*
- *Unconfined Compressive Strength (UCS) tests,*
- *Durability Index,*
- *Linear Expansion tests,*
- *Sulphate (SO_3) tests,*
- *Thermogravimetric analysis (TGA) and*
- *X-ray Diffraction (XRD).*

The first six tests were chosen as they represent, or relate to, tests outlined in the Design and Construction of Lime Stabilised Capping Specifications (DoT, 1995). The analytical techniques (TGA and XRD) were undertaken in order to understand the phase and mineralogical changes of the stabilised LOC, especially during mellowing and the early stages of curing with lime.

6.1 Consistency (Atterberg) Limits

The consistency limit tests were carried out in accordance with BS 1377 (1990) Part 2 – Classification Tests (British Standard Methods of Test for Soils for Civil Engineering Purposes) on Lower Oxford Clay (LOC) that was dried, crushed and sieved passing 425 μm (in accordance with the standard). Additionally, tests were carried out with various additions of lime (i.e. quicklime (CaO) or hydrated lime ($Ca(OH)_2$)) in order to establish the effects of increased lime addition to a pyrites-bearing clay soil and to determine the differences, if any, between CaO and $Ca(OH)_2$ on Atterberg limits. In order to ascertain the effects of mellowing, tests were carried out on material that had been mellowed at or 20°C for 3 days (Table 6.1). The British standard referring to consistency limit tests does not address the issue of mellowing. Therefore an original approach was employed where the mixed material was placed in sealed polythene bags after an addition of 40 wt.% water prior to mellowing. After the mellowing period, the mixed material was tested in a similar way to unmellowed material.

Table 6.1 Samples subjected to consistency (Atterberg) limit tests.

Modifier	Stabiliser	Unmellowed	Mellowed	
			6 hours	3 days
2% $Ca(OH)_2$		✓	✓	✓
	4% $Ca(OH)_2$	✓	✓	✓
	6% $Ca(OH)_2$	✓	✓	✓
	8% $Ca(OH)_2$	✓	✓	✓
1.5% CaO		✓	✓	✓
	3% CaO	✓	✓	
	4.5% CaO	✓	✓	✓
	6% CaO	✓	✓	✓

6.1.1 Liquid Limit

The dry material(s) were initially mixed with around 40 wt.% water using palette knives until the consistency of the material was considered suitable. In accordance with BS 1377 (1990), the material was then used to fill a brass cup (56mm in diameter and 41mm deep) (see Plate 6.1). A metal cone (angle 30±1°C and 35mm 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 was removed from the cup near to the zone of penetration in order to determine the moisture content (again in accordance with BS 1377 (1990)). After removal of material for the determination of the moisture content, the residual material in the cup was removed and mixed with the remainder of the material in the presence of more water. Further penetration tests, together with their corresponding moisture contents were performed so as to obtain a set of points in the penetration range 5 – 30mm. The LL was taken as the moisture content corresponding to a penetration of 20mm, from a graph of penetration (mm) against moisture content (%).

6.1.2 Plastic Limit

In order to determine the plastic limit (PL), material set aside after initial mixing during liquid limit determination was gently rolled on a flat plate into rods and rolling continued until the rods crumbled when they were of approximate diameter of 3 mm. When the desired crumbling occurred, a few crumbs were taken for moisture content determination. This moisture content is defined as the plastic limit of the material. From the liquid limit and the plastic limit, the plasticity index (PI) of the material was obtained as the difference between the two. The Design and Construction of Lime Stabilised Capping Specifications (DoT, 1995) states that clay soil must have a PI of 10% or more in order to be considered for lime stabilisation.

6.2 Proctor Compaction Tests

Compaction tests, in accordance with BS 1377 (1990) – Proctor Compaction Test procedure, were used to determine the maximum dry density (MDD) and the optimum moisture content (OMC) of LOC with, and without, various additions of both CaO and

$Ca(OH)_2$ after three different mellowing periods and two different temperatures (see Table 6.2).

Table 6.2 Samples subjected to Proctor compaction tests.

Modifier	Stabiliser	Unmellowed	Mellowed			
			6 hours		3 days	
			Temperature (°C)			
			10	20	10	20
2% $Ca(OH)_2$		✓	✓	✓	✓	✓
	4% $Ca(OH)_2$	✓		✓		✓
	6% $Ca(OH)_2$	✓		✓		✓
	8% $Ca(OH)_2$	✓		✓		✓
1.5%CaO		✓	✓	✓	✓	✓
	3% CaO	✓		✓		✓
	4.5% CaO	✓		✓		✓
	6% CaO	✓		✓		✓

Similar to the Atterberg limits, the relevant British standards (BS 1377 and BS 1924) do not address the issue of mellowing in Proctor compaction tests. Therefore it was necessary to add an original component to the test to deal with the problem of mellowing. During mellowing, care was taken not to introduce moisture in excess of optimum moisture content. The dry materials (i.e. LOC and lime) were mixed with 20-wt.% water and placed in sealed plastic bags for the period of mellowing. After mellowing the mixed materials were removed from the bag and treated in a similar way to the unmellowed mixes. The MDD and OMC attained as a result of the Proctor tests were later used for the preparation of samples for the determination of unconfined compressive strength (UCS), durability and for linear expansion measurements. Mixing of the dry materials was achieved using a Model SE-401 Hobart 40 Qt mixer. The material was compacted in 3 equal layers in a mould of dimensions 105±0.5 mm in diameter and 115±1 mm in height, each layer being subjected to 27 blows using a 2.5kg ram (see Plate 6.2). After weighing the mould together with the compacted material, a small amount of material was taken from the interior and used for moisture content determination. A dry density / moisture content curve was then used to determine the MDD and the OMC.

Tests on LOC were carried out with and without lime (2%$Ca(OH)_2$ and 1.5% CaO) firstly without mellowing, and then after 6-hours or 3-days mellowing at 10°C or 20°C (again, it should be noted that 1.5%CaO is equivalent to 2%$Ca(OH)_2$). To further examine the role of mellowing and lime type additional Proctor compaction tests were carried out on samples containing 3%, 4.5% and 6%CaO and 4%, 6% and 8% $Ca(OH)_2$.

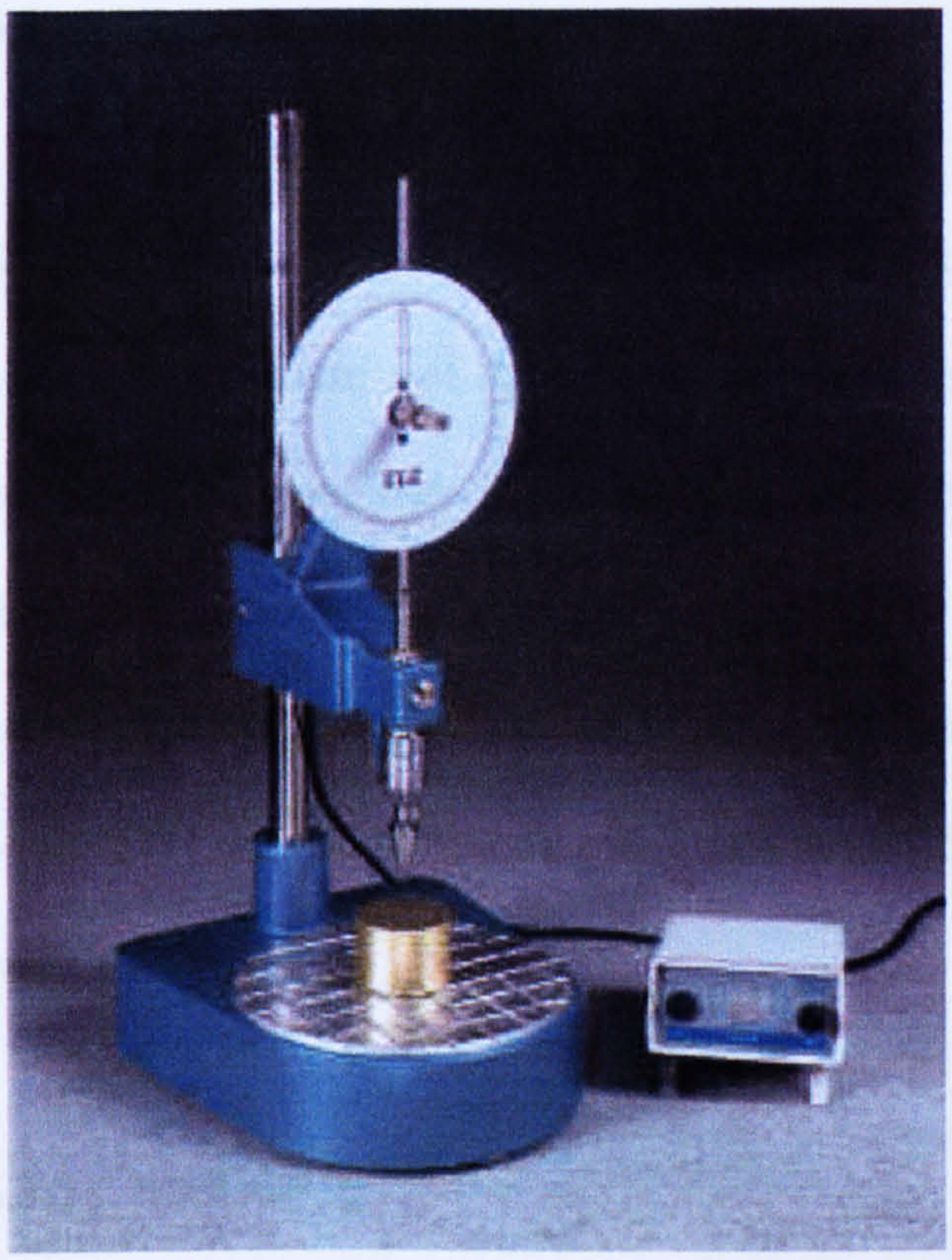


Plate 6.1 Falling cone penetrometer used in Atterberg (consistency) limits.

Plate 6.2 Compaction equipment used in the Proctor compaction tests.

6.3 Sample Preparation

Strength tests (UCS), durability tests and linear expansion tests were carried out using compacted cylinders of the LOC with added lime with and without additions of GGBS or PC. The material used in the analytical techniques (i.e. SO_3 determination, thermogravimetric analysis (TGA) and X-ray diffraction (XRD)) was obtained from compacted cylinders either during, or on completion of, the expansion tests (in the case of the SO_3 tests) and on completion of the UCS tests (in the case of the TGA and XRD work).

6.3.1 Mellowing

As previously mentioned, the British Standards do not address the issue of mellowing. Therefore mixes of clay, lime (both quicklime and hydrated lime) and water, that were to undergo mellowing were mixed at a moisture content of optimum (OMC), the value for which was attained as a result of the Proctor compaction tests, and stored for 3 days at 20°C. On completion of the mellowing period, the material was removed from the sealed bags and placed into a mixing bowl whereupon a calculated amount of water was added in order that the mix was wet of OMC. (The results established that a uniform moisture content of 32% was sufficient to compact all specimens wet of optimum.) Depending on the amount and type of lime, the Proctor compaction characteristics (i.e. MDD and OMC) of a given mix will vary. Wild et al (1999) found that a reduction in potential expansion can be achieved if samples are mixed and compacted "wet of optimum" (i.e. the moisture content added to the material before final compaction is in excess of the optimum moisture content (OMC) established during the Proctor compaction tests), as this increases the inter-particle void space allowing the accommodation of developing expansive products. For selected samples the appropriate amount of GGBS or PC was added at this point along with a calculated amount of water (attributed by weight to the amount of GGBS or PC added). From this point, all samples (mellowed or unmellowed) were treated in exactly the same manner.

Enough material to produce one cylindrical sample was mixed in a Kenwood Chef Excel mixer for 2 minutes before slowly adding the calculated amount of water. Automatic mixing was followed by a manual-mixing phase with palette knives until a homogenous mix was achieved. The mixed material was then fed into a cylindrical stainless-steel split mould and compacted using a hydraulic jack. Based on pre-calculated material weights, the soil sample was weighed to ensure the anticipated calculated weight was achieved. Finally, the cylindrical specimens were cleaned of releasing oil, wrapped in cling film to limit moisture loss, labelled and stored in the appropriate curing environment as described below.

6.3.2 Curing Conditions

To allow an assessment of the rate of cementation within the specimens at different temperatures, curing temperatures of 5°C, 10 °C and 20°C were chosen as these reflect the range of typical annual soil temperatures in the UK (British Earth Sheltering Association, 1994). Curing at 5°C and 10°C was achieved using refrigerators, whilst a sealed constant temperature room provided a curing environment of 20°C. Regular checks ensured temperatures were kept within a range of ± 2°C. To monitor strength characteristics over time, curing periods of 1, 4, 12, 24 and 52 weeks were employed.

6.4 Unconfined Compressive Strength (UCS)

It is necessary to precisely define the strength of a material, as the strength obtained is influenced by the way in which it is measured and this should where possible reflect conditions in use. The Design and Construction of Lime Stabilised Capping Specifications (DoT, 1995) endorse the California Bearing Ratio (CBR) test as the preferred method of determining strength. Although the CBR is practical in the field it is impractical in a laboratory-based investigation as firstly, it uses a great deal of the raw materials (clay, lime etc.) and secondly, is very time consuming. Researchers such as Kinuthia (1997) and Wild et al. (1998) employed unconfined compressive strength (UCS) tests in order to assess the strength of stabilised clay soils under laboratory conditions. More recently, Veith (2000) combined this method with undrained, unconsolidated shear strength and indirect tensile strength measurements and found that strength development exhibited similar trends for all methods of testing. In the current work the UCS method is utilised.

Unconfined Compressive Strength (UCS) of stabilised clay samples was determined using a JJ 30 MK compression-testing machine at a loading rate of 1mm/min. A self-levelling device was placed between the top of the sample and the upper platten in order to achieve uniaxial stress. Load was then applied at a rate of 1mm/min until failure was recorded. Three samples for each mix composition (see Table 6.3) were tested and the mean value was taken. Anomalous values (i.e. values that differed from the other two values by 20%) were discarded. UCS tests were carried out on mellowed LOC-lime samples that were cured for 1 and 4 weeks at 5°C, 10°C and 20°C. To assess the effects of mellowing on strength development of mellowed (3 days at 20°C) and unmellowed material, unmellowed samples were also produced and cured for 1 and 4 weeks. Similarly UCS tests were carried out on mellowed GGBS or PC stabilised samples that had been cured for 1, 4, 12, 24 and 52 weeks at 5°C, 10°C and 20°C. Samples cured at 5°C and 10°C were allowed to reach room temperature before testing.

The Design and Construction of Lime Stabilised Capping Specifications (DoT, 1995) states that the initial consumption of lime (ICL) of a clay soil will depend upon the mineralogy of the unstabilised material, with typical ICL's ranging from 1.5% to 3.5% for $Ca(OH)_2$. The ICL value is given by the amount of lime required to raise the pH of a standard clay-lime slurry to 12.4. Veith (2000) found the ICL of LOC to be 2.5%. However, Veith commented that lime additions of only 1% or 2% lifted the pH of the slurry to almost 12.4. Based on these observations and the fact that Wild et al. (1996) had obtained a high degree of GGBS activation with additions of only 1% lime for a kaolinitic soil, 2% $Ca(OH)_2$ was chosen as the initial modifier of the clay-lime material, and activator for GGBS. Laboratory-based research in the area of lime-stabilised soils has concentrated on the addition of hydrated lime ($Ca(OH)_2$), rather than quicklime (CaO), to clay soils. However, in practice quicklime is generally used to stabilise clay soils as it has a higher available lime content per unit weight and a very fast drying action on wet soils, particularly in temperate climates. Therefore both hydrated lime and quicklime are used in the current work, with quicklime (1.5% CaO) being employed for the bulk of the work (Table 6.3.).

Table 6.3 Mix Compositions with Lower Oxford Clay subjected to UCS and durability tests.

<table>
<tr><th colspan="2">Modifier</th><th colspan="2">Stabiliser</th></tr>
<tr><td colspan="2">2%$Ca(OH)_2$</td><td colspan="2">-</td></tr>
<tr><td colspan="2">-</td><td colspan="2">4%$Ca(OH)_2$</td></tr>
<tr><td colspan="2">-</td><td colspan="2">6%$Ca(OH)_2$</td></tr>
<tr><td colspan="2">-</td><td colspan="2">8%$Ca(OH)_2$</td></tr>
<tr><td colspan="2">1.5%CaO</td><td colspan="2">-</td></tr>
<tr><th>$Ca(OH)_2$ (wt.%)</th><th>CaO (wt.%)</th><th>PC (wt.%)</th><th>GGBS (wt.%)</th></tr>
<tr><td>-</td><td>1.5</td><td>2</td><td>-</td></tr>
<tr><td>-</td><td>1.5</td><td>4</td><td>-</td></tr>
<tr><td>-</td><td>1.5</td><td>6</td><td>-</td></tr>
<tr><td>-</td><td>1.5</td><td>8</td><td>-</td></tr>
<tr><td>2</td><td>-</td><td>4</td><td>-</td></tr>
<tr><td>2</td><td>-</td><td>8</td><td>-</td></tr>
<tr><td>-</td><td>1.5</td><td>-</td><td>2</td></tr>
<tr><td>-</td><td>1.5</td><td>-</td><td>4</td></tr>
<tr><td>-</td><td>1.5</td><td>-</td><td>6</td></tr>
<tr><td>-</td><td>1.5</td><td>-</td><td>8</td></tr>
<tr><td>2</td><td>-</td><td>-</td><td>4</td></tr>
<tr><td>2</td><td>-</td><td>-</td><td>8</td></tr>
</table>

6.5 Durability Tests

In order to determine the influence of lime and/or GGBS and PC addition on the durability of stabilised clay soils a modified durability test (BS 1924, Section 4.3: Specification for Highway Works for cement bound materials) was employed. The test was first used by the Transport Research Laboratory (TRL) in their report no.408 where durability is determined by a parameter called durability index (DI). As the hardening rates are slower in lime stabilised and lime modified GGBS stabilised soils, compared to lime/cement stabilised soils, TRL decided to lengthen the test to allow sufficient time in order for strength to develop. The test involves curing specimens at 20°C for 21 days followed by soaking in water at 20°C for 7 days and then determining the unconfined compressive strength. A control set of specimens is also cured for 28 days at 20°C and the compressive strength determined without being subjected to soaking in water. The durability index is obtained by determining the compressive strength of the soaked specimens as a percentage of the compressive strength of the control specimen. It is this test that is employed in the current work (see Table 6.3)

Soaking of the specimens was carried out in plastic containers wherein two samples of similar consistency were placed in 500 ml of water to minimise cross contamination. The samples were unrestrained except for a thin layer of cling film (50mm wide) positioned around the middle of the compacted cylinder, thus allowing the free ingress of moisture but maintaining some of the cylinders' dimensional stability during soaking. Curing took place at 20°C and at 5°C for both mellowed (3 days at 20°C) and unmellowed cases.

6.6 Linear Expansion

Expansion and heave in lime stabilised clay soils is common and is discussed in depth in Chapter 3. The Design and Construction of Lime Stabilised Capping Specifications (DoT, 1995) stipulate that samples of lime-stabilised material (in a standard 127mm high CBR mould) should not expand more than 5mm after 28 days with no sample swelling more than 10mm. As mentioned in section 6.4, CBR tests require a great deal of material and are unsuitable for a large number of expansion tests in laboratory investigations.

Therefore, in order to assess the linear expansion of mellowed and unmellowed cylindrical clay soil samples (100mmX50mmϕ) due to chemical reactions and water absorption, an experimental method developed at the University of Glamorgan was employed. The original method involved a water-tight tank in which a complete series of samples was accommodated and their expansions monitored. Wild and Tasong (1999) and Veith (2000) improved this experimental set-up utilising individual sealed plastic cells to avoid cross-contamination between samples with differing constituents. The method determines the linear expansion of the compacted cylinder from readings taken from a sensitive dial gauge in contact with a Perspex disc resting on top of the specimen. Samples were placed on a stage in the watertight Perspex cell in such a way that expansion could be continually monitored. After 7 days of moist curing, 500ml of water was added. The experimental set up is illustrated in Plate 6.3. The linear expansions of the samples were continually monitored on a daily basis, both during curing and after soaking.

As mentioned in Chapter 3, pyrites is thought to oxidise under particluar conditions to produce sulphates, which in turn are known to increase the potential for expansion in stabilised clay soils (Hawkins, 1992; Cassanova et al. (1997); Snedker and Temporal (1990); Wild and Tasong (1999)). The Lower Oxford Clay (LOC) is known to contain a significant amount of pyrites and when stabilised is thought to be susceptible to sulphate attack particularly in oxidising conditions. To monitor the effects of pyrites oxidation the soaking water in which selected samples were placed was intentionally and continuously aerated in order to accelerate pyrites oxidation. The laboratory system is a static enclosed system, thus after the initial and possibly quite rapid removal of oxygen from the soaking water repletion of oxygen may be limited. Therefore oxidation in such a closed system might be expected to be severely retarded or terminated. The water was constantly aerated by means of a tube that was connected to a fish tank aspirator. The test was carried out in order to assess the influence of mellowing, temperature, stabiliser content and the intentional aeration of the soaking water on the linear expansion characteristics of stabilised LOC.

pH values of soaking waters play an important role with regards to the type of reaction product formed. As previously stated, Gaze and Crammond (2000) reported that the reaction product ettringite was abundant in crushed mortar tablets that were soaked in a solution of high pH. However, the pH value dropped when the mortar was exposed to the air and subsequently the dominant reaction product became gypsum. Also, pyrites oxidation produces an acidic environment. Thus as the pH of the soaking water is so important, the soaking waters containing the clay-lime samples were monitored at 7 day intervals using pH sensitive strips (Whatman CF, range 0-14). A list of the compositions subjected to this process can be seen in Table 6.4:

Table 6.4 Samples subjected to linear expansion tests.

Modifier	Stabiliser	Unmellowed				Mellowed	
		Aerated		*Non- aerated*		*Aerated*	
		Temp.(°C)		Temp.(°C)		Temp.(°C)	
		20	5	20	5	20	5
1.5% CaO		✓		✓		✓	✓
	4 and 8%PC					✓	✓
	4 and 8*%GGBS	*✓		*✓		✓	✓
2% $Ca(OH)_2$		✓		✓		✓	✓
	4% $Ca(OH)_2$	✓		✓		✓	✓
	6% $Ca(OH)_2$	✓		✓		✓	✓
	8% $Ca(OH)_2$	✓		✓		✓	✓

*only 8%GGBS tested

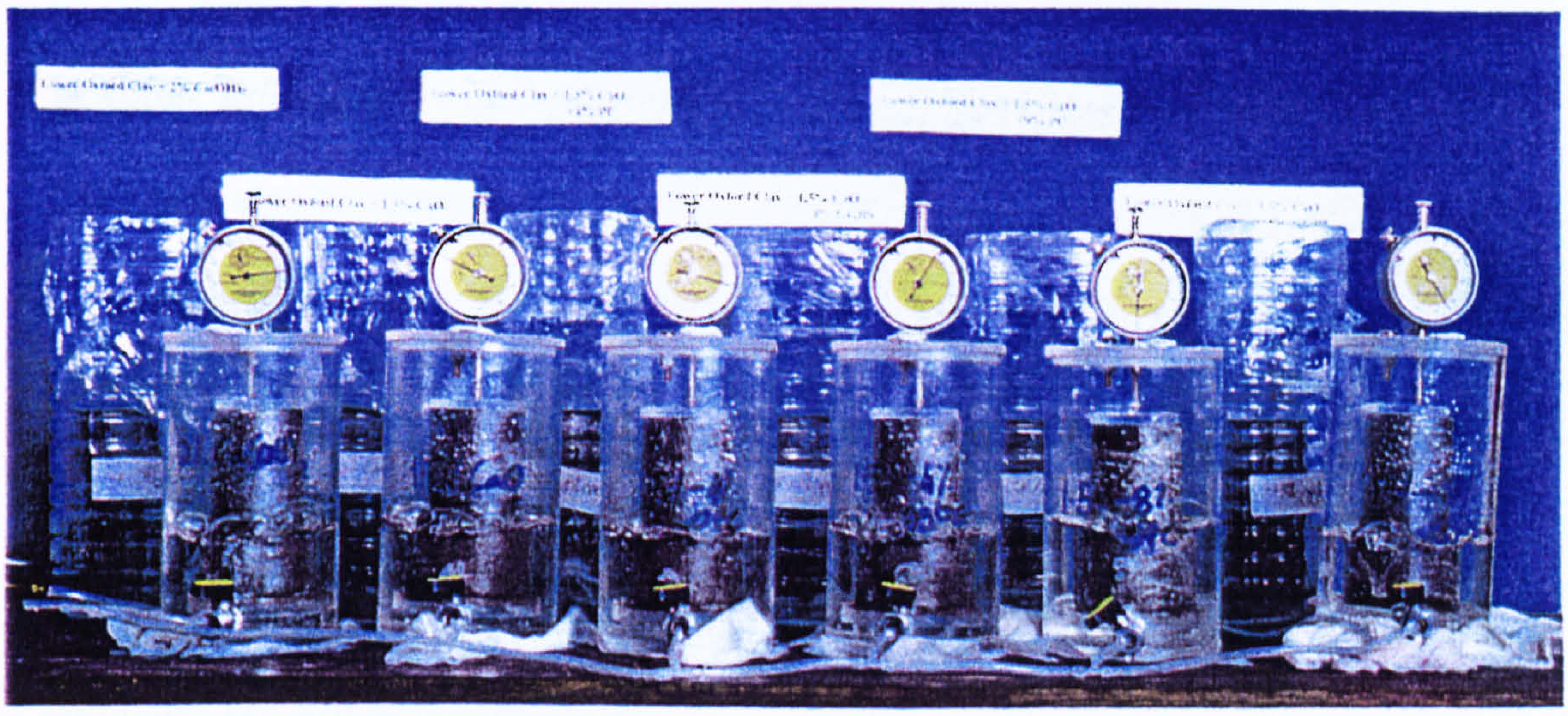


Plate 6.3 Linear Expansion Apparatus

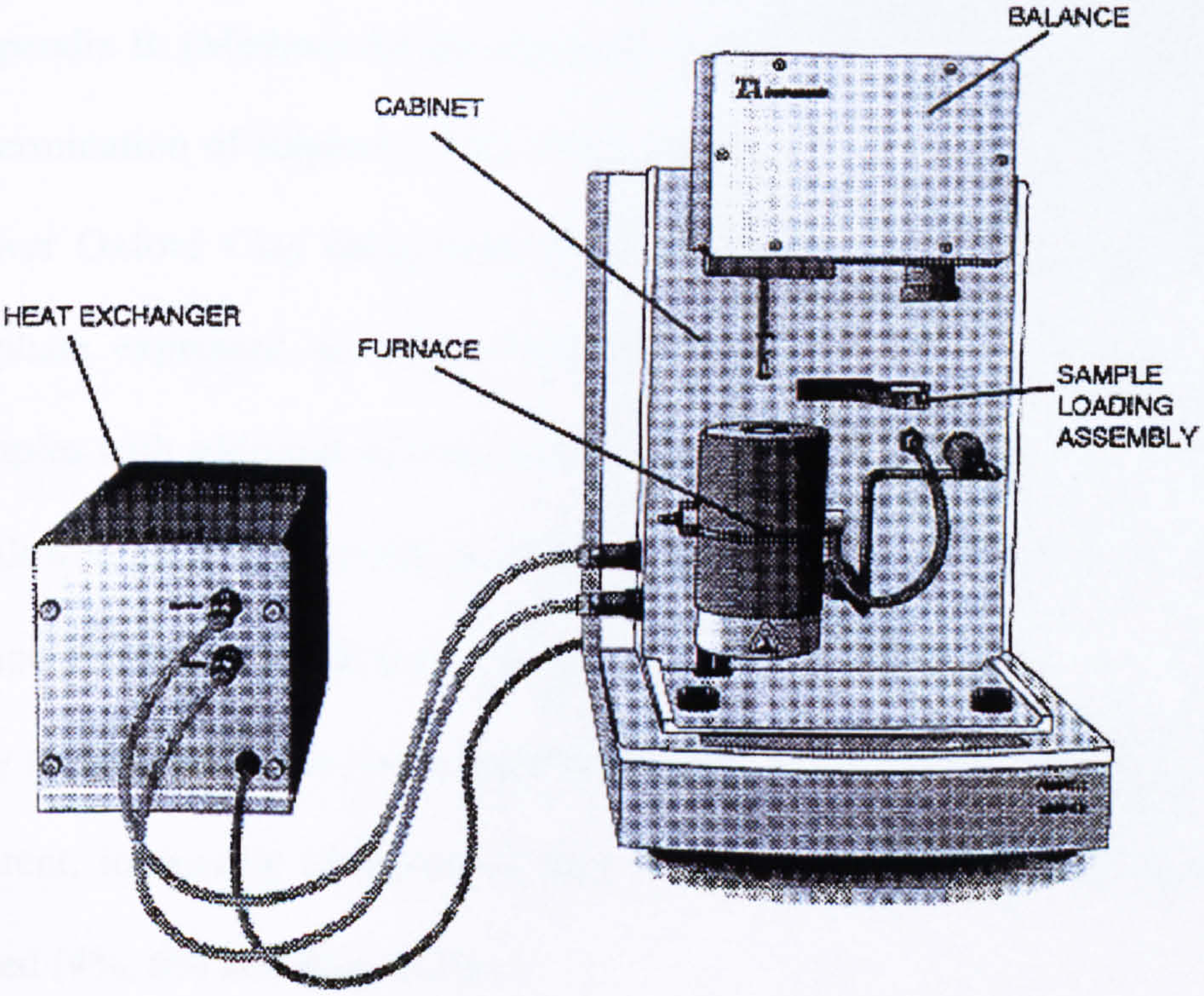


Plate 6.4 Diagram of a thermogravimetric analyser TGA 2950.

6.7 Sulphate (SO_3) Analysis

In order to determine the amount of sulphate potentially available in Lower Oxford Clay, and also to monitor the change in sulphate level with time in the stabilised LOC it is necessary to test for both sulphate and total sulphur. In their natural state sulphates occur as SO_4. The Building Research Establishment has revised its Digest on the effects of sulphates on concrete from expressing sulphates as SO_3 in BRE Digest 25 (BRE, 1981) to sulphates as SO_4 in BRE Digest 363 (BRE, 1991). However in soil testing, sulphates are still expressed as SO_3.

Tests were carried out on LOC to establish the total sulphur content using a modified version of BS 1047 (Air cooled blastfurnace slag aggregate for use in construction) – Appendix B. (Methods for the chemical analysis of blastfurnace slag) – B2. (Method for determination of sulphur) :1983. Tests were also carried out to find the SO_3 content of Lower Oxford Clay using method B3 (Method for the determination of acid soluble sulphate expressed as SO_3). Subsequently sulphate tests were also carried out on samples with additions of lime (both CaO and $Ca(OH)_2$) which had been unmellowed or mellowed for 3 days, moist cured for 7 days and soaked in a range of environments and temperatures (see Table 6.6). The material used in sulphate tests was soaked in the same way as samples in the linear expansion work. To further investigate the changes in SO_3 content, increasing additions of lime were also added to the LOC and subsequently tested (4%, 6% and 8%$Ca(OH)_2$).

Pyrites oxidation ceases with the absence of air and/or water. In order to halt the oxidation process at the desired times it was necessary to modify the test outlined in BS

1047. Both the original and modified tests are illustrated in Table 6.6. To stop further oxidation after sampling at a particular stage, the samples were weighed, their moisture contents determined and they were immediately transferred to 20ml of 2Molar hydrochloric acid (HCl).

Tests were carried out on mellowed (3 days at 20°C) or unmellowed stabilised material that had undergone 7 days of curing, 14 days soaking in the appropriate environment and at the end of the soaking test (105 days) at either 20 or 5°C. The samples used in this test are listed in Table 6.5.

Table 6.5 Samples subjected to sulphate analysis.

Modifier	**Stabiliser**	**Unmellowed**				**Mellowed**	
		Oxidised		*Non-oxidised*		*Oxidised*	
		Temp.(°C)		Temp.(°C)		Temp.(°C)	
		20	5	20	5	20	5
1.5% CaO		✓		✓		✓	✓
2% $Ca(OH)_2$		✓		✓		✓	✓
	4% $Ca(OH)_2$	✓		✓		✓	✓
	6% $Ca(OH)_2$	✓		✓		✓	✓
	8% $Ca(OH)_2$	✓		✓		✓	✓

Table 6.6 Comparison of BS 1047 :1983 and the modified test used in this work.

BS 1047 :1983	**Modified Version of BS:1047**
Bring to the boil 20 ml of 2 molar HCL.	Remove soil cylinder from expansion cell and independently determine the average moisture content of the sample (using the oven dry method). Immediately extract four samples of between 1 and 5g from the cylinder for testing (recording the weights) and transfer to sealable plastic bottles containing 20 ml molar HCL.
Brush in 1g of dry, crushed material and continue to heat for 5-6 minutes.	Carefully transfer the material and washings from the bottle into a suitable beaker and bring to boiling point for 5-6 minutes.
Add 100 ml of boiling water, filter paper pulp and make alkaline to methyl red by means of ammonia.	Add 100 ml of boiling water, filter paper pulp and make alkaline to methyl red by means of ammonia
Filter under gentle suction reserving the filtrates. Transfer the filter paper to a beaker and re-dissolve in 5 ml HCL and 70 ml hot water	Filter under gentle suction reserving the filtrates. Transfer the filter paper to a beaker and re-dissolve in 5 ml HCL and 70 ml hot water
Boil, precipitate, filter and wash, rejecting the precipitate. Make the combined filtrates acid using HCL and add, in drops, 10ml of 10% barium chloride. Stand in a warm place over night and filter by means of a weighed sintered silica filter. Ignite slowly to 800°C, weigh and calculate the total percentage of SO_3 from the mass of $BaSO_4$ precipitate.	Boil, precipitate, filter and wash, rejecting the precipitate. Make the combined filtrates acid using HCL and add, in drops, 10ml of 10% barium chloride. Stand in a warm place over night and filter by means of a weighed porcelain crucible. Ignite slowly to 800°C, weigh and calculate the total percentage of SO_3 from the mass of $BaSO_4$ precipitate.
$\%SO_3$ = Mass of precipitate x 13.74 / Mass of sample	$\%SO_3$ = Mass of precipitate x 13.74 / Mass of sample. Before calculating SO_3, one must take into account the amount of modifier and/or stabiliser in the material and the moisture content. This will markedly reduce the mass of the sample.

6.8 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) is a thermal analysis technique used for measuring the amount and rate of change in sample mass as a function of temperature and time. TGA can be used to characterise any material that exhibits weight change as a result of, for example, dehydration (loss of water of crystallisation) dehydroxylation (loss of OH ions), oxidation (e.g. combustion of organic matter), or decarbonation (loss of CO_2).

Heating of clays results in a pattern of weight loss that is characterised by the attractive force with which water is retained within or on the clay structure at different temperatures. Similar weight losses occur on heating hydrated cement. During the hydration of cement a number of chemical changes occur resulting in the formation of various phases. These include:

- Formation of ettringite,
- Formation of C-S-H gel,
- Formation of $Ca(OH)_2$,
- Carbonation of $Ca(OH)_2$ to give $CaCO_3$.

On heating, each of the above phases shows a weight loss over a specific temperature region due either to partial or total decomposition. The weight loss results from the loss of water (dehydration or dehydroxylation) or carbon dioxide (from decarbonation). From the thermogravimetric measurements it is therefore possible to estimate, and in some cases accurately determine, the amount of each phase which is present at different stages of the hydration process.

In thermal analysis tests the specimens are heated at a constant rate and the weight changes can be recorded in two ways - (i) percentage weight loss against temperature (TG), and/or (ii) rate of loss in weight against temperature (DTG), this being the derivative of the above curve in (i).

A weight change at a specific temperature produces a step in (i) and a peak (maximum) in (ii). The curves are useful in illustrating the manner in which the amount of any particular phase present changes with curing time, and also in providing reliable quantitative data giving the actual amounts of particular phases present. However, this technique requires a previous knowledge of the chemical compositions of the individual phases and their characteristic TG and DTG curves or decomposition temperature

The major thermogravimetric effects that characterise clay soils can be observed at temperatures ranging between 50°C and 300°C (loss of absorbed water and water of hydration) and between 450°C and 1000°C (dehydroxylation). At temperatures beyond 900°C most clay minerals undergo an exothermic recrystallisation phase and new crystals form from amorphous materials or from old crystals destroyed at lower temperatures (Mitchell, 1993). However, it should be noted that the thermal behaviour of clay soils can differ considerably from that of pure clay minerals due to the presence of various elements such as organic material or carbonates which decompose on heating.

There are a number of factors that influence the values of the peak temperatures observed on DTG plots.

- The amount of the sample being tested,
- The heating rate,
- The furnace atmosphere,
- The particle size of the sample,
- The degree of crystallinity of the compound being tested.

In order to ensure consistency the first three of the above factors were standardised throughout the testing period. The last two factors depend on the nature of the starting material and the physical and chemical changes that occur with time and cannot therefore be standardised. The current TGA work was carried out using a thermogravimetric analyser Hi-Res^{TM} TGA 2950 with a TA5000 Thermal Analyst Controller and appropriate software (Plate 6.4). The heating rate was chosen as 10°C per minute within a temperature range of 25 to 1000°C. The sample was taken from the interior of a compacted cylinder (used in the UCS tests) and was dried at 50°C (±2°C) in an oven for at least 48 hours. After drying the sample was crushed to a powder in a pestle and mortar, and between 8 to 20mg of the crushed sample was transferred to an open alumina pan, which was then heated in a nitrogen atmosphere. Weight loss and temperature increase is logged during the test and the resulting graph supplies the TGA weight loss curve (%) and the derivative weight loss curve (DTG) (dw%/dt°C). The former plots the total weight loss in percent over the temperature range to which the sample was subjected, whereas the latter shows the derivative of the weight loss with increase in temperature, resulting in a graph with pronounced peaks, allowing conclusions and calculations to be made as to the identity and quality of particular compounds or phases present.

An example of this can be seen in Figure 6.1. Gypsum, which is commonly found in clay soils, has the chemical formula $CaSO_4.2H_2O$. Therefore, at a given temperature gypsum loses 2 water molecules. The theoretical weight loss of the bound water is based on a molecular weight for gypsum of 172 atomic mass units (amu).

$$\begin{array}{ccc} CaSO_4 & + & 2H_2O \\ (40 + 32 + (16x4)) & + & (2x\,[2x1 + 16]) \\ 136 & + & 36 \end{array}$$

$$= 172 \text{ amu.}$$

The loss of water (36 amu) is therefore 20.9% relative to the gypsum molecule. The observed weight loss of gypsum during a TGA run in a sealed aluminium pan with a pin-hole lid was found to be 19.92%, which shows satisfactory agreement with the calculated result (Figure 6.1). Interestingly it can be seen that gypsum typically has two weight loss peaks (represented by peaks 1 and 2 on Figure 6.1).

Peak 1 represents the transformation of gypsum to *hemi-hydrate:*

$$\mathbf{CaSO_4.2H_2O \quad \rightarrow \quad CaSO_4.0.5H_2O}$$

Whereas Peak 2 shows the complete loss of water to form *anhydrite:*

$$CaSO_4.0.5H_2O \rightarrow CaSO_4.$$

However these two decompositions occur over a relatively narrow temperature range and the temperature at which each decomposition occurs is sensitive to the level of water vapour in the atmosphere in the immediate environment of the specimen. For specimens in an open crucible in a dry nitrogen atmosphere the typical heating rates employed for TG work are sufficiently rapid for the two decompositions to occur simultaneously and only one peak is observed (Total weight loss = 20.20%, Figure 6.2). If however the atmosphere above the specimen is partially enclosed (by covering the aluminium crucible containing the sample with an aluminium lid with a pinhole in it) then water vapour will build up in the atmosphere above the sample. Hence the two decomposition temperatures will separate and a double weight loss peak will be observed as shown in Figure 6.1. In the current work on LOC, aluminium crucibles were unsuitable because of the their upper temperature limit (around 600°C). Therefore open alumina crucibles were employed, for which the gypsum decomposition produces a single weight loss peak. This is in fact preferable in that a double peak occupies a wider temperature range and is more likely to interfere with decomposition from other phases present.

Figure 6.1 TG curves of analytical gypsum ($CaSO_4.2H_2O$) in a sealed crucible with pinhole lid.

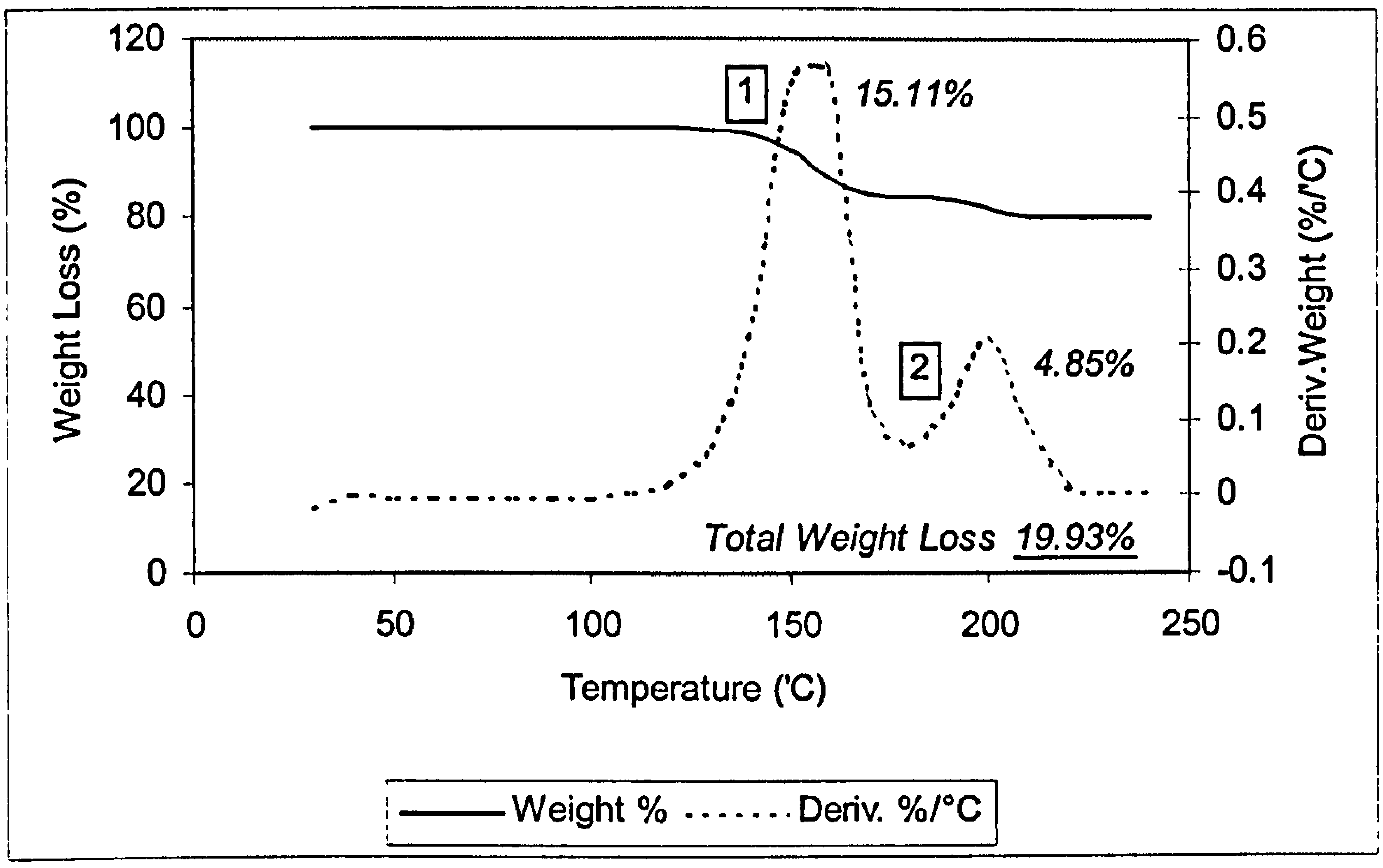
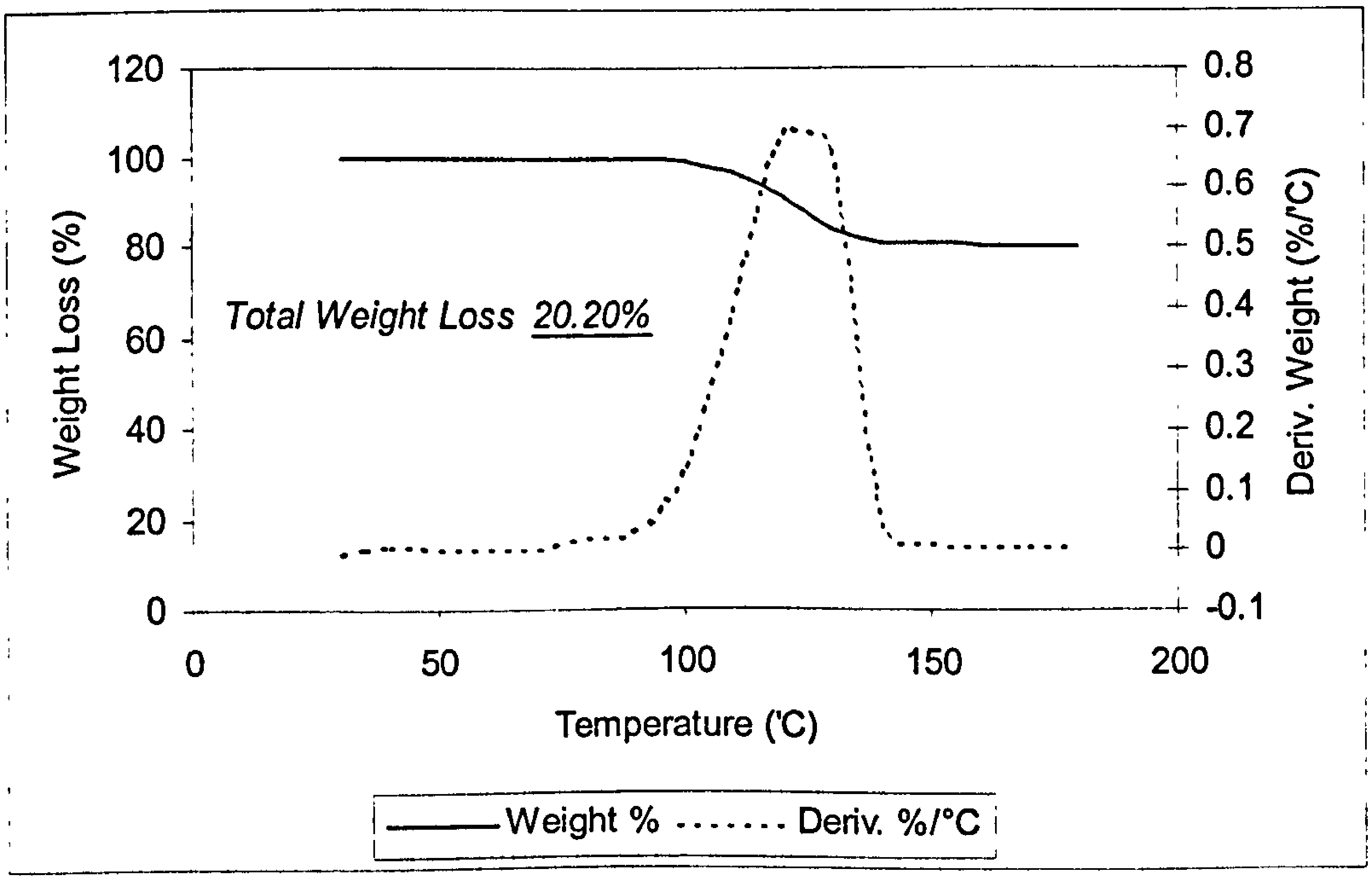


Figure 6.2 TG curves of gypsum ($CaSO_4.2H_2O$) in an open alumina crucible



A second example of dehydration is that of hydrated lime ($Ca(OH)_2$) which is used to modify and stabilise the LOC.

$$\begin{array}{lclcl}
\mathbf{Ca(OH)_2} & = & \mathbf{CaO} & + & \mathbf{H_2O} \\
\mathbf{(40 + (18x2))} & = & \mathbf{(56)} & + & \mathbf{(18)} \\
\mathbf{(74)amu} & & & & \mathbf{(18)amu}
\end{array}$$

In this case total moisture loss =18 amu/74 (total) amu = 24.32% relative to the hydrated lime molecule. Figure 8.3 shows total weight loss to be 24.49%, which appears to be in satisfactory agreement to the calculated result. However, it is only Peak 1 on Figure 6.3 that represents weight loss due to loss of water (weight loss = 20.51%). The other 3.98% weight loss (Peak 2) has occurred due to CO_2 loss, implying that the $Ca(OH)_2$ had undergone a degree of carbonation before testing. Using simple calculations, one can determine how much of the hydrated lime has carbonated.

$$\begin{array}{lclcl}
\mathbf{CaCO_3} & \rightarrow & \mathbf{CaO} & + & \mathbf{CO_2} \\
\mathbf{40+12+48} & \mathbf{56} & & \mathbf{44} & \\
\mathbf{100} & \mathbf{56} & & \mathbf{44} &
\end{array}$$

Therefore, 44 (amu)/100 (amu) = the loss of weight due to CO_2 loss is 44%. If Peak 2 shows a weight loss of 3.98%, then 3.98/44 x 100 = 9.05% $CaCO_3$. Hence, there is 90.95% $Ca(OH)_2$ in the sample tested.

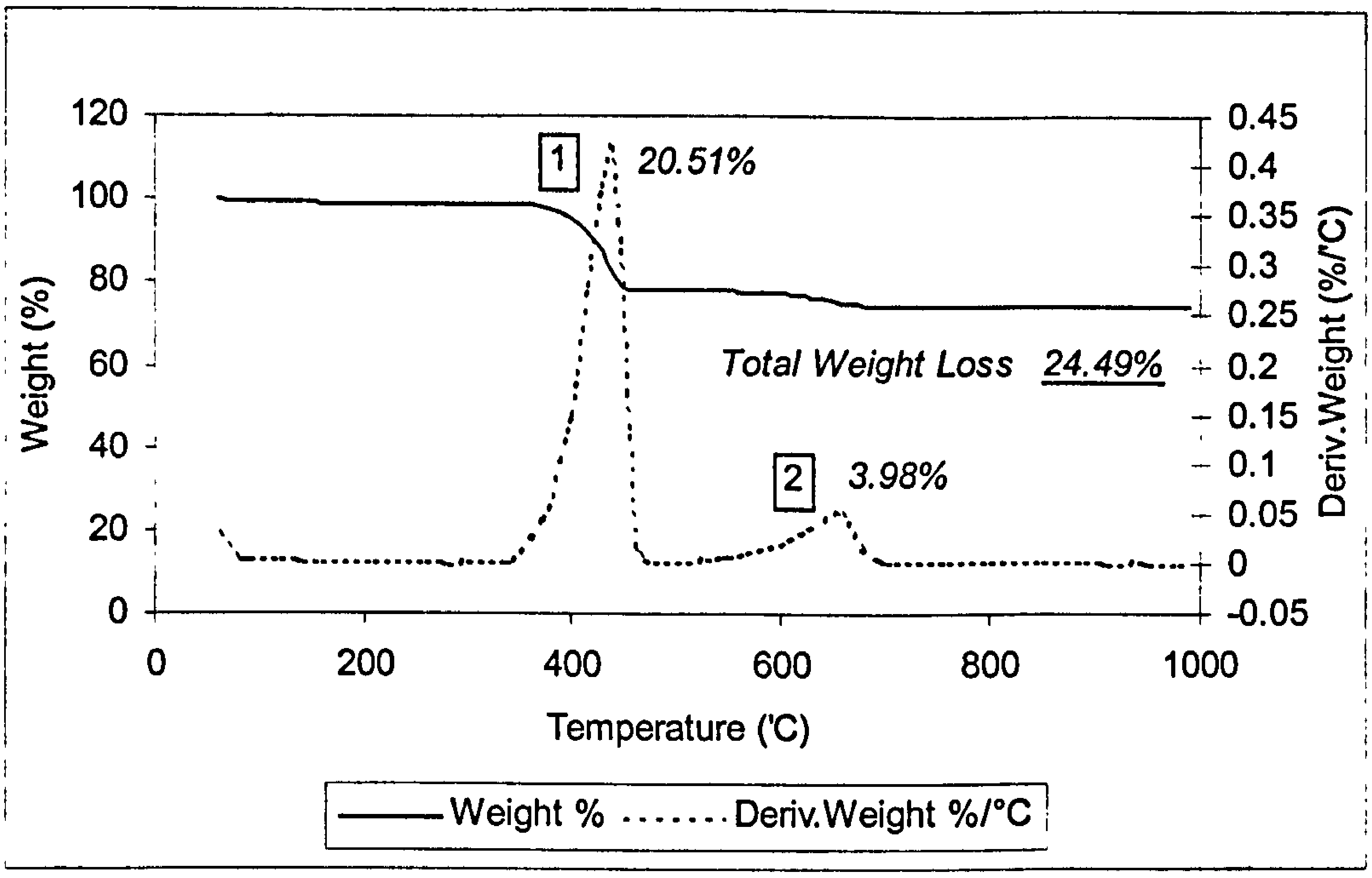


Figure 6.3 TG Curve of $Ca(OH)_2$ in open alumina crucible.

Finally an example of weight loss due to dehydroxylation of clay minerals can be seen in Figure 6.4 where standard porcelain "kaolinite" was subjected to TG analysis in an open pan crucible.

$\mathbf{Al_2O_32SiO_22H_2O}$

$\mathbf{Al_2O_3\,2SiO_22H_2O \rightarrow 2(H_2O)}$

100+120+36 → 36

256 (amu) → 36 (amu)

Therefore total weight loss of kaolinite clay minerals due to dehydroxylation is 36 (amu) / 256 (amu) = 13.51%. However Figure 6.4 shows a weight loss of kaolinite (i.e. standard porcelain) of only 10.95%. This is because the standard porcelain "kaolinite" clay used in the current work is not 100% pure and contains mica and other compounds that may lose water after heating and therefore affect the weight loss of the sample. If there is 84% kaolinite clay minerals in standard porcelain, then 84% of 13.53% (calculated total weight loss) = 11.36% (corrected calculated total weight loss), compared to a 10.95% weight loss using TG techniques. This suggests that there is in fact only 81% kaolinite clay minerals in the standard porcelain "kaolinite" clay and not 84% as given in the data provided by Imerys Group Ltd. (1987).

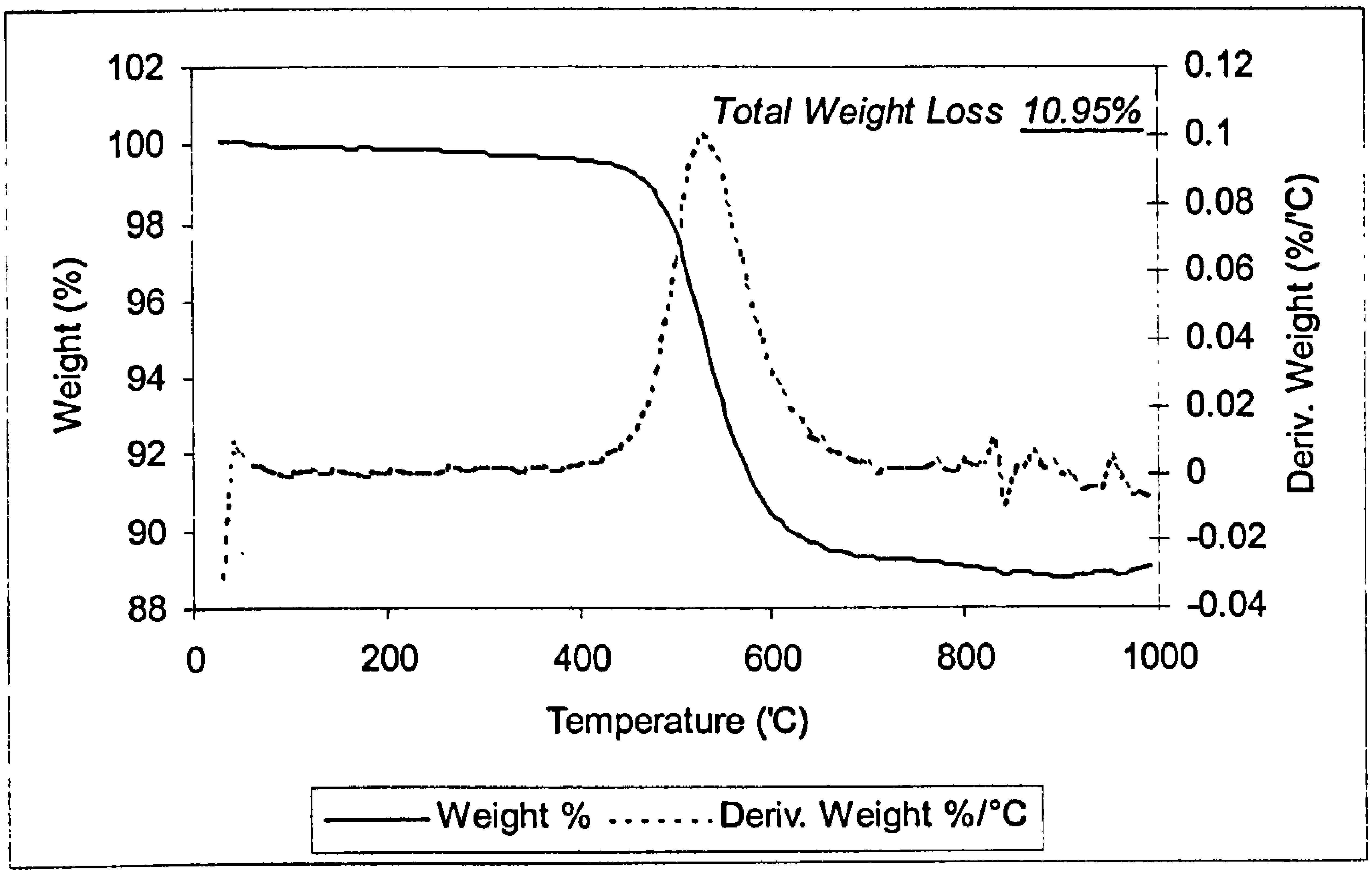
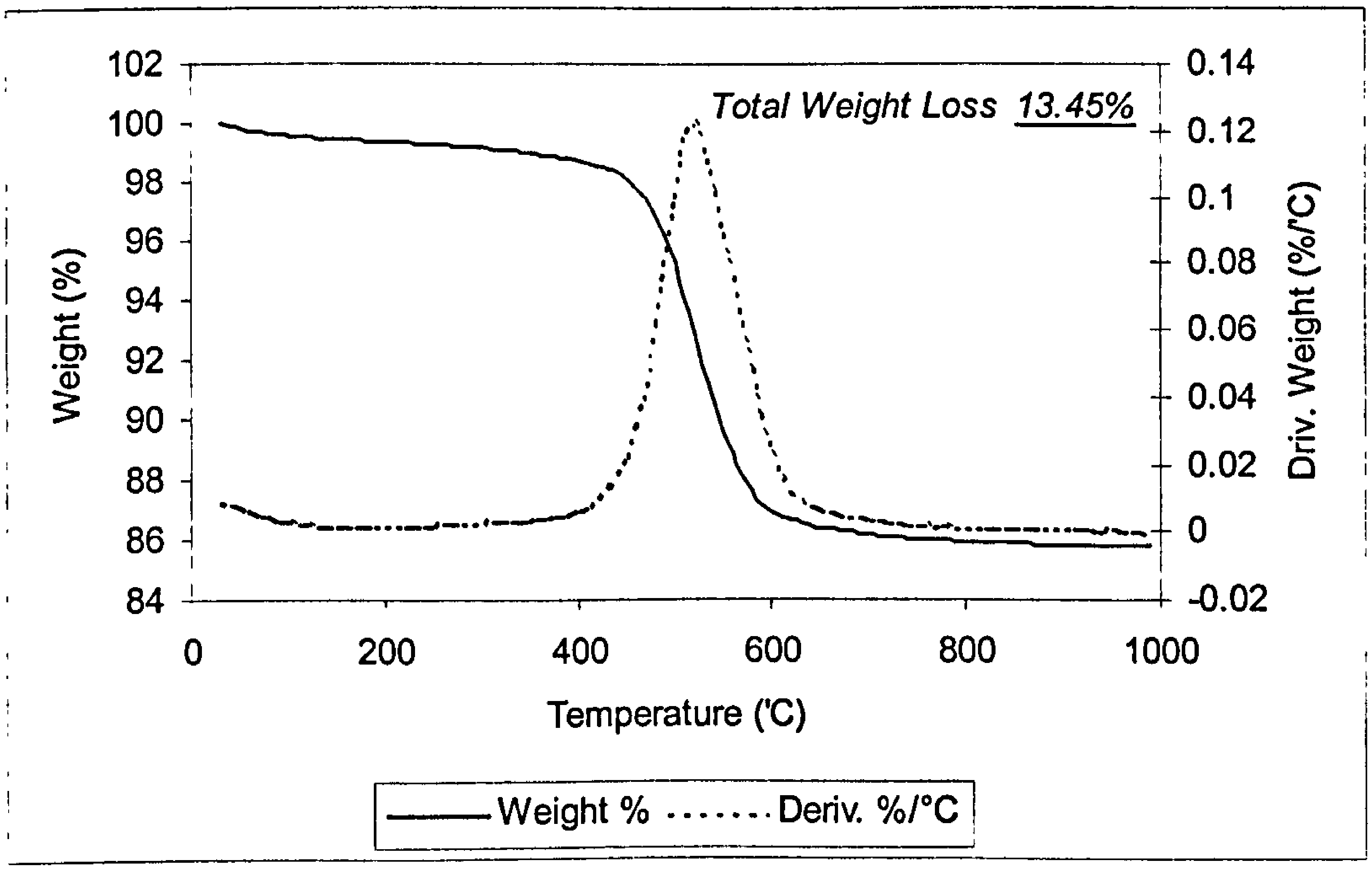


Figure 6.4 TG curves of kaolinite (standard porcelain) in an open alumina crucible

Figure 6.5 illustrates the TG trace of coarse kaolin crystals from Australia (supplied by Imerys Group Ltd.). Unlike the standard porcelain "kaolinite" (Figure 6.4), the calculated weight loss of the kaolinite clay mineral (13.51% weight loss) is almost identical to the weight loss observed in the "pure" kaolin sample (13.45% weight loss) due to dehydroxylation. This not only establishes that the standard porcelain "kaolinite" used in the current work contains less than 84% kaolinite clay minerals, but also that the TG analysis is an accurate tool in the identification of hydrous compounds such as kaolin.

Figure 6.5 TG curves of kaolin crystals (supplied by Imerys Group Ltd.) in an open alumina crucible.



Detailed thermogravimetric analysis of the LOC with varying amounts of added lime ($Ca(OH)_2$ or CaO) will allow a better understanding of the processes of mellowing and of the reactions occurring during the early curing periods. It will also enable the effect of lime addition, on the oxidation of pyrites and the subsequent formation of gypsum and ettringite during the initial period of modification, to be established.

6.9 X-ray Diffraction (XRD)

In the current work X-ray diffraction (XRD) methods were used for the observation and characterisation of crystalline clay and non-clay minerals in the LOC as well as for identification of the crystalline reaction products. XRD analysis was employed in the LOC-CaO and LOC-$Ca(OH)_2$ systems.

Each crystalline substance has its own atomic structure, which diffracts X-rays in a characteristic pattern (Barr et al, 1995). Recognition of this unique pattern establishes the diffracting substance and therefore this method is useful for the confirmation and/or identification of crystalline products. The method may be used to give a quantitative indication of phase content from the relative intensities of the adjacent diffraction lines from different crystalline components. However accurate quantitative analysis requires the use of internal standards and is made difficult by factors such as preferred orientation and line broadening which are a function of crystallite shape and size. The complete absence of diffraction lines indicates amorphous substances, which cannot therefore be quantified by this technique. In the current work XRD was used principally for phase identification, to underpin the TGA observations.

XRD may be represented by Bragg's law (Eq. 6.1). From Figure 6.6, 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 Figure 6.5 it is apparent that AB=BC=d$\sin\theta$. Consequently, length ABC = 2d$\sin\theta$. Constructive interference occurs when the X-rays scattered from the two planes are in phase. This occurs when their path difference is an integral number of wavelengths (nλ). That is when:

$$\mathbf{n\lambda = 2d\sin\theta} \text{ (Braggs Law)} \qquad \text{Eq. 6.1}$$

where: λ = X-ray wavelength

n = integer.

Crystalline phases are identified by matching the d-spacing calculated from the above equation with those from known crystalline compounds. There are certain advantages in using X-ray analysis over many 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 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.

In the current work, XRD analysis was conducted, on LOC modified/stabilised with additions of 8%$Ca(OH)_2$ or 6%CaO for a variety of curing times and environments; that is:

- a dry mix,
- an unmellowed mix,
- a mellowed mix (3 days at 20°C),

- unmellowed, compacted specimens cured for 1 week and 4 weeks at 20°C,
- mellowed, compacted specimens cured for 1 week and 4 weeks at 20°C.

Specimens with the highest lime contents used were selected in order to detect any changes in the crystalline phases present, as the technique is not sufficiently sensitive to detect very small changes. The specimens themselves were taken from the interior of compacted soil samples and dried in an oven at 50°C (±2°C) for at least 48 hours. Powdered, dried specimens used for X-ray analysis were a few grams in weight.

The work 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 1.54179 A. The specimens used for XRD work were selected to coincide with some of those used for the TGA work. The work was aimed at establishing (together with the TGA work), the influence of mellowing, curing time and lime type on the phase composition of the LOC, specifically in relation to calcium hydroxide, sulphates and ettringite.

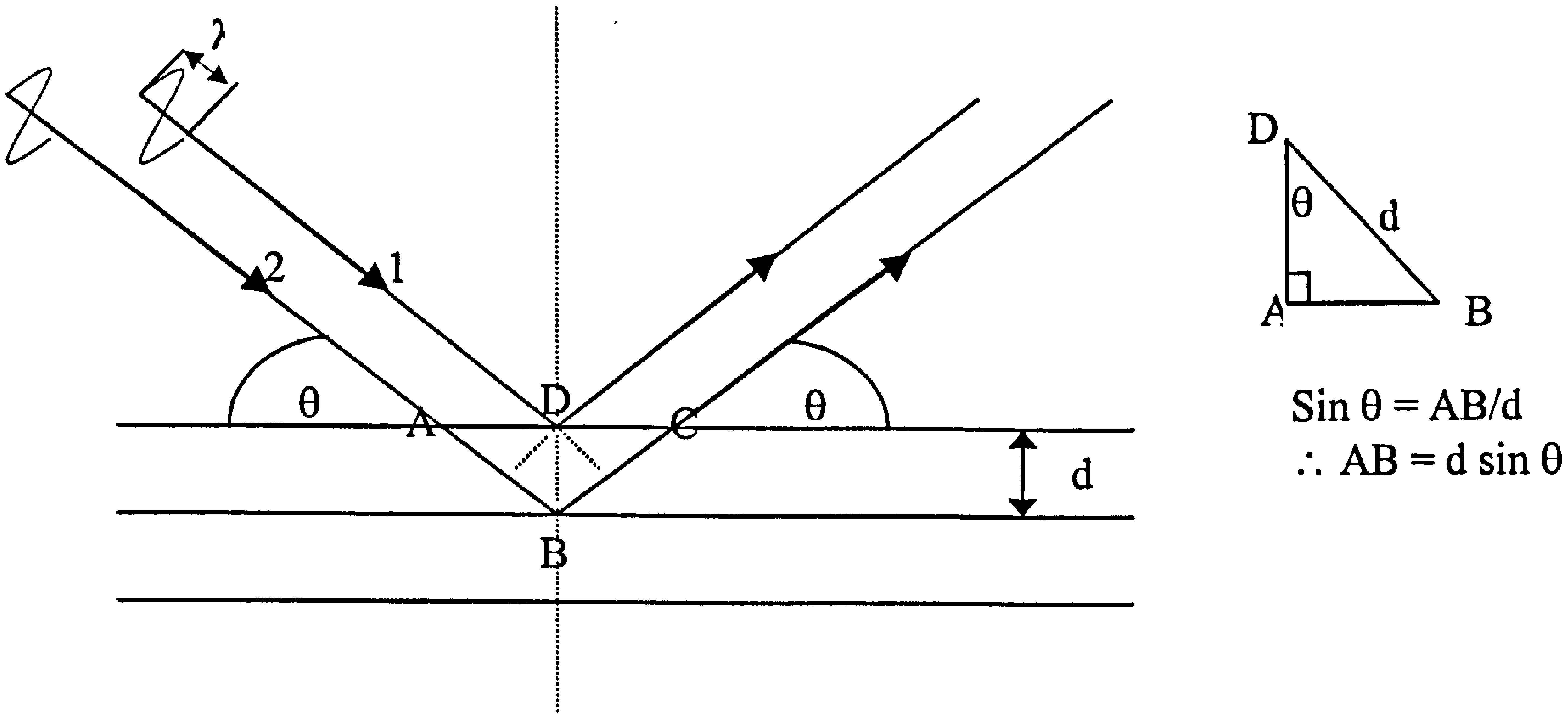


Figure 6.6 X-ray diffraction according to Bragg's Law (from Whiston, 1987).

7. Experimental Results: Lower Oxford Clay - Lime System

The experimental results of the current work are separated into two chapters. Chapter 7 deals with the interaction of Lower Oxford Clay with lime. It involves the effects of mellowing, temperature, lime content and lime type ($Ca(OH)_2$ or CaO) on the fabric and properties of Lower Oxford Clay (LOC)-lime combinations. The results are presented in Sections 7.1 to 7.7. The experimental test results include consistency (Atterberg) limits test, Proctor compaction tests, unconfined compressive strength (UCS) tests, durability tests, linear expansion tests, pH measurements and sulphate (SO_3) analysis. Also the results of the analytical tests employed (thermogravimetric analysis (TGA) and X-ray diffraction (XRD)) are presented in this chapter.
Chapter 8 deals with the stabilisation of lime-modified LOC stabilised with either GGBS or PC. It includes the results of long-term (up to 52 weeks) strength, linear expansion and durability measurements of stabilised LOC cured at various temperatures and in different environments.

7.1 Consistency (Atterberg) Limits

7.1.1 LOC-$Ca(OH)_2$ System

Figure 7.1.1 illustrates the changes in liquid limit, plastic limit and plasticity index of mellowed and unmellowed LOC with increasing additions of $Ca(OH)_2$ (2%, 4%, 6% and 8%). Mellowing was carried out for 3 days at 20°C.

The liquid limit (LL) of the LOC increased rapidly from 59% to 69% with the addition of 2%$Ca(OH)_2$ (Figure 7.1.1). Further additions of $Ca(OH)_2$ resulted in a slight overall increase in LL with the highest LL occurring after an addition of 6%$Ca(OH)_2$. Similarly, the plastic limit (PL) increased when LOC was mixed with 2%$Ca(OH)_2$ from 32% to 38% and continued to increase with increasing lime content up to 6%$Ca(OH)_2$

addition, and then a decline occurred. The LL and PL results showed an increase in plasticity index (PI) from 27% for untreated LOC to 31% when 2%$Ca(OH)_2$ was added. Further additions of $Ca(OH)_2$ resulted in reduced PI with an 8%$Ca(OH)_2$ addition producing a PI of 20%. As mentioned in chapter 3, additions of $Ca(OH)_2$ modify the consistency limits of a clay soil as the calcium from the lime causes flocculation, which enables the mixed material to incorporate a greater volume of water. Further additions of lime generally increase flocculation (and hence increase the capacity to hold water) up to a certain point. Beyond a certain lime addition it is known that lime will not continue to participate in flocculation due to calcium saturation of the clay particles. This point, when the soil has satisfied the affinity for lime is termed the lime fixation point (Hilt and Davidson, 1960). It is clear that after an addition of 6%$Ca(OH)_2$ to the LOC, the PL and LL values are reduced suggesting that the lime fixation point of the LOC is around 6%$Ca(OH)_2$.

Mellowing (3 days at 20°C) of the LOC-2%$Ca(OH)_2$ mix had little effect on the consistency limits. However, further increases of $Ca(OH)_2$ resulted in increased PL and LL up to an addition of 6%$Ca(OH)_2$, thereafter a reduction occurred. The plasticity index of mellowed LOC-4%$Ca(OH)_2$ mixes showed the highest PI (38%) primarily due to the significant increases in LL without similar increases in PL. Further additions of $Ca(OH)_2$ resulted in a reduction of PI. The PI of mellowed mixes of LOC and $Ca(OH)_2$ are generally higher than similar unmellowed mixes.

It is suggested that mellowing of clay-lime mixtures allows extra time for the clay-lime reactions (such as flocculation and the formation of various phases containing alumina, silica, calcium and if present sulphate). Therefore it is thought that mellowing would further increase the consistency limits of LOC-lime mixes due to increased flocculation and thus a greater ability to contain water. Mellowing of LOC with a small addition of $Ca(OH)_2$ has little effect on consistency limits, indicating that the added lime is consumed in reactions immediately on mixing. However, with increasing lime additions the consistency limit values (especially LL) increase as flocculation continues unhindered for 3 days. Again the addition of >6%$Ca(OH)_2$ resulted in slightly reduced consistency limits indicating that additions of $Ca(OH)_2$ in excess of 6% only result in supplying an excess of calcium to the mix.

7.1.2 LOC-CaO System

Figure 7.1.2 illustrates the changes in liquid limit, plastic limit and plasticity index of mellowed and unmellowed LOC with increasing additions of CaO (1.5%, 3%, 4.5% and 6%). For ease of comparison between Figures 7.1.1 and 7.1.2 the lime content in the latter is also presented in terms of equivalent $Ca(OH)_2$ additions. Again, mellowing was carried out for 3 days at 20°C.

The liquid limit (LL) increased from 59% to 72% when 1.5%CaO (equivalent to 2%$Ca(OH)_2$) was added to the LOC. However further additions of CaO only showed a small increase up to an addition of 4.5% (6%$Ca(OH)_2$), then a decrease was apparent. The plastic limit (PL) steadily increased when CaO was added to the LOC, with the highest PL exhibited by the LOC-4.5%CaO mix (equivalent to 6%$Ca(OH)_2$) specimen at 51%. The plasticity index (PI) of the LOC is initially increased with 1.5%CaO addition though generally a decrease was apparent with further increases in CaO content. In a similar way to the LOC-$Ca(OH)_2$ systems, a small addition of CaO to the

LOC resulted in increased consistency limits due to flocculation. However, it is apparent that values obtained using 1.5%CaO are slightly higher than those obtained when 2%$Ca(OH)_2$ is used. One fundamental difference between CaO and $Ca(OH)_2$ is the hydration of the oxide, which is a strong exothermic reaction, producing 0.882kJ/g of heat. It is suggested that as increased heat results in elevated chemical reactivity, this feature may accelerate the flocculation of the material and therefore results in increased PL and LL values. Increasing additions of CaO generally increase the LL and PL of the LOC up to an addition of 4.5%CaO (equivalent to 6%$Ca(OH)_2$). However although the increase in PL and LL is higher in LOC-1.5%CaO mixes (compared to LOC-2%$Ca(OH)_2$ mixes), further increases with increasing additions of CaO are much smaller and less pronounced (especially after mellowing), clearly indicating the flocculation is influenced by the exothermic reaction that accompanies CaO hydration.

The introduction of a mellowing period modifies the consistency limits of LOC-CaO mixes. A period of mellowing slightly increases the LL of LOC-1.5%CaO and LOC-6%CaO mixes (equivalent to 2% and 8%$Ca(OH)_2$ respectively). However additions of 3% and 4.5%CaO (equivalent to 4% and 6%$Ca(OH)_2$ respectively) showed significantly raised LL compared to unmellowed mixes. Similarly the PL of all LOC-CaO mixes is increased after mellowing, especially at lower CaO additions. The PI of LOC-CaO is generally reduced with increasing CaO contents with or without mellowing, except for the LOC-1.5%CaO in the unmellowed system. Mellowing of the LOC-CaO mixes had a similar effect on PL and LL to mellowing of the LOC-$Ca(OH)_2$ mix producing an overall increase in these parameters.

Summary

- The addition of a small amount of lime (2%$Ca(OH)_2$ or 1.5%CaO) as a soil modifier to the LOC increases LL, PL and PI of the material due to flocculation as a result of cation exchange between the lime and the clay particles present in the soil. Consistency limit values are slightly higher when CaO is used as it is thought the strong exothermic reaction that accompanies CaO hydration encourages greater flocculation [values can be found in Appendix B].
- Increasing additions of lime up to 6%$Ca(OH)_2$ or 4.5%CaO further increase the PL and LL of the LOC, but even higher additions only result in supplying an excess of calcium to the mix resulting in a slight decline in these parameters. Therefore, it is suggested that this point is the lime fixation point of the LOC.
- Mellowing (3 days at 20°C) of the LOC-2%$Ca(OH)_2$ mix has little effect on the consistency limits because the small additions of added lime react immediately with the LOC upon mixing. However, the LOC-1.5%CaO mix showed increases in both PL and LL after mellowing.
- Mellowing of the LOC with increasing additions of $Ca(OH)_2$ or CaO results in increased LL and PL values as it is thought mellowing allows extra time for increased flocculation and therefore allows the mixed material to incorporate more moisture.

7.2 Proctor Compaction Tests

7.2.1 Proctor Compaction of Lime-Modified LOC

Figures 7.2.1 and 7.2.2 illustrate the compaction characteristics (that is: the optimum moisture content (OMC) and maximum dry density (MDD)) of the LOC with and without additions of 2%$Ca(OH)_2$ or 1.5%CaO, which had been mellowed at 10°C or 20°C for either 6 hours or 3 days. Mellowing was achieved with an addition of 20wt.% water.

Increasing the mellowing time (i.e. from 6 hours to 3 days) had little effect on the optimum moisture content (OMC) of LOC-2%$Ca(OH)_2$ mixes, although OMC values were slightly greater after mellowing at 10°C than at 20°C (Figure 7.2.1(A)). Similarly, increasing the mellowing time did not appreciably affect the maximum dry density (MDD) of the mellowed LOC-2%$Ca(OH)_2$ mixes, although MDD values were less when mellowing took place at 10°C compared to 20°C (Figure 7.2.1(B)). The differences in compaction data (especially with regard to MDD) after mellowing at different temperatures suggest that higher mellowing temperatures slightly increase density. A possible explanation of this phenomenon could be that as higher temperatures encourage chemical reactivity, the formation of reaction products such as ettringite and gypsum due to pyrites oxidation may be enhanced resulting in higher MDD values. However, regardless of mellowing temperature or time, the OMC and MDD of the LOC are increased and reduced respectively when $Ca(OH)_2$ is added.

A similar pattern was observed when LOC-1.5%CaO mixes were mellowed as mellowing time had little significant effect on OMC values (Figure 7.2.2(A)). However, mellowing at 10°C resulted in slightly higher OMC values than mellowing at 20°C. MDD values of the same mixes were slightly lower when the mixes were mellowed at 10°C compared to values for mixes mellowed at 20°C (Figure 7.2.2 (B)). Again this suggests that the products of the clay-lime reaction may have slightly increased the density of LOC-lime mixes at higher temperatures. Regardless of mellowing time or temperature, the OMC and MDD values of the LOC were respectively increased and reduced with a small addition of CaO.

As stated in Section 7.1, the addition of lime to a clay soil results in the immediate structural disruption of the material due to flocculation. As the flocculated material is more friable than untreated clay then the ability to contain moisture (and therefore to reduce density) is increased when lime is added. It is thought that the slightly higher MDD values experienced at 20°C (compared to those at 10°C) may be a result of accelerated clay-lime reaction that are, over time, known to produce particular reaction products. In the LOC, pyrites (FeS_2) may affect the reaction products, as it is known that in the presence of lime, pyrite oxidation (which is accelerated in an alkaline environment) leads to gypsum formation. It is probable that the differences in density after mellowing at different temperatures are due to the formation of reaction products, which will be more crystalline and better formed at higher temperatures. The unexpected similarity in compaction data after mellowing for 6 hours and 3 days is probably a result of the small amount of lime added to the LOC. That is, after 6 hours the lime would have been consumed during the clay-lime reactions and therefore little further change in compaction values would be expected with further mellowing time.

In order to better understand the LOC-lime reaction during mellowing at 20°C, the following sections present Proctor compaction data, giving the OMC and MDD values of mellowed and unmellowed LOC mixes with increasing additions of $Ca(OH)_2$ and CaO.

7.2.2 Proctor Compaction of the LOC-$Ca(OH)_2$ System

Figure 7.2.3 (A and B) illustrates, respectively, the OMC and MDD values of the LOC with 2%, 4%, 6% and 8% $Ca(OH)_2$. either unmellowed or mellowed (6 hours or 3 days at 20°C). Mellowing was achieved with an addition of 20wt.% water.

Increases in lime content produced systematic increases in OMC and decreases in MDD in the LOC-$Ca(OH)_2$ system with the greatest differences occurring after an 8%$Ca(OH)_2$ addition to the LOC (from 27% to 28% OMC, and 1.39 Mg/m^3 to 1.36 Mg/m^3 MDD). The OMC of the LOC-lime mixes increase progressively with increase in lime content after 6 hours of mellowing and further increase after a mellowing period of 3 days for lime additions of up to 6%$Ca(OH)_2$. It should be noted that additions of lime in excess of 6%$Ca(OH)_2$ result in a slight reduction in OMC values. The converse applies for MDD values which decrease with increase in mellowing time up to an addition of 6%$Ca(OH)_2$. Further additions of lime result in little change or a slight increase in density.

7.2.3 Proctor Compaction of the LOC-CaO System

Figure 7.2.4 (A and B) illustrate, respectively, the OMC and MDD values of the LOC with 1.5%, 3%, 4.5% and 6%CaO (equivalent to 2%, 4%, 6% and 8%$Ca(OH)_2$) either unmellowed or mellowed for 6 hours or 3 days at 20°C. Mellowing was achieved with an addition of 20wt.% water. The trends are very similar to those when $Ca(OH)_2$ is added although the increases in OMC and the decreases in MDD are generally greater when CaO is used.

Although an initial addition of CaO (i.e.1.5%) increased the OMC of the LOC, further additions of CaO resulted in steadily reduced OMC values. However, after a period of mellowing (6 hours or 3 days), the OMC of the LOC generally increased with increasing lime content. The MDD of the LOC was initially reduced after a lime addition of up to 3%CaO(equivalent to 4%$Ca(OH)_2$) (to 1.35 Mg/m^3), but then increased with the LOC-6%CaO (equivalent to 8%$Ca(OH)_2$) showing an MDD of 1.355 Mg/m^3. A similar pattern was seen after 6 hours mellowing, with an initial decrease in MDD after an addition of up to 3%CaO and then a slight relative increase with further CaO additions. Further mellowing (3-days) resulted in further decreased MDD values up to an addition of 3%CaO. Further increases in CaO content showed increased density.

It is clear that increasing additions of lime to the LOC result in increased OMC values and decreased MDD values due to increased flocculation and agglomeration caused by cation exchange between the lime and the clay particles in the LOC. However, lime in excess of 6%$Ca(OH)_2$ had little further effect on the compaction characteristics of the LOC as it is thought that the reactive constituents in the LOC had been consumed, supporting the theory that 6%$Ca(OH)_2$ or 4.5%CaO is the lime fixation point of the LOC. As stated above, the LOC-CaO mixes tend to give higher OMC values and lower MDD values than the LOC-$Ca(OH)_2$ mixes. It is thought that the strong exothermic reaction that accompanies CaO hydration and produces $Ca(OH)_2$ accelerates flocculation, explaining the observed differences in compaction values. The introduction of a mellowing period elevates the OMC and decreases the MDD values as a result of increased flocculation, with increased mellowing time generally producing higher and lower OMC and MDD values respectively.

Summary

- Small additions of lime (2%$Ca(OH)_2$ or 1.5%CaO) to the LOC result in increased OMC and decreased MDD values, irrespective of mellowing time or curing temperature. However, it is apparent that the aforementioned changes in OMC and MDD values are greater when mellowing takes place at 10°C compared to mellowing at 20°C. It is thought that this feature is due to the formation of reaction products that would be more crystalline and better formed at higher temperatures.
- The similarity between the compaction data of mixes with 2%$Ca(OH)_2$ or 1.5%CaO mellowed for 6 hours or 3 days suggest that such a small amount of added lime would be consumed within the first 6 hours of mellowing and therefore little further change in compaction values would be expected with further mellowing time.
- Increasing additions of lime (up to 6%$Ca(OH)_2$ or 4.5%CaO) to the LOC resulted in increasing OMC values and decreasing MDD values. However these changes in compaction values were unaffected or slightly reversed when the lime content was

further increased. This supports the evidence from Section 7.1 that the lime fixation point of the LOC is 6%$Ca(OH)_2$ or 4.5%CaO and further additions of lime result only in supplying an excess of lime to the material. Mellowing of LOC-lime mixes generally further increases OMC values and decreases MDD values with increased mellowing time, as flocculation is thought to continue unhindered. The effects tend to peak at >6% lime addition and then stabilise or reverse slightly.

In order to further assess the role of mellowing in LOC-lime mixes, Section 7.3 compares the short-term strength development (1 and 4 weeks curing), of unmellowed and mellowed (3 days at 20°C) lime-modified LOC samples cured over a range of different temperatures. Section 7.3 also reports the influence of increasing additions of $Ca(OH)_2$ on the strength development of the LOC, again over a range of different temperatures.

7.3 Unconfined Compressive Strength (UCS)

7.3.1 UCS of Lime-Modified LOC

Figure 7.3.1 (A-D) presents the unconfined compressive strength (UCS) data for 50ϕx100mm cylindrical specimens consisting of LOC modified with 2%$Ca(OH)_2$ or 1.5%CaO, both unmellowed and mellowed (3 days at 20°C) and cured for 1 or 4 weeks at 5°C, 10°C and 20°C. Mellowing was carried out for 3 days at 20°C after an addition of water (OMC). The cylinders were compacted at their respective MDD (Section 7.2) and at a moisture content of 32%.

Although the highest strength occurred in the unmellowed samples at 20°C, curing temperature and mellowing has little overall effect on the UCS of LOC-2%$Ca(OH)_2$ samples after a curing period of 1 week, with no UCS value found in excess of 350kN/m^2 (Figure 7.3.1 (A) [Appendix B]). Further curing (4 weeks) generally resulted in increased UCS development, with the unmellowed samples consistently exhibiting higher strengths than similar mellowed samples (Figure 7.3.1 (B)). Similar behaviour was observed when the LOC was modified with 1.5%CaO, although after 1 week curing, the strength of mellowed material exceeded that of the unmellowed material, especially at 5°C (Figure 7.3.1 (C)). After 4 weeks curing the strength was, overall, increased with the unmellowed LOC-1.5%CaO samples generally showing higher strengths compared to similar mellowed samples, although a reduction in strength was apparent at 5°C (Figure 7.3.1 (D)). Generally no UCS values were in excess of 400 kN/m^2.

It is clear that although extended curing time generally results in greater strength development of lime-modified LOC, especially after curing at 20°C compared to similar samples cured at 5°C, the changes are relatively small and not very systematic. This is attributed to the fact that only a small amount of lime was added to these specimens, and there is an immediate adsorption of lime by the clay particles, which produces flocculation (as explained in Sections 7.1 and 7.2). Also if sulphates are present rapid reaction might be expected to form gypsum and/or ettringite. Curing time allows the formation of various C-S-H gels and C-A-H phases due to pozzolanic reactions between the clay particles and the added lime. However, at these small levels of lime addition it is thought that there is insufficient lime remaining (after flocculation and the formation of initial reaction products) to provide any significant pozzolanic activity. It is therefore difficult to interpret the effect of mellowing on the strength development of compacted, lime-modified samples as the amount of added lime is probably insufficient to form adequate cementing gels and phases after the initial, rapid flocculation and interaction of the mixed material. Therefore, the UCS of the LOC was also investigated for increasing additions of $Ca(OH)_2$ in the mix. The results are presented in the following Section.

7.3.2 UCS of the LOC-$Ca(OH)_2$ System.

Figure 7.3.2 (A-D) and 7.3.3 (A-D) illustrate the UCS of unmellowed and mellowed (3 days at 20°C) LOC with increasing addition of $Ca(OH)_2$ (2%, 4%, 6% and 8%) after curing at 5°C, 10°C and 20°C for periods of 1 and 4 weeks respectively. Samples were compacted at their relevant MDD and at a moisture content of 32%.

Strength generally increased with increasing lime content and increasing temperature, with the greatest 1 week strength exhibited by the mellowed LOC-8%$Ca(OH)_2$ sample at 20°C (703 kN/m^2), and after 4 weeks in the unmellowed LOC-8%$Ca(OH)_2$ sample cured at 20°C (955 KN/m^2). The increase in strength with increasing temperature is not surprising as it is known that higher temperatures encourage more rapid reactions and better-formed cementitious products (i.e. C-S-H gels and C-A-H phases) and therefore superior strengths. The amount of added lime also affects the strength development of clay soils as the addition of increased calcium ions usually results in an increased volume of cementitious reaction products. However, this is dependent on the volume of pozzolanic material present in the clay soil because if the critical amount of available calcium ions to react with the available pozzolanic material is exceeded, then little further strength gain will be achieved by increases in lime content. As stated earlier the increase in UCS with time and with temperature is negligible when 2%$Ca(OH)_2$ is added to the LOC as clay containing such small additions of lime shows modification but little stabilisation because there is insufficient lime to produce significant amounts of cementitous reaction products.

A feature of the test results is that after 1 week of curing it is the mellowed samples that generally show the higher strengths compared to the unmellowed samples. However, after 4 weeks curing the reverse is usually the case where unmellowed samples are generally stronger than mellowed samples. Therefore, the processes and reactions between the lime and the LOC that take place during mellowing contribute to the early strength of lime modified LOC, but are superseded by other reactions (probably pozzolanic reactions) with increasing time. The addition of lime to a sulphate-bearing clay soil (such as the LOC) is known to react with pozzolanic material and the sulphate to form ettringite, which in itself is known to contribute to the early strength of PC mortars and is the principal strength-giving phase in super-sulphated cement (SSC). It is thought that the mellowing period would encourage crystalline ettringite formation in LOC-lime mixes, explaining the mellowed samples' superior strength development after 1 week's curing. However, this process (ettringite formation) will consume calcium ions introduced to the mixture by the lime. Therefore it is probable that this calcium depletion in mellowed samples will result in inferior strengths when compared with unmellowed samples after 4 weeks curing, as the strength giving gels and phases must be less in volume. Thus, it is probable that mellowed lime-modified LOC samples would show lower strengths compared to unmellowed samples after longer curing periods. In addition, in the unmellowed samples the initial ettringite formation reaction is known to be expansive which could depress the early strength gain in the unmellowed material, whereas in the mellowed material a significant part of the ettringite forming reaction would have been completed during the mellowing period.

Summary

- Increased curing time and increased curing temperature generally results in increased unconfined compressive strength (UCS) values for lime-modified (2%$Ca(OH)_2$ or 1.5%CaO) LOC samples, although the changes are small and non-systematic. Therefore the increases in UCS with time and temperature, and the differences between mellowed and unmellowed samples are difficult to interpret because such small additions of lime show modification but little stabilisation, as there is insufficient lime to produce significant amounts of cementitious reaction products.
- The addition of increasing amounts of $Ca(OH)_2$ to the LOC results in increased strength development. After 1 week curing, UCS values are greater for samples that have undergone a period of mellowing (3 days at 20°C) than for unmellowed samples.
- However, after 4 weeks curing it is generally the unmellowed samples that exhibit higher UCS values. It is thought that during mellowing crystalline ettringite is formed, which will contribute to the early strength of the material. However, this process consumes calcium ions, which are required in the formation of the various strength giving gels and phases over time. Therefore it is probable that unmellowed lime-stabilised LOC samples would show slightly higher strengths after longer curing periods than similar mellowed samples. In addition the early stages of

ettringite formation are expansive which may retard early strength gain in unmellowed samples.

The previous sections have established that when LOC-lime mixes have undergone a period of mellowing (for 3 days at 20°C) prior to compaction and subsequent testing then significant changes in Atterberg (consistency) limits, Proctor compaction values and short term strength development (UCS) occur compared to similar unmellowed mixes. It is thought that these changes are the result of increased flocculation and the formation of various reaction products as a consequence of the clay-lime reactions. As stated earlier (Chapter 3), expansion due to sulphate attack is common in lime-stabilised clay soils. Section 7.4 examines the role of mellowing and pyrite oxidation on the expansion characteristics of lime-stabilised Lower Oxford Clay.

7.4 Linear Expansion, pH Measurements and SO_3 Analysis

7.4.1 Lime Modified LOC

7.4.1.1 Linear Expansion

Figures 7.4.1 and 7.4.2 illustrate the linear expansion of LOC with additions of 2%$Ca(OH)_2$ and 1.5%CaO in four differing soaking environments; a static soaking environment at 20°C (Figure 7.4.1 (A)); an aerated soaking environment at 20°C (Figure 7.4.1 (B)); an aerated soaking environment at 20°C where the samples have been mellowed for 3 days at 20°C before compaction (Figure 7.4.2 (A)); and an aerated environment, stored at 5°C, where the samples have been mellowed for 3 days at 20°C

(Figure 7.4.2 (B)). Before soaking, a curing period of 7 days was employed in all cases. Mellowing was achieved with a moisture addition at OMC. The cylinders were compacted at their respective MDD values (Section 7.2) and at a moisture content of 32%.

When, after a 7-day curing period, soaking water saturates compacted LOC-lime samples, linear expansion is immediate regardless of lime type, soaking environment and temperature (Figure 7.4.1 (A-B) and Figure 7.4.2 (A-B)). During the first 7-14 days of soaking, expansion is rapid in all CaO and $Ca(OH)_2$ modified specimens and thereafter expansion continues at a reduced rate (Figure 7.4.1 (A)). The pattern and rate of linear expansion of the LOC-2%$Ca(OH)_2$ and LOC-1.5%CaO samples varied somewhat when soaked in a static environment, where the LOC-2%$Ca(OH)_2$ sample showed slightly greater "ultimate" expansion (8% expansion at 105 days) than the LOC-1.5%CaO sample (6% expansion at 105 days). Soaking in aerated water (Figure 7.4.1 (B)) had little effect on the expansion characteristics of the samples, compared to soaking in a static environment. However, a period of mellowing before compaction results in reduced expansion in both mixes (3.9% expansion at 105 days) (Figure 7.4.2 (A)). Lowering the soaking temperature to 5°C resulted in slightly increased expansion in both samples (Figure 7.4.2 (B)). Maximum expansion was observed in the LOC-2%$Ca(OH)_2$ sample as it expanded by almost 10% after 110 days. In general, the expansion patterns of the CaO and $Ca(OH)_2$ modified LOC samples were very similar throughout the test, implying that lime type, at these low lime additions, had little effect on the linear expansion of the LOC. The observation that mellowing produces a significant reduction in expansion indicates that chemical reaction during the mellowing period is a critical factor influencing subsequent expansion. It is thought that the mellowing process consumes calcium ions, firstly during flocculation of the mixed material and secondly in the formation of ettringite. If this is the case the sulphate ions will also be consumed by the process of ettringite formation, resulting in lower available sulphate ions in mellowed samples (compared to unmellowed samples) when saturated with water. It is known that ettringite formation in the presence of excess water will lead to expansion and deterioration of lime-stabilised clay soils. Therefore it is probable that the reduced expansion apparent in mellowed compacted, lime-modified LOC samples is a result of calcium and sulphate depletion due to the formation of crystalline ettringite during the mellowing period. This subsequently reduces ettringite formation and therefore expansion upon soaking. Another theory to explain reduced expansion in mellowed LOC-lime samples compared to unmellowed samples could be due to the reduction in density (and therefore increased porosity) of the mellowed material, as seen in Section 7.2. Mellowing allows ettringite to form unhindered in a less restricted environment, thus causing less disruption and expansion. The increased expansion of lime-modified LOC when tested at 5°C may be due to the insufficient production of cementitious products at lower temperatures, resulting in lower strength and therefore less resistance to expansive reactions. However, Figure 7.3.1 (A) and (C) show that the differences in UCS values after 1 week's curing (i.e. the curing period before saturation in the expansive test) between the mellowed samples cured at 5°C and 20°C are not significantly different. The 7-day curing period prior to soaking does allow ettringite to form (as it does during mellowing) in a moist rather than a saturated environment where it is much less expansive. Thus, material cured at 20°C where reaction is more rapid will expand less on soaking than material cured at 5°C.

7.4.1.2 Sulphate (SO_3) Analysis of Lime-Modified LOC

Figure 7.4.3 (A-D) shows the SO_3 content of the LOC-2%$Ca(OH)_2$ and 1.5%LOC-CaO samples that have been subjected to the linear expansion experiments outlined in Section 7.4.1.1. The SO_3 contents of the samples were determined after a 7-day moist curing period, after 14 and 105 days soaking (21 days and 112 days as shown on the figures).

The total sulphur content of the LOC was determined as 2.45% and the SO_3 content as 0.97% as determined by BS 1377 (Chapter 6). Therefore the potential additional SO_3 of the LOC, if all the sulphur is oxidised is:

Total S x (amu of SO_3 / amu of S) – Determined SO_3

2.45 x (80/32) – 0.97 = <u>5.14</u>%

Thus, if all S (sulphur) as sulphide or organic sulphur was to convert to SO_3, then the total potential SO_3 that could be provided by the LOC= <u>6.12</u>% (i.e. 5.14 + 0.97)

A mellowed, compacted sample of LOC without any added lime which was cured for 7 days at 20°C (i.e. the curing period before moisture is added during linear expansion experiments), was found to have an SO_3 content of 0.88% (i.e. the SO_3 content at zero lime addition in Figure 7.4.3 (A-D)), which within the expected variability of the LOC, is the same as that determined for the untreated uncompacted LOC (0.97% SO_3). This illustrates that the sulphate level of the LOC does not increase when mixed with water, compacted and cured for 7 days. The addition of lime to the LOC resulted in a marked increase of the SO_3 content after 7 days curing from 0.88% to 1.53% for the LOC-2%$Ca(OH)_2$ sample, and to 2.32% for the 1.5%CaO sample (Figure 7.4.3 (A-B)). Mellowing of similar samples, again cured for 7 days, showed increased SO_3 content with the LOC-2%$Ca(OH)_2$ and LOC-1.5%CaO samples increasing to 1.92% and to 2.11% respectively (Figure 7.4.3 (C-D)).

Soaking the lime-modified LOC samples for 14 days (21 days into the test) resulted in further substantial increases in SO_3 content. Surprisingly however, after prolonged soaking periods, not only was the total potential SO_3 content of the LOC not achieved, but also the SO_3 content reduced substantially when aerated water constituted the soaking water. Soaking in a static environment for 14 days resulted in an increase in SO_3 content of the LOC-2%$Ca(OH)_2$ samples from 1.53 (7days) to 2.86% (at 21 days) (Figure 7.4.3 (A)). However the LOC-1.5%CaO samples decreased in SO_3 content from 2.32% to 1.46% over the same period. Only a relatively small reduction in SO_3 content was observed in both samples after 105 days to 2.22% and 1.06% respectively. Soaking in aerated water for 14 days consistently raised the SO_3 content of the 1.5%CaO samples to above 4% whereas the SO_3 content of the LOC-2%$Ca(OH)_2$ sample increased by a lesser degree. In all tests SO_3 contents did not reach the total potential value of 6.12% and in the tests involving aerated soaking water at 20°C, SO_3 values were reduced to below 2% after 105 days (112 days into the test).

In an attempt to explain the phenomenon of reduced SO_3 contents after soaking in aerated water, data from thermogravimetric analysis (TGA) of the mellowed LOC-2%Ca(OH) and LOC-1.5%CaO samples soaked in aerated water was undertaken at various stages of the expansion test (i.e. after 3 days mellowing, after 7 days moist curing; after 14 days soaking and after 105 days soaking). It was found that the gypsum content increased during the mellowing period, but during curing and subsequent soaking the gypsum content (expressed as a percentage of the LOC) fell in both samples (Figure 7.4.4 (A)). However, the calcium carbonate ($CaCO_3$) content of both samples fell during the mellowing period but increased to a maximum level of 17.3% after 108 days soaking (Figure 7.4.4 (B)). This suggests that during mellowing gypsum was formed at the expense of calcium carbonate due to the oxidation of pyrites (FeS_2) in the soil. This is common in clay soils containing pyrites (Russell and Parker (1970); Hawkins and Pinches (1987); Hawkins and Wilson (1990)) as oxidised pyrites produces weak sulphuric acid:

$$2FeS_2 + 2H_2O + 7O_2 \quad \rightarrow \quad 2FeSO_4 + 2H_2SO_4$$

The sulphuric acid will then attack calcite (calcium carbonate) in the soil to form gypsum:

$$H_2SO_4 + CaCO_3 + H_2O \quad \rightarrow \quad CaSO_4.2H_2O + CO_2$$

However, with prolonged soaking in aerated water, surprisingly the calcium carbonate content increases whilst the gypsum content decreases or remains stable.

In order to understand the reactions and processes at work throughout the expansion experiments on lime-modified LOC, especially during the mellowing period, it is necessary to introduce a greater volume of lime to the LOC. The following section compares the linear expansion, pH measurements and SO_3 values of LOC with increasing additions of $Ca(OH)_2$.

7.4.2 Lime-Stabilised LOC - Linear Expansion, pH Measurements and SO_3 Analysis of LOC-$Ca(OH)_2$ samples.

Figures 7.4.5–7.4.8 (A) illustrate the linear expansion of LOC with various additions of $Ca(OH)_2$ (2%,4%,6% and 8%) which were subjected to soaking in a variety of environments and temperatures. Secondly, Figures 7.4.5–7.4.8 (B) show the pH values of the soaking waters containing the various compacted samples. Finally Figures 7.4.5–7.4.8 (C) illustrate the changes in SO_3 content of the various samples after moist curing (7 days), after soaking for 14 days and after soaking for 105 days (21 and 112 days on the figures). In addition Figure 7.4.9 shows the changes in pH of the soaking water from the unmellowed LOC-8%$Ca(OH)_2$, in which the air that was bubbled through the soaking water was first passed through a sealed flask containing soda lime or "carbsorb" to remove CO_2 prior to bubbling.

7.4.2.1 Unmellowed Samples in a Static Soaking Environment 20°C

Expansion: Expansion of compacted lime-stabilised LOC cylinders when soaked in a static environment after 7 days curing, was immediate with all samples showing the same rate of expansion over the first 7 days soaking (14 days into the test) (Figure 7.4.5 (A)). After 21 days soaking the sample containing the greatest $Ca(OH)_2$ content exhibited the greatest linear expansion, with samples expanding between 6.1% and 9% respectively for samples containing between 2% and LOC-8%$Ca(OH)_2$. Expansion slowed down after about 50 days in all samples and thereafter was minimal. The greatest and least amount of linear expansion, at the end of the test (after 105 days soaking), was 8.1% and 15.5% in, respectively, the LOC-2%$Ca(OH)_2$ and LOC-8%$Ca(OH)_2$ samples.

pH: The pH of the static soaking waters containing LOC-$Ca(OH)_2$ samples showed increased values after 7 days soaking, with, as expected, higher pH values occurring in samples containing higher amounts of $Ca(OH)_2$ (e.g. LOC-2%$Ca(OH)_2$ sample – pH 10.5, 8%$Ca(OH)_2$ - pH12.5) (Figure 7.4.5 (B)). A reduction in pH of around 1.5 was then observed in all soaking waters after a further 7 days soaking, though further soaking increased the pH of the soaking waters between 1 and 2 pH. This pH level was then maintained for 70 days whereupon a slight decrease in pH occurred. The pH monitoring of the soaking water containing the LOC-4%$Ca(OH)_2$ sample was terminated after 77 days as the sample expanded beyond the limit of the expansion cell and was therefore open to the air, though linear expansion could still be monitored.

SO_3 Content: As previously established (Section 7.4.1.2), the SO_3 content of the LOC to which 1.5%CaO or 2%$Ca(OH)_2$ had been added increased substantially after a period of curing (7 days) and subsequent soaking. In these experiments up to 8%$Ca(OH)_2$ was added to the LOC. Soaking of unmellowed, compacted LOC samples with various additions of lime in a static environment for 14 days resulted in a further increase in SO_3 content (Figure 7.4.5 (C)). Also sulphate content was generally higher at higher lime contents with the highest SO_3 content displayed by the LOC-8%$Ca(OH)_2$ sample (3.9%). After 105 days soaking (112 on the figure) in a static environment the SO_3 content of the stabilised LOC samples showed either further increases or in two cases a slight decrease but still maintained values in excess of 2%. In fact, the LOC-6%$Ca(OH)_2$ samples showed a substantial increase in SO_3 (to 5.55%). This increase in

SO_3 content must be due to pyrites oxidation as discussed in Section 7.4.1.2. Clearly, even in a static system, there is sufficient oxygen available to provide substantial oxidation and the maximum SO_3 value obtained (5.8%) is only slightly below the maximum potential SO_3 content of 6.12%.

7.4.2.2 Unmellowed Samples in an Aerated Soaking Environment at 20°C

Expansion: Soaking compacted samples of LOC with various additions of $Ca(OH)_2$ in aerated water generally resulted in slightly increased expansion compared to samples soaked in a static environment, except for the LOC-2%$Ca(OH)_2$ sample which showed slightly less expansion (Figure 7.4.6 (A)). However, Figure 7.4.1 shows the opposite with the LOC-2%$Ca(OH)_2$ samples soaked in aerated water expanding less than similar samples in static water. The reason for this must simply be due to sample variability, rather than increased expansion due to chemical reactions. The greatest expansion was seen in the LOC-6%$Ca(OH)_2$ sample (16.3%) after 105 days soaking. Although the object of soaking samples in aerated water was to artificially oxidise the pyrites present in the LOC and hence increase sulphate levels, it would appear from both the sulphate analyses and the expansion measurements that there is adequate oxygen available in the static system to oxidise most if not all of the pyrites.

pH: Soaking of the various samples in aerated water produced a rather different pH pattern compared to the static soaking waters (Figure 7.4.6 (B)). The maximum pH of the soaking waters occurred after 14 days soaking, with the LOC- 4%, 6% and 8%$Ca(OH)_2$ samples showing pH values of around 12.5, whilst the LOC-2%$Ca(OH)_2$ sample exhibited a maximum pH of 9. Further soaking resulted in gradually decreased pH values until 56 days, whereupon all soaking waters showed pH values of neutral (7) until the end of the test. As the patterns of the static and aerated soaking waters varied so dramatically, a separate test was undertaken to establish the effects of aerating the water with specific regard to atmospheric CO_2 on pH values. Figure 7.4.9 compares the pH values of the aerated soaking water containing LOC-8%$Ca(OH)_2$ sample, with the pH values of similarly aerated soaking water where the air had first been passed through a sealed flask containing soda lime or "carbsorb" prior to its introduction to the water in order to remove CO_2 from the system. The figure clearly shows that the pH values of the CO_2-free water remain at around 12.4pH whereas the CO_2-rich water displayed an obvious decline in pH. It would appear therefore that it is the carbonation of the soaked samples that is resulting in the marked decline of the pH after 30 to 40 days of soaking.

SO_3 Content: Soaking of the various lime stabilised LOC samples for 14 days in aerated water resulted in increased SO_3 content (Figure 7.4.6 (C)). The LOC-8%$Ca(OH)_2$ sample again exhibited the highest increase in SO_3 content (from 2.0% to 3.9%). However, the SO_3 contents of the LOC-2% and 4%$Ca(OH)_2$ samples after 122 days soaking dropped to values below that of the 7 day cured unsoaked sample and the value for the LOC-8%$Ca(OH)_2$ sample decreased from 3.9% to 2.6%. Although the LOC-6%$Ca(OH)_2$ sample showed a slight increase in SO_3 content and exhibited the highest value at 105 days soaking (3.3%), the value was substantially less than the 5.5% exhibited by the sample soaked in a static environment (Figure 7.4.5 (C)).

7.4.2.3 Mellowed Samples in an Aerated Soaking Environment at 20°C

Expansion: Mellowing of LOC-$Ca(OH)_2$ samples prior to compaction resulted in reduced expansion in all samples soaked in aerated water, with the greatest reduction in expansion due to mellowing occurring in the LOC-6%$Ca(OH)_2$ sample after 105 days (from 16.3% to 9.7% expansion) (Figure 7.4.7 (A)). The expansion profile of the LOC-8%$Ca(OH)_2$ mix showed renewed expansion after 50 days, at which point the sample expanded beyond the limit of the expansion cell and thereafter expansion measurements were terminated. The expansion characteristics of the LOC with 4% and 6% $Ca(OH)_2$ additions were very similar throughout the test (between 9.5% and 10% expansion after 105 days). The 2%$Ca(OH)_2$ mix showed good dimensional stability after 40 days of the test.

pH: The introduction of a mellowing period before compaction and subsequent soaking (3 days at 20°C) further modified the pH of the aerated soaking waters, as maximum pH was not observed until after 35-42 days soaking with the waters containing the higher amounts of lime again displaying the highest pH values (Figure 7.4.7 (B)). The maximum pH values for the aerated water containing mellowed samples of LOC and 2%, 4%, 6% and 8% $Ca(OH)_2$ were 7.5, 9.5, 11.5 and 12.5 respectively. A decline in pH value was then observed after 56 days, and after 84 days the pH values of all soaking waters were neutral (7) until the completion of the test.

SO_3 Content: Mellowing (3 days at 20°C) of samples before compaction resulted in generally reduced SO_3 increases after soaking in aerated water for 14 days compared to similar unmellowed samples (Figure 7.4.7 (C)). For LOC samples containing 2% and 4%$Ca(OH)_2$ the increase after soaking was <0.5% SO_3, whereas for samples containing 6% and 8%$Ca(OH)_2$ the increase after the same soaking time was >1% SO_3. After soaking for 105 days, a noticeable decrease in SO_3 content was observed in all samples so that regardless of lime content, the %SO_3 was found to be less than before soaking (between 1.1% and 1.7%). It is probable that the carbonation of the lime and the subsequent drop in pH values, which is known to lead to ettringite decomposition and the leaching of sulphate ions into the soaking waters, was achieved more effectively in the less dense, more porous mellowed specimens explaining the significant reduction in SO_3 levels compared to unmellowed samples.

The three soaking environments (static, aerated, and aerated and mellowed) have shown markedly differing pH value patterns, even though the samples are essentially of the same compositions (i.e. LOC-lime). It is thought that CO_2 introduced into the soaking waters via the aeration process is responsible for the reduction of pH values when samples are soaked in aerated environments. The CO_2 will carbonate the lime present in the sample and therefore lower the pH value, simultaneously providing an unstable environment for ettringite and ultimately causing ettringite decomposition. It is interesting to note that the pH values of all aerated samples "level-off" at a value of neutral (7), the pH value of gypsum in solution (Figure 5.1). It is thought that the pH values of the mellowed LOC-$Ca(OH)_2$ mixes exhibit a slightly different trend as they are less dense than the unmellowed samples (Section 7.2) and therefore have a higher porosity, explaining the gradual "build up" in pH levels as it simply took longer for the OH ions to diffuse into the surrounding water. The higher porosity of the material would also explain the marked drop in pH when the $Ca(OH)_2$ was eventually completely carbonated.

7.4.2.4 Mellowed Samples in an Aerated Soaking Environment at 5°C

Expansion Lowering the temperature of the soaking environment from 20°C to 5°C resulted in very rapid initial expansion and then collapse (Figure 7.4.8 (A)). In fact the magnitude of expansion prior to failure, even for specimens with low lime content was similar to that of the mellowed LOC-8%$Ca(OH)_2$ sample after 50 days soaked at 20°C in aerated water. (Figure 7.4.7 (A)) After 14 days soaking all samples failed (i.e. collapsed), indicating very poor cementation coupled with excessive expansion.

pH:, It is difficult to interpret the pH values of the aerated soaking waters of the mellowed samples stored at 5°C (Figure 7.4.8 (B)) because the lime stabilised LOC samples failed after only 3 weeks soaking. The pH patterns of the LOC with 6% and 8% $Ca(OH)_2$ showed slightly higher values after less soaking time in this test compared to the soaking waters containing similar samples stored at 20°C.

SO_3 Content: When the soaking temperature was reduced from 20°C to 5°C (Figure 7.4.8 (C)), the SO_3 content of mellowed, compacted and cured LOC-lime samples, soaked in aerated water (14 days), increased even further. The LOC samples containing 2% and 4%$Ca(OH)_2$ increased their SO_3 content by increments of about 1.3% (from 2% and 1.4% to 3.2% and 3.2% respectively), whilst the samples containing 6% and 8%$Ca(OH)_2$ increased by increments of about around 3.5% (from 1.4% to 4.9% and 4.8% respectively) after 14 days soaking at 5°C. Because the soaked specimens failed after less than 3 weeks soaking, the long-term changes in SO_3 content could not be determined.

Summary

- On soaking after 7 days moist curing, linear expansion of lime-modified LOC samples (either 2%$Ca(OH)_2$ or 1.5%CaO) was immediate regardless of the soaking environment.
- An addition of lime (either 2%$Ca(OH)_2$ or 1.5%CaO) to the LOC resulted in increased SO_3 levels after mellowing (3 days at 20°C and 7 days moist curing at 20°C) due to the oxidation of pyrites.
- Increases in lime content to the LOC generally resulted in increased linear expansion, increased pH levels of the surrounding waters and increased SO_3 contents after soaking.
- Other than at high lime contents, aerating the surrounding soaking waters of lime-stabilised LOC samples produced a marked fall in measured SO_3 contents at extended soaking times to levels below that prior to soaking. Also the introduction, as a result of aeration, of CO_2 into the soaking waters resulted in a marked fall in pH values after 56 days soaking.
- A period of mellowing (3 days at 20°C) prior to compaction of LOC-lime samples resulted in reduced linear expansion and in lower sulphate contents during soaking.
- A drop in temperature from 20°C to 5°C resulted in a significant increase in measured sulphate values after 14 days soaking and an increase in the initial expansion experienced on soaking.
- The observations establish that increased lime content and reductions in temperature produce increased expansion. Also, aerating the soaking water has limited influence

on expansion, and mellowing substantially reduces expansion of the Lower Oxford Clay (LOC).

7.5 Durability Index (DI)

7.5.1 LOC-$Ca(OH)_2$ System

Figure 7.5.1 (A and B) shows the durability index (DI) of the LOC with various percentage additions of $Ca(OH)_2$ (2%, 4%, 6% and 8%) cured at either 5 or 20°C with and without a period of mellowing (3 days at 20°C). The samples were compacted at their relevant MDD and at 32% MC.

Unlike strength (Section 7.3) increasing additions of lime to the LOC samples cured at 20°C did not result in increased durability index (DI) values (Figures 7.5.1 (A-B)). Instead a gentle overall decline in DI was observed with increasing lime content (Figure 7.5.1 (A-B)). However, increasing lime content improved the DI of all samples cured at 5°C, with the mellowed material showing slightly elevated DI values compared to unmellowed samples. The DI's of the LOC-$Ca(OH)_2$ samples were reduced when cured at 5°C compared to similar samples cured at 20°C with the LOC-2%$Ca(OH)_2$ soaked samples exhibiting no measurable strength at all at 5°C. This is clearly a result of the absence of the formation of cementitious bonding at 5°C as demonstrated in Figure 7.3.3. At 20°C the LOC-2%$Ca(OH)_2$ sample showed the greatest DI. Also at 20°C it is apparent that the LOC-6%$Ca(OH)_2$ samples showed better DI values than the LOC-8%$Ca(OH)_2$ samples with or without mellowing. Mellowing improved the DI of all samples when cured at 20°C (except the LOC-2%$Ca(OH)_2$ sample which showed little change) (Figure 7.5.1 (B) [Appendix B]).

It is thought that ettringite forms in the LOC-lime system and that in the presence of excess moisture, ettringite formation causes disruption and swelling. From the previous sections (Figure 7.3.3), it is clear large additions of lime to the LOC result in higher strengths compared to samples containing 2%$Ca(OH)_2$. However, specimens with high lime contents expand far more than samples containing small amounts of lime (Figure 7.4.5-7.4.7). Therefore it is probable that the reduction in durability index (DI) samples containing high lime contents is due to the greater propensity of those samples to swell, though this feature is less for mellowed samples.

It is proposed that the higher DI values shown in mellowed LOC-lime samples, compared to unmellowed samples is due to a combination of two factors: 1) reduced density and increased porosity allowing room to accommodate the formation of deleterious phases (such as ettringite or at low temperatures thaumasite) and therefore reducing disruption, and 2) reduced available calcium and sulphate contents as it is thought mellowing encourages ettringite formation prior to compaction, subsequently depleting the system of the necessary ingredients to form deleterious phases in the presence of water.

Summary

- Increased lime contents resulted in increased durability values at 5°C, except at low lime levels, although the reverse occurred when testing took place at 20°C, as samples with high lime contents are known to expand in the presence of water.
- The DI values of LOC-$Ca(OH)_2$ samples tested at 20°C are greater than those tested at 5°C. This is attributed to the absence of the formation of cementitious bonding at lower temperatures (see Figure 7.3.3).
- Mellowing of the LOC-$Ca(OH)_2$ generally resulted in better durability, especially at 20°C (except in the LOC-2%$Ca(OH)_2$ sample). This increase in durability is a result of a combination of increased porosity, allowing more room for the formation of deleterious ettringite during soaking and the depletion of available calcium and sulphate ions due to reactions taking place during mellowing.
- Results suggest that there is a maximum lime limit of 6%$Ca(OH)_2$ addition to the LOC, above which the DI reduces.

In order to better understand the processes by which these observed changes occur a series of analyses were carried out on specimens at different stages in their development, using thermogravimetric analysis and X-ray diffraction analysis. The results of these are reported in Sections 7.6 and 7.7.

7.6 Thermogravimetric Analysis

7.6.1 LOC

Figure 7.6.1 illustrates the derivative thermogravimetric (DTG) trace of dried Lower Oxford Clay that was subjected to heating up to 1000°C at a rate of 10°C/min in an open alumina pan in a nitrogen atmosphere. There are 5 Regions of the LOC DTG trace that relate to weight loss due to either loss of H_2O or CO_2.

- **Region 1 (<80°C)** represents moisture loss due to adsorbed moisture on the material not lost during the drying process. Moisture loss, and therefore weight loss, at this temperature range (i.e. <80°C) represents the driving off of the uncombined water present in the LOC.
- **Region 2 (90-140°C)** represents weight loss due to the water loss of gypsum when heated to around 110°C to 130°C. Parsons et al. (1997) attributed a similar weight-loss peak to gypsum at these temperatures when analysing LOC using evolved gas analysis (EGA) techniques. Calculations using the TG curve show the gypsum content of the LOC to be 1.45%. This value is slightly less than the value given by Smith (1999) of 2% gypsum in the LOC. Because the LOC is heated in an open alumina pan, the characteristic double weight-loss peak of gypsum (as explained in Chapter 6) is not seen here.
- **Region 3 (300-600°C)** represents the loss of water due to dehydroxylation of clay minerals. The LOC is a natural clay soil containing kaolinite (10%), illite (23%) and chlorite (7%) and the dehydroxylation weight-loss peaks overlap producing a large,

broad double peak between 300°C and 600°C (Figure 7.6.1). The dehydroxylation of clay minerals is known to occur around 500°C and more specifically kaolinite loses its combined water at 570°C (Liptay, 1974). The report by Parsons et al. (1997) on LOC suggest that organic matter is oxidised in this temperature region (300°C to 500°C), and it is also thought that SO_2 evolution peaks are located between 300°C and 500°C that are due to the oxidation of organic bound sulphur and the oxidation of pyrites (Parsons et al. 1997). However it is unlikely these peaks would be present in the current work as all TG analyses are run in an oxygen free, nitrogen environment.

- **Region 4 (620-760°C)** represents the loss of CO_2 from calcium carbonate. This is confirmed by comparison of dried, untreated LOC with LOC that has been subjected to dilute (2Molar) HCl (Figure 7.6.2). The figure shows clearly that the weight loss in region 4, present in the LOC at around 700°C disappears on dissolution in HCl. The acid combines with the calcium carbonate to produce calcium chloride (CaCl), thus driving off CO_2, which results in the loss of $CaCO_3$ material. This is represented below:

$$CaCO_3 + 2HCl \qquad \rightarrow \qquad CaCl_2 + CO_2 + H_2O$$

In addition there is an increase in the weight loss peak at around 120°C due to gypsum dehydration. The liberation of CO_2 from $CaCO_3$ will result in an increase in available calcium content in the system, and it is suggested that this released calcium reacts with the sulphate released from the pyrites in the soil in the acid environment to produce extra gypsum

- **Region 5 (800-900°C)**. The exact origin of this small peak at around 900°C is unclear. Parsons et al. (1997) assigns this peak to water evolution or CO_2 evolution, depending on the heating environment, though they do not specifically state how the peak is produced. An alternative for the weight loss is the loss of SO_3 from the gypsum at high temperatures, thus explaining the increase in this peak with increased gypsum content. However, Figure 7.6.3 shows clearly that the peak in this region is unconnected with gypsum. Another possibility is the decomposition of sulphides and other carbonates, which are, according to Dunham (1992), thought to occur between 400-950°C.

7.6.2 LOC-$Ca(OH)_2$ System

Figures 7.6.4, 7.6.5, 7.6.6 and 7.6.7 show the DTG traces of the LOC containing respectively 2%, 4%, 6% and 8%$Ca(OH)_2$. The figures include the traces for specimens with the components (i.e. LOC and $Ca(OH)_2$) mixed together in the dry state; in the unmellowed state; after mellowing (3 days at 20°C); and after 1 and 4 weeks moist curing at 20°C (with and without a period of mellowing). For purposes of comparison the individual DTG traces of the LOC and $Ca(OH)_2$ are also displayed in each figure. Table 7.2 gives the gypsum contents of the various mixes expressed as a percentage of the LOC. Unfortunately, due to time constraints it was not possible to analyse specimens that had also been soaked in static and aerated water.

Table 7.2 Gypsum contents (%) of the LOC with various additions of $Ca(OH)_2$ after mixing and after various curing times.

	LOC	$2\%Ca(OH)_2$	$4\%Ca(OH)_2$	$6\%Ca(OH)_2$	$8\%Ca(OH)$
Dry Mix	1.45	1.87	1.75	1.54	1.65
Unmellowed	-	4.42	3.39	4.23	2.52
Mellowed	-	3.55	3.83	2.05	3.21
1 Weeks Curing (Unmellowed)	-	1.88	3.86	3.35	3.05
1 Weeks Curing (Mellowed)	-	1.72	1.40	2.79	2.58
4 Weeks Curing (Unmellowed)	-	4.36	3.31	2.38	3.04
4 Weeks Curing (Mellowed)	-	5.11	5.96	3.16	3.16
Theoretical Limit*	1.45	6.10	10.73	15.37	20.01

* This assumes that all added lime forms gypsum and contributes to the 1.45% already present in the LOC.

It is apparent that on mixing the LOC with $2\%Ca(OH)_2$, the gypsum content of the material immediately increased from 1.45% to 1.87% implying that either the LOC or $Ca(OH)_2$ were not fully dry, or that the materials had reacted with moisture in the air to partially oxidise the pyrites in the LOC and thus slightly increase the gypsum content (Figure 7.6.4). In the dry state, the addition of $2\%Ca(OH)_2$ also resulted in the formation of a small peak at 400°C attributable to the dehydration of unreacted $Ca(OH)_2$. The addition of water to the mix (32wt.%) further increased the gypsum content of the material (from 1.45%to 4.42%) implying that the oxidation of pyrites and subsequent formation of gypsum was immediate in the presence of moisture, confirming the sulphate analysis reported in Section 7.4. Also, as expected, the $Ca(OH)_2$ peak vanished confirming that the lime had reacted with the components in the LOC. A similar pattern was observed after a period of mellowing (3 days at 20°C), and also a small peak was present below 100°C. A curing period of 1 week at 20°C reduced the gypsum content of both the mellowed and unmellowed material, with the mellowed material exhibiting a peak around 80-90°C. Further curing (4 weeks at 20°C) resulted in increased gypsum content with the unmellowed and mellowed mixes displaying gypsum contents of 4.36% and 5.11% respectively. In both mixes the peak forming at around 80°C was stronger and better defined. The excess sulphate was clearly consumed in the formation of an additional sulphate-containing phase or phases. It is suggested that this phase is ettringite, which exhibits a weight loss in the region 70-120°C.

An addition of 4%$Ca(OH)_2$ resulted in an increased $Ca(OH)_2$ peak (Figure 7.6.5). The introduction of water increased the gypsum content from 1.45% to 3.39% and reduced the $Ca(OH)_2$ peak. After mellowing the gypsum content of the mix further increased to 3.83% with the $Ca(OH)_2$ now fully consumed. A strong peak was observed at around 80°C indicating a new phase had been formed during the mellowing period. Curing for 1 week initially resulted in a further increase in gypsum to 3.86%. However, further curing (4 weeks) reduced the gypsum content of the material to 3.31% whilst the peak that represents the phase produced during mellowing had more than doubled. Increased curing after mellowing resulted in a similar trend for the unmellowed material, though the gypsum content of the mellowed material was greater than in the unmellowed material.

Figure 7.6.6 shows that an addition of 6%$Ca(OH)_2$ to the LOC resulted in an increased $Ca(OH)_2$ peak and an increase in gypsum content (from 1.45% to 1.54%). After the addition of water the gypsum content further increased (to 4.23%). Also some of the added lime that had not yet reacted with the other components in the LOC remained.

Mellowing resulted in a reduction in gypsum content, though there was still unreacted $Ca(OH)_2$ present in the system. The TG trace of the LOC-6%$Ca(OH)_2$, cured for 1 week, again illustrates that a portion of the added $Ca(OH)_2$ had not reacted with the LOC. Also, the gypsum peak had reduced whilst the peak formed at around 80°C increased in size. Further curing resulted in the almost complete disappearance of gypsum whilst the phase represented by the peak at around 80°C (attributed to ettringite) had increased significantly. The TG curves of the mellowed samples after curing followed a similar pattern, though the gypsum content was higher after 4 weeks curing (3.16%). Whether the samples were mellowed or unmellowed, the added $Ca(OH)_2$ had fully reacted with the clay after 4 weeks curing.

Adding moisture to the LOC-8%$Ca(OH)_2$ slightly increased the gypsum content of the material from 1.45% to 1.65% (Figure 7.6.7). Mellowing of the mix resulted in a further increase of the gypsum content (3.21%) and a strong peak was observed at 80°C. Curing for 1 and 4 weeks resulted in a gradual reduction in gypsum content with the new phase (thought to be ettringite) with a weight loss peak around 80°C being more prominent with increases in curing time. Curing the mellowed samples for the same time period had the same affect, though the gypsum peak was more prominent. Throughout all mellowed mixes, the presence of $Ca(OH)_2$ indicated that even after mellowing and 4 weeks moist curing some of the added lime had not reacted with the LOC. In general at low lime addition there is a tendency, after prolonged curing, for most of the added lime to be present as gypsum, whereas the converse is the case for high lime additions in that the gypsum contents tend to be lower although the potential gypsum contents are much higher. Most of the added lime in this case is fixed as ettringite which gives a weight loss peak in the region of 70°C to 100°C, and there is also, in the case of the LOC-8%$Ca(OH)_2$ sample, evidence of some residual lime remaining even after 4 weeks.

7.6.3 LOC-CaO System

Figures 7.6.8, 7.6.9, 7.6.10 and 7.6.11 illustrate the DTG traces of the LOC mixed with 1.5%, 3%, 4.5% and 6% CaO with increasing time. The figures show the curves of the components (i.e. LOC and CaO) mixed together in the dry state; in the unmellowed state; after mellowing (3 days at 20°C); and after 1 and 4 weeks moist curing at 20°C (with and without a period of mellowing). For clarity the DTG trace of the LOC is also displayed. Table 7.3 exhibits the gypsum contents of the various mixes as a percentage of the clay.

Table 7.3 Gypsum contents (%) of the LOC with various additions of CaO after a number of mixing and curing times.

	LOC	1.5%CaO	3%CaO	4.5%CaO	6%CaO
Dry Mix	1.45	2.19	3.30	4.23	4.20
Unmellowed	-	4.59	4.25	5.13	4.62
Mellowed	-	4.08	4.91	4.30	5.04
1 Weeks Cured (Unmellowed)	-	2.80	3.02	2.81	2.67
1 Weeks Cured (Mellowed)	-	3.90	4.77	5.32	4.42
4 Weeks Cured (Unmellowed)	-	2.13	0	0	0
4 Weeks Cured (Mellowed)	-	4.08	4.39	3.77	4.00
Theoretical Limit*	1.45	6.10	10.73	15.37	20.0

*This assumes that all added lime forms gypsum and contributes to the 1.45% already present in the LOC.

Mixing of the dry LOC-1.5%CaO material with water immediately increased the gypsum content of the LOC (from 1.45% to 4.59%), though this was slightly reduced after mellowing (3 days at 20°C) to 4.08% (Table 7.2). This reduction in gypsum content coincided with an increase in the size of the peak found at a temperature of around 80°C. Curing for 1 and 4 weeks resulted in further reductions in gypsum content, and an increase occurred in the phase represented by the peak found at around 80°C, attributed to ettringite. However, curing for 1 and 4 weeks after mellowing showed much greater gypsum contents and relatively smaller increases in the ettringite peak.

Figure 7.6.9 illustrates that the addition of 3%CaO to the LOC resulted in an increase in the gypsum content from 1.45% to 3.30%. The addition of water further increased the gypsum content of the mix (to 4.25%) and a period of mellowing resulted in a further increase to a gypsum content of 4.91%. During mellowing the new phase occurred represented by the peak at around 80°C. Curing for 1 and 4 weeks resulted in the reduction and eventual disappearance of the gypsum peak, whilst the phase represented by the peak formed at around 80°C became more dominant until it was the only clearly visible peak after 4 weeks curing. However curing for the same period after mellowing showed that the gypsum content was still relatively high (between 4.3% and 4.7%) compared to the unmellowed DTG traces.

A further addition of CaO to the LOC (i.e. 4.5%CaO) again resulted in an immediate increase in gypsum content (from 1.45% to 4.23%), which further increased when moisture was added to 5.13% (Figure 7.6.10). Mellowing of the mix reduced the gypsum peak and the new phase, ettringite formed, represented by the peak at a temperature of around 80°C. Curing for 1 and 4 weeks resulted in decreased gypsum content with time until the gypsum completely disappeared having reacted with the components of the LOC, whilst the ettringite phase formed during mellowing increased. Curing of the mellowed mixes (1 and 4 weeks) again showed a reduction of the gypsum peak and an increase in the ettringite peak formed during mellowing. However, after 4 weeks there was still 3.77% gypsum in the mellowed system compared with a complete absence of gypsum in the unmellowed system. Also the ettringite peak found at around 80°C was not as pronounced in the mellowed material as in the unmellowed material. In the mellowed or unmellowed mixes that have been cured for 1 and 4 weeks, a $Ca(OH)_2$ peak is apparent, implying that the CaO had hydrated to form $Ca(OH)_2$, and that the lime had not completely reacted with the components in the LOC.

Figure 7.6.11 shows that the addition of 6%CaO to the LOC again resulted in increased gypsum content (from 1.45% to 4.20%). The addition of water to the mix slightly increased the gypsum content, and the added water also reacted with the CaO to form a $Ca(OH)_2$ peak at around 400°C. Mellowing of the mix increased the gypsum content to 5.04% and also resulted in the formation of ettringite, as shown by the peak at around 80°C. Similar to Figures 7.6.8-7.6.10, curing for 1 and 4 weeks reduced the gypsum content of the material to 2.67% and 0% respectively, whilst the DTG peak representing the ettringite phase formed during mellowing continued to increase. Curing for 1 and 4 weeks of mellowed samples again showed a decrease of the gypsum content to 4.42% and 4.00% respectively whilst the ettringite phase formed during mellowing continued to increase, though at a slower rate than in unmellowed samples.

From this section it is clear that the gypsum content of the LOC increases when lime is added (whether mixed in a "dry" state or mixed with water). This phenomenon must be due to the rapid oxidation of pyrites in the LOC, which produces sulphuric acid, which in turn attacks the lime and possibly also the calcite present and produces gypsum. It is also clear that gypsum and ettringite are the two main reaction products of LOC-lime mixtures. However, the type and amount of the reaction products depend largely on three factors: 1) the effect of quicklime as opposed to hydrated lime, 2) the effect of mellowing as opposed to not mellowing, and 3) the effect of lime content. As discussed previously the balance between the relative amounts of gypsum and ettringite produced is particularly sensitive to lime content and there is a tendency for gypsum to be the dominant phase at low lime contents and ettringite at high lime contents.

Summary

- **Quicklime Vs. Hydrated Lime:** The two fundamental differences between the LOC-$Ca(OH)_2$ and LOC-CaO system are that: 1) in the dry mixes the gypsum content of the LOC increases to a greater level when mixed with CaO compared to $Ca(OH)_2$. It is known that CaO is more reactive than $Ca(OH)_2$ and therefore may produce gypsum, via pyrites oxidation at an advanced rate; and 2) after 4 weeks curing the unmellowed LOC-$Ca(OH)_2$ samples show a gypsum content of between 3% and 4.4% whereas in the LOC-CaO samples at lime levels above 1.5%CaO there is a complete absence of the gypsum peak. Instead, a large ettringite peak is exhibited. As both systems contain excess lime at high lime additions after 4 weeks curing, it is probable that the differences in gypsum contents with differing lime type show that CaO is more effective in oxidising pyrites to form gypsum. The more rapid oxidation of pyrites in the LOC-CaO system would lead to more gypsum being consumed during ettringite formation, ultimately resulting in the complete oxidation of pyrites and the full consumption of gypsum to form ettringite.

- **Mellowed vs. Unmellowed.** In all samples (regardless of the system), ettringite forms during the mellowing period at the expense of gypsum. This is a result of the extended oxidation time of pyrites (producing gypsum, which is consumed in the presence of lime and water) and also the reduced density resulting in a more open LOC-lime matrix allowing ettringite development during the 3 days mellowing period. The major difference between the mellowed and unmellowed samples after 4 weeks curing is that the mellowed samples consistently contain between 3.16% and 5.96% gypsum, whereas the unmellowed sample contained considerably less gypsum (in the case of the LOC-CaO system, no gypsum is found at all at CaO levels above 1.5%). It has been shown that at low lime addition, pyrites oxidation occurs during mellowing to form gypsum at the expense of calcium carbonate in the LOC. Also gypsum, in the presence of water and lime, will form ettringite during mellowing. Both these reactions consume lime and water prior to compaction and subsequent curing. Therefore not only will the mellowed compacted LOC-lime samples be depleted in available sulphate and lime, but also available water. Thus it is evident that the gypsum present in mellowed samples after 4 weeks curing is not fully consumed in the formation of ettringite, perhaps due to the lack of available moisture.
- **Lime Content.** The DTG figures in this section established that the amount and type of reaction product depend largely on the amount of lime added to the LOC. When only a small amount (2%$Ca(OH)_2$ or 1.5%CaO) is added it is clear that gypsum is the dominant reaction product before compaction. After compaction and subsequent curing of these low-lime samples it is the gypsum peaks, which are

generally larger than the ettringite peaks (especially after mellowing). When larger amounts of lime (8%$Ca(OH)_2$ or 6%CaO) are added it is clear that after compaction the largest reaction-product DTG peaks are exhibited by water loss attributed to ettringite in the cured, unmellowed samples. When a period of mellowing is employed prior to compaction ettringite is still the dominant reaction product, though unlike in the unmellowed sample, a significant amount of gypsum remains. It is likely that this feature is a result of differing pH values when differing amounts of lime are added to the LOC (as seen in section 7.4). From the DTG data it is clear that small amounts of added lime are consumed in various reactions before 1 week curing. However, large amounts of added lime are not fully consumed even after 4 weeks curing, resulting in higher pH levels and of course more available lime. As it has been reported (Gaze and Crammond, 2000) that ettringite is unstable at pH levels below 10, it is unsurprising that the DTG traces of the LOC-8%$Ca(OH)_2$ or 6%CaO exhibit higher ettringite: gypsum ratios and that at low lime levels the reverse is noted.

In order to corroborate the above deductions, the next section examines the phase changes of the LOC with 8%$Ca(OH)_2$ or 6%CaO using X-ray diffraction (XRD) techniques.

7.7 X-ray Diffraction (XRD) Analysis

7.7.1 Lower Oxford Clay (LOC)

Figure 7.7.1 illustrates the X-ray diffraction (XRD) trace of the Lower Oxford Clay (LOC). The 2θ values and d-spacings of the peaks can be seen in Appendix C.

Only the major peaks representing illite, gypsum, kaolinite, calcite, quartz, siderite, hemi-hydrate, plagioclase feldspar and pyrites are labelled on the XRD trace of the LOC. The minerals represented in Figure 7.7.1 are in good agreement with mineralogical analysis of the LOC reported by Wild et al. (1996) and Smith (1999) (Table 5.2)

7.7.2 LOC-8%$Ca(OH)_2$ System

Figure 7.7.2 (A) illustrates the XRD trace of the LOC-8%$Ca(OH)_2$ in the dry mix; the unmellowed mix; and compacted unmellowed samples after 1 and 4 weeks curing at 20°C. Figure 7.7.2 (B) illustrates the XRD trace of the LOC-8%$Ca(OH)_2$ in the dry mix; in the mellowed mix (3 days at 20°C); and compacted mellowed samples after 1 and 4 weeks curing at 20°C.

Mixing of the two dry constituents resulted in the appearance of two large $Ca(OH)_2$ peaks, and these peaks diminished in size on addition of water (32%) (Figure 7.7.2 (A)). Also the strong gypsum peak disappeared on mixing with water, indicating that both the

$Ca(OH)_2$ and the gypsum had reacted. After compaction and curing (1 week) it is noticeable that the gypsum peak is again present. This is clearly a result of pyrites oxidation, which is known to produce gypsum when free calcium is present. Also the small amount of hemi-hydrate ($CaSO_4.0.5H_2O$) observed was consumed along with more $Ca(OH)_2$ in the formation of ettringite. Further curing (4 weeks) showed that the gypsum peak was reduced along with the $Ca(OH)_2$ peak, whilst the ettringite peak had increased. As the gypsum was now being reduced and $Ca(OH)_2$ was still present in the system, it is probable that pyrites oxidation had terminated after 4 weeks, though it is thought ettringite would continue to form with further curing.

A period of mellowing modified the proportion and types of reaction products present prior to compaction as ettringite is clearly produced and hemi-hydrate disappears (Figure 7.7.2(B)). Gypsum is also clearly present and appears to increase slightly, indicating that pyrites oxidation is continuing at an enhanced rate compared to the unmellowed mix. Curing of the compacted, mellowed LOC-8%$Ca(OH)_2$ sample shows that $Ca(OH)_2$ is consumed to a greater extent than in the unmellowed samples (also see Figure 7.6.7) and that both ettringite and gypsum are present after 4 weeks. The results of the X-ray analysis generally confirm and support the results obtained from thermogravimetric analysis in Figure 7.6.7.

7.7.3 LOC-6%CaO System

Figure 7.7.3 (A) illustrate the XRD trace of the LOC-6%CaO in the dry mix; in the unmellowed mix; and compacted unmellowed samples after 1 and 4 weeks curing at 20°C. Figure 7.7.3 (B) illustrates the XRD trace of the LOC-6%CaO in the dry mix; in the mellowed mix (3 days at 20°C); and compacted mellowed samples after 1 and 4 weeks curing at 20°C.

Surprisingly, the addition of up to 6%CaO to the LOC did not result in the appearance of crystalline CaO, and $Ca(OH)_2$ was observed in the XRD trace of the "dry" mix (Figure 7.7.3 (A)). Similar to the LOC-8%$Ca(OH)_2$ mix, the addition of water resulted in the reduction of the $Ca(OH)_2$ peak and the strong gypsum peak was very much reduced, again indicating that in the presence of water, the lime and the gypsum had reacted. Compaction and curing for 1 week resulted in ettringite formation at the expense of hemi-hydrate and lime, and the continued presence of gypsum and $Ca(OH)_2$ in the system indicated that pyrites oxidation was continuing. Further curing produced increased ettringite formation, this time at the expense of gypsum and lime. After 4 weeks curing the complete disappearance of gypsum, coupled with the presence of a small amount of lime strongly suggests that pyrites oxidation had terminated. Again the X-ray diffraction data generally support the results of the thermogravimetric analysis of these specimens reported in 7.6.11.

The presence of ettringite and the disappearance of hemi-hydrate confirm the theory that a period of mellowing allows the reactions between the added lime and the sulphates to occur prior to compaction (Figure 7.7.3 (B)). Compaction and curing of the mellowed LOC-6%CaO mixes illustrates gypsum is still abundant together with ettringite even after 4 weeks curing and that much of the added lime had been consumed. This is in excellent agreement with Figure 7.6.11.

Summary

- Immediately on mixing lime with the LOC in the presence of water, reactions involving $Ca(OH)_2$ and sulphates take place.
- After compaction and curing (1 week), ettringite is formed at the expense of hemi-hydrate, lime and water. After 4 weeks curing, the reduction or complete disappearance of gypsum, coupled with the presence of lime, indicates pyrites oxidation has terminated.
- A period of mellowing prior to compaction and curing results in the formation of ettringite at the expense of lime and sulphates. The fact that gypsum continues to be present during curing and appears to increase with time suggests that pyrites oxidation occurs at an enhanced rate in mellowed mixes compared to unmellowed mixes.
- After curing it is clear that mellowed samples contain both gypsum and ettringite and that lime levels are reduced, whereas unmellowed samples, although following a similar pattern, tend to show less gypsum and greater amounts of ettringite. This may be as a result of the fact that mellowed samples are susceptible to carbonation during the mellowing period and depression in pH (relative to samples that are not mellowed) which tends to favour gypsum stability relative to ettringite.

7.8 LOC-Lime Summary

It is apparent that in sulphate and sulphide bearing clays the addition of lime leads to increased levels of sulphate (from enhanced pyrites oxidation), ettringite formation and increased expansion on soaking. Mellowing reduces the expansion on soaking because it allows some of the expansive reactions to take place prior to compaction. Also mellowing depresses pH values in the early stages of soaking which also appears to depress pyrites oxidation and sulphate levels. This may be due to carbonation during mellowing. To effectively stabilise soil and to achieve long-term pozzolanic activity and strength enhancement the amount of added lime must be above lime fixation point. However this, as explained above leads to increasing pyrites oxidation and sulphate contents and increasing levels of expansion during soaking. A solution to this problem is to use lime not as a stabiliser, but as a soil modifier and use a second material as a stabiliser. Ground granulated blastfurnace slag (GGBS) would act as an ideal stabiliser as its hydration is activated in an alkaline environment and it provides long term cementation and good sulphate resistance. If lime is added to the soil as a modifier and the soil is allowed to mellow, sulphates will be released during the mellowing period. Also some of the damaging reaction products, which are expansive if formed under saturated conditions, will form during the mellowing period in circumstances where they will do no damage. The amount of lime that is added should, from an economic standpoint, be as small as possible, but should be sufficient to both maintain an alkaline environment for a prolonged period, to facilitate GGBS activation and also to promote pyrites oxidation and release sulphate, and allow some of the damaging expansive products to form during the mellowing period. It should also be noted that where GGBS is to be used as a stabiliser the presence of gypsum could be advantageous because if lime is used as an activator, gypsum is known to accelerate GGBS hydration and therefore provide early strength.

From an assessment of the results obtained on the LOC-lime system and their analysis and interpretation it was decided to use either 2%$Ca(OH)_2$ or 1.5%CaO as a soil modifier for the LOC and use various levels of GGBS as stabiliser to establish an appropriate GGBS level. In addition, for purposes of comparison and evaluation, PC was also used as a stabiliser.

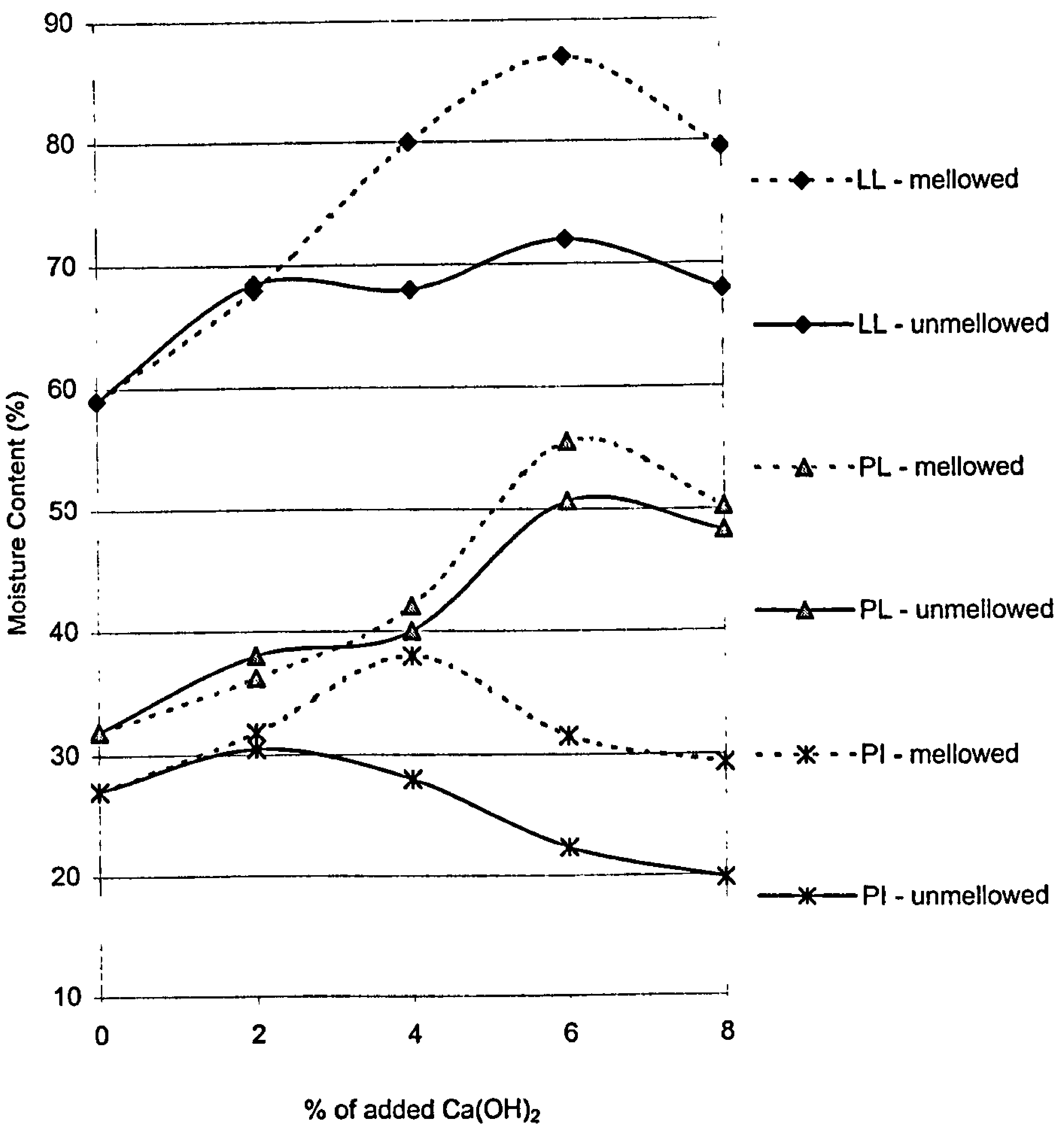


Figure 7.1.1 Atterberg (consistency) limits of LOC with various additions of $Ca(OH)_2$ before and after mellowing for 3 days at 20°C.

LL= liquid limit
PL = plastic limit
PI = plasticity index

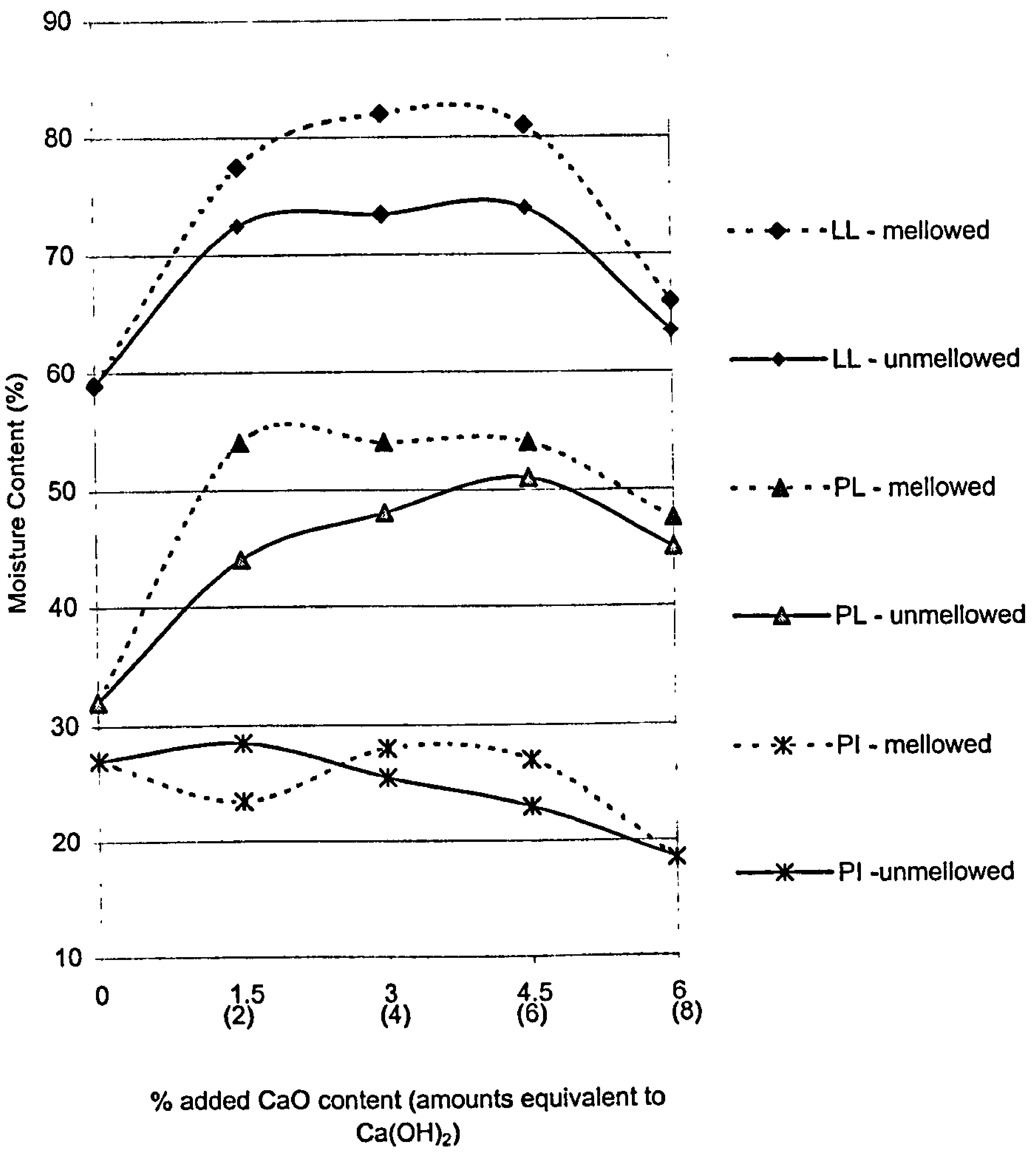


Figure 7.1.2 Atterberg (consistency) limits of LOC with various additions of CaO before and after mellowing for 3 days at 20°C.

LL= liquid limit
PL = plastic limit
PI = plasticity index

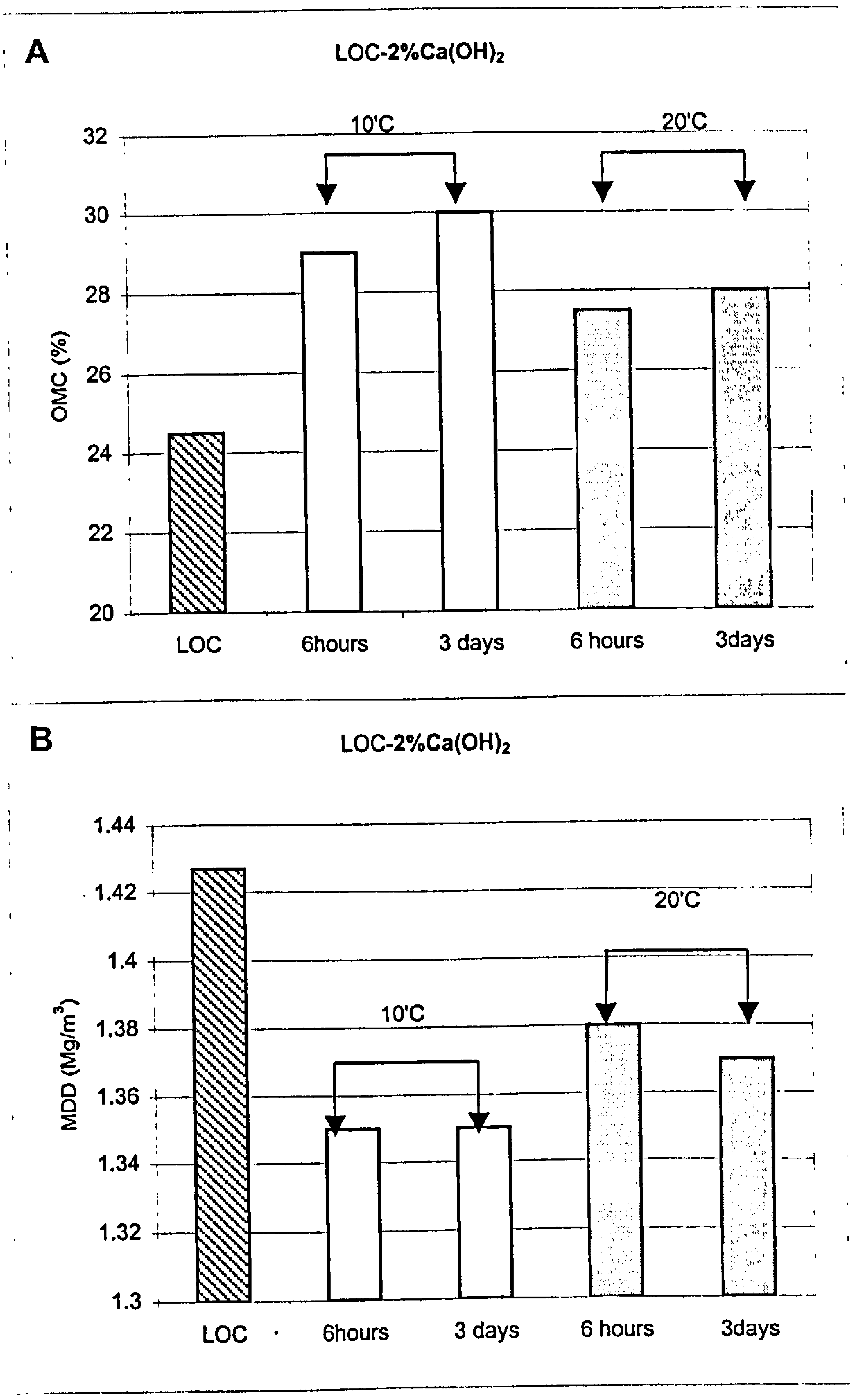


Figure 7.2.1 (A) Optimum moisture content (OMC) and (B) maximum dry density (MDD) values of LOC-2%$Ca(OH)_2$ mellowed for either 6 hours or 3 days at 10°C or 20°C

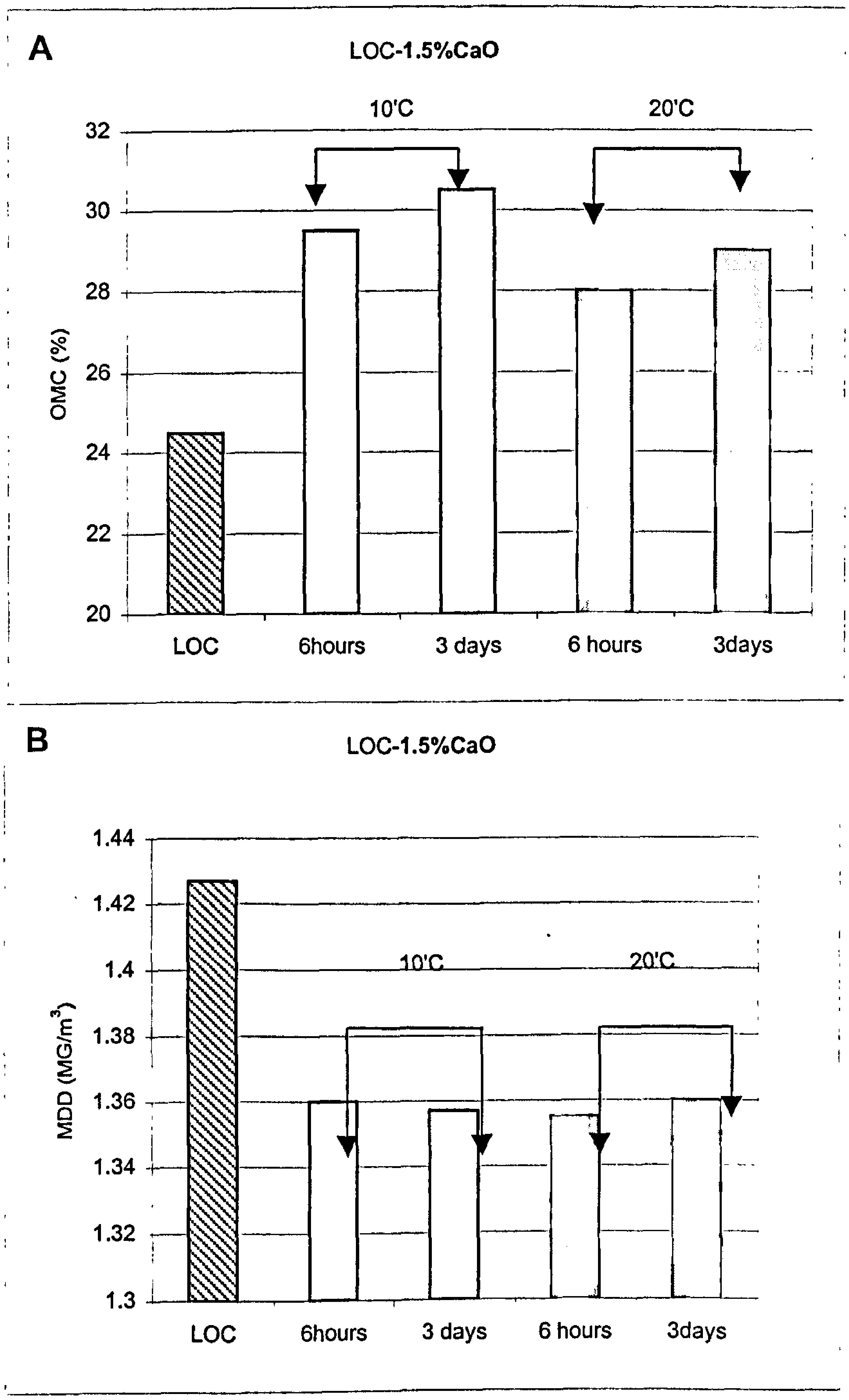


Figure 7.2.2 (A) Optimum moisture content (OMC) and (B) maximum dry density (MDD) values of LOC-1.5%CaO mellowed for either 6 hours or 3 days at 10°C or 20°C

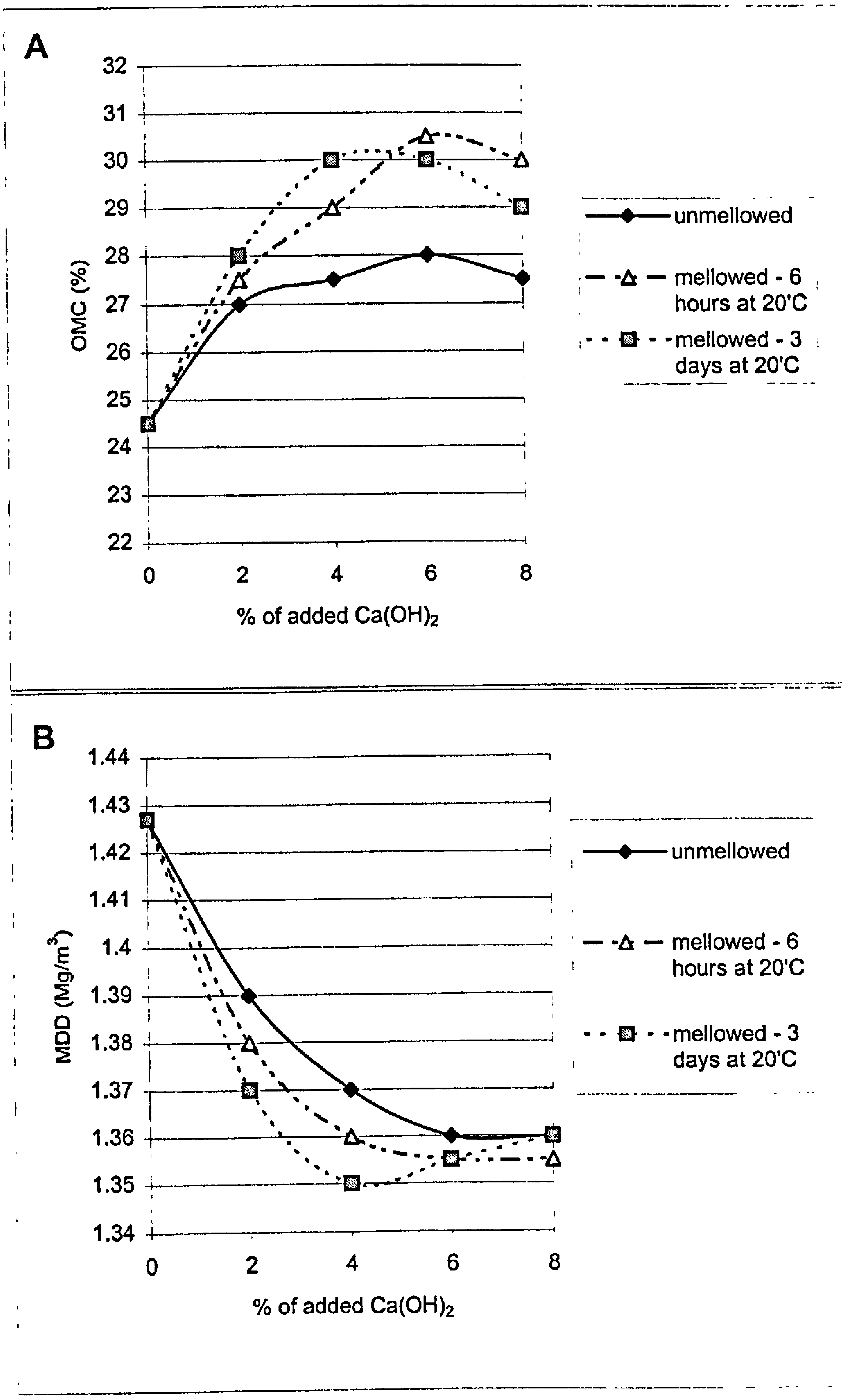


Figure 7.2.3 Compaction parameters of mellowed (6 hour or 3 days at 20°C) and unmellowed LOC treated with various additions of $Ca(OH)_2$ at 20°C.

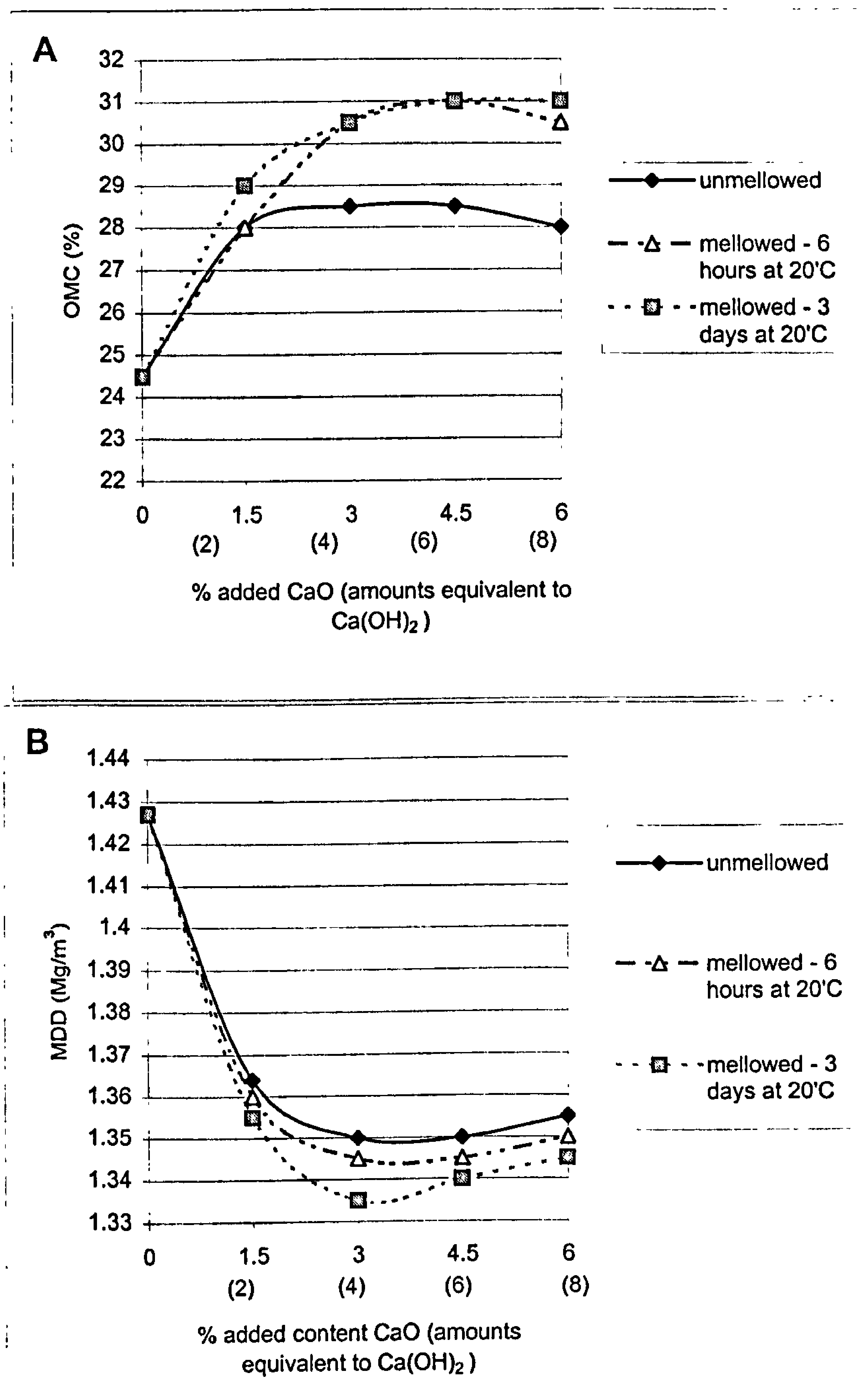


Figure 7.2.4 Compaction parameters of mellowed (6 hour or 3 days at 20°C) and unmellowed LOC treated with various additions of CaO at 20°C.

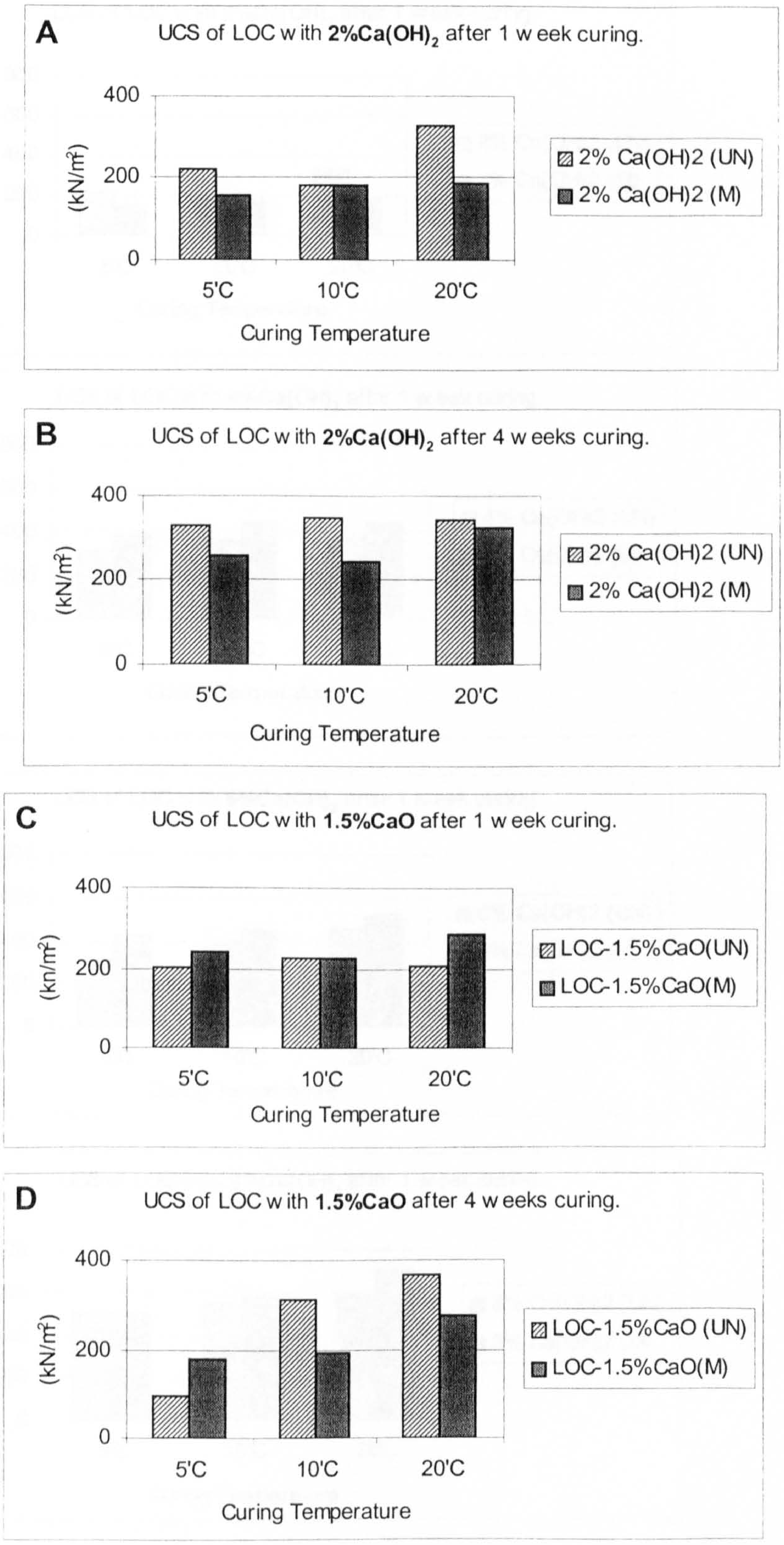


Figure 7.3.1 Unconfined compressive strength (UCS in kN/m^2) of compacted lime-modified (i.e. 2%$Ca(OH)_2$ or 1.5%CaO) LOC samples cured at 5°C, 10°C or 20°C for 1 and 4 weeks.
(M) = Mellowed
(UN) = Unmellowed

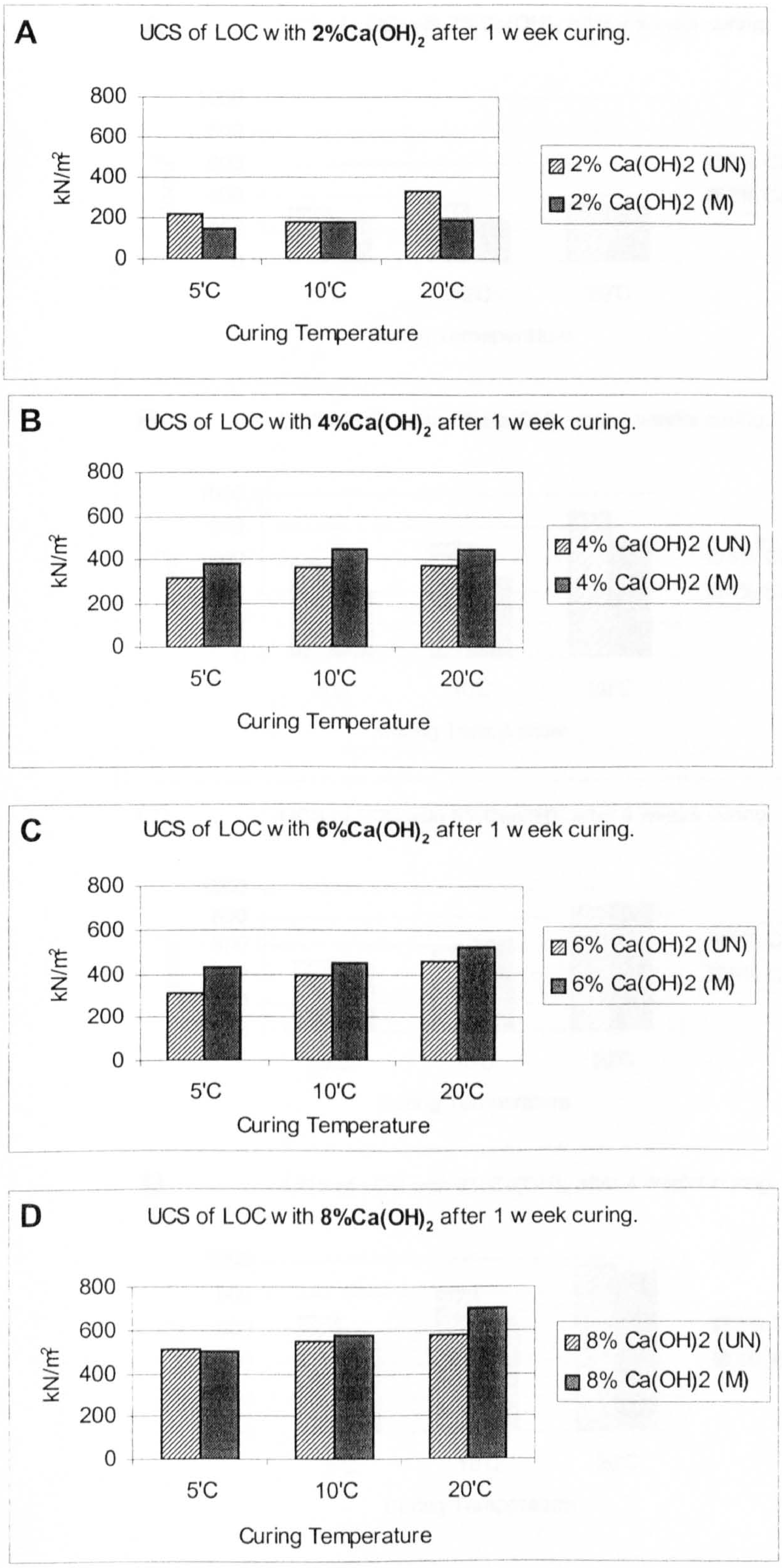


Figure 7.3.2 Unconfined compressive strength (UCS in kN/m^2) of compacted lime-LOC samples with various additions of $Ca(OH)_2$ cured at 5°C, 10°C or 20°C for 1week.
(M) = Mellowed
(UN) = Unmellowed

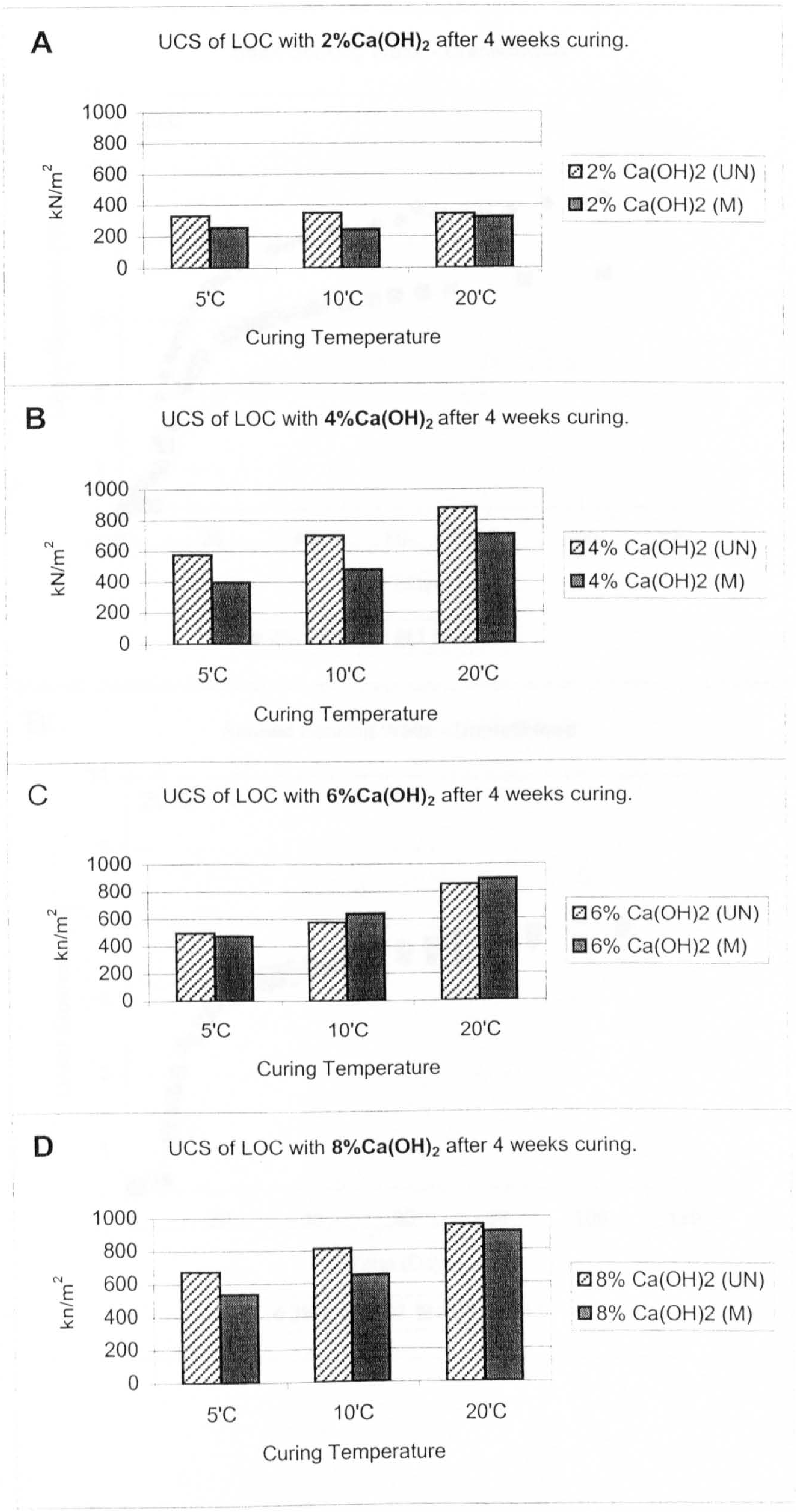


Figure 7.3.3 Unconfined compressive strength (UCS in kN/m^2) of compacted lime-LOC samples with various additions of $Ca(OH)_2$ cured at 5°C, 10°C or 20°C for 4 weeks.
(M) = Mellowed
(UN) = Unmellowed

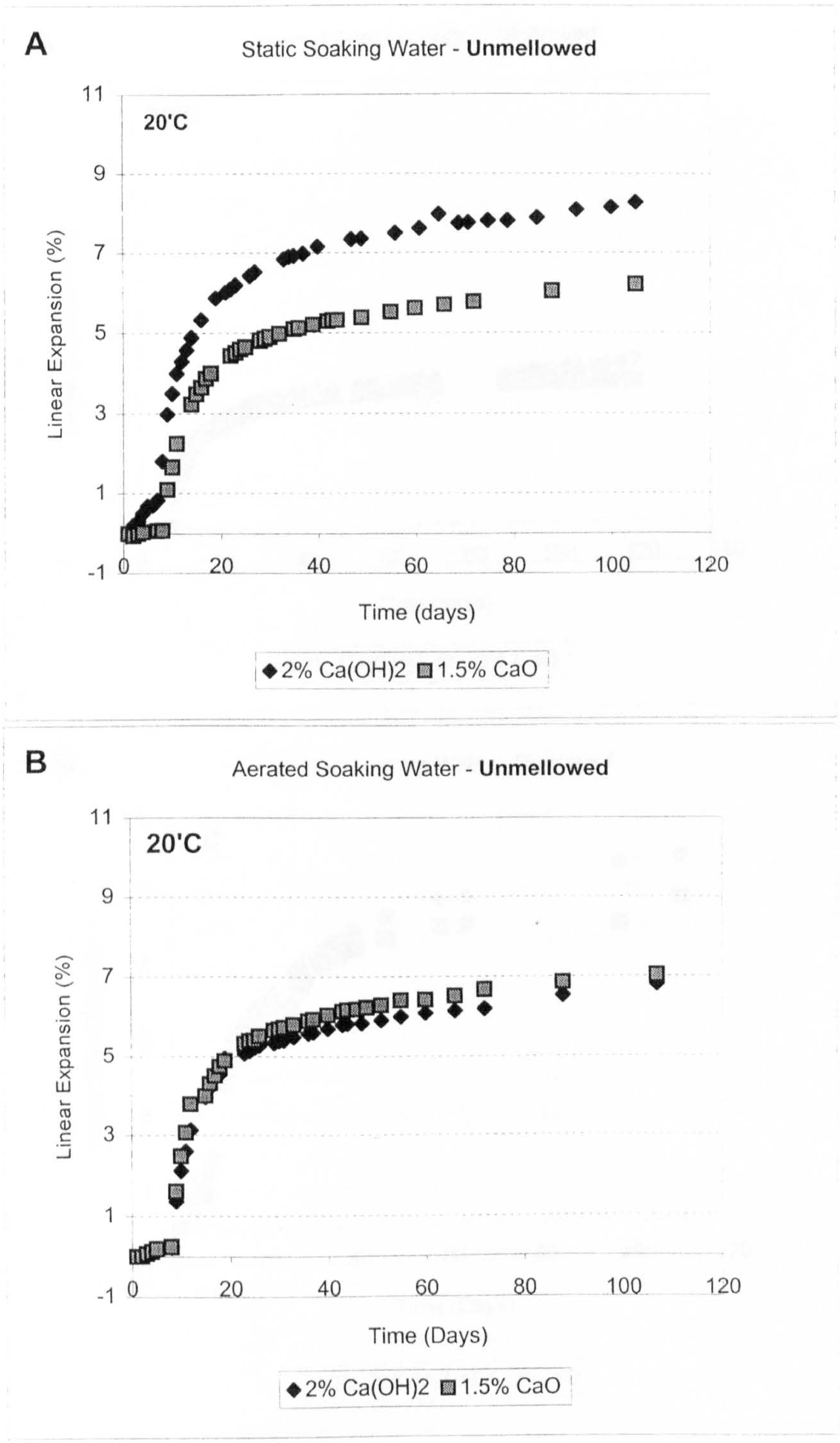


Figure 7.4.1 Linear expansion vs. soaking time of compacted, lime-modified (2%$Ca(OH)_2$ or 1.5%CaO) LOC in (A) a static soaking environment at 20°C; or (B) an aerated soaking environment at 20°C.

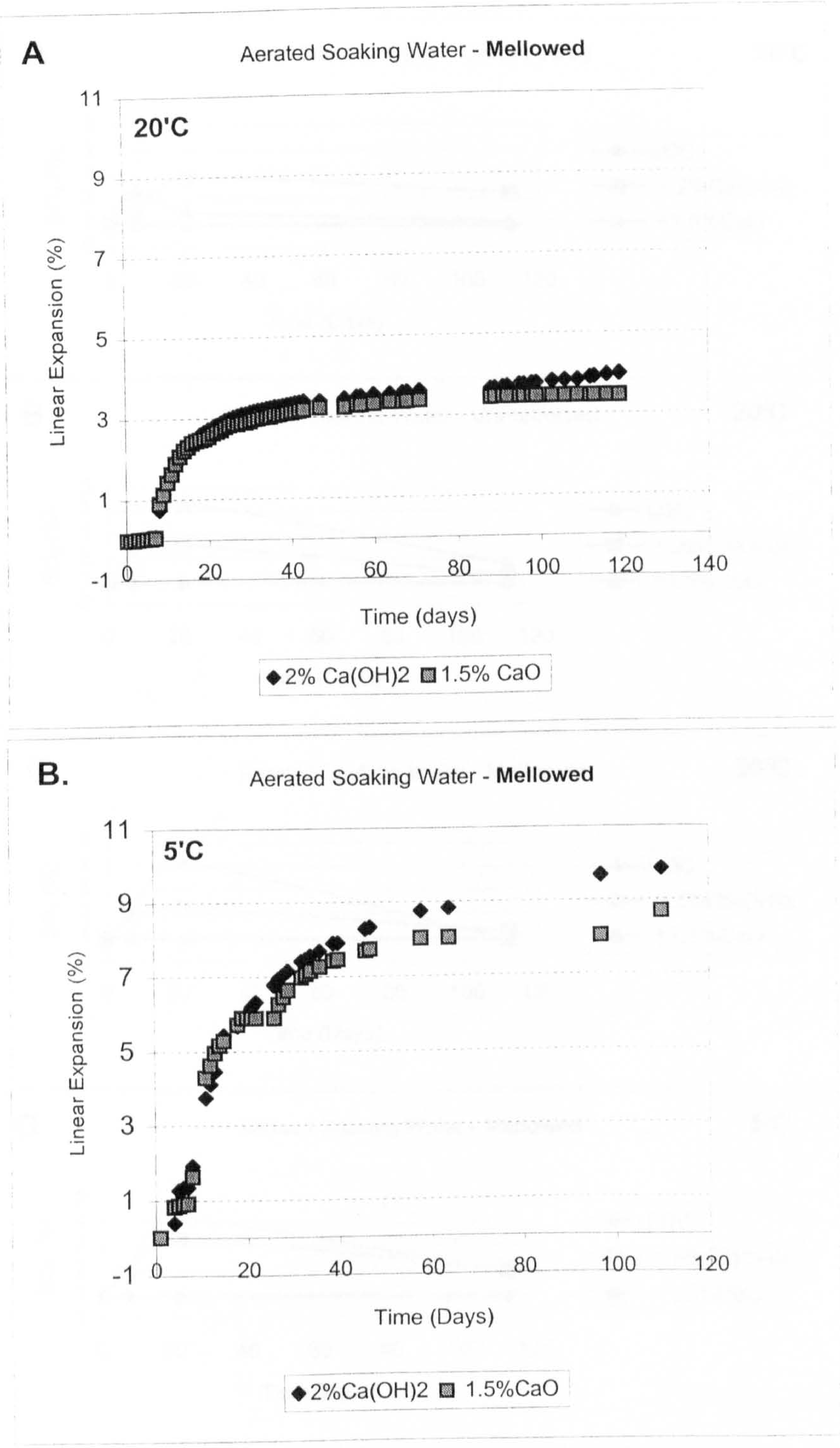


Figure 7.4.2 Linear expansion vs. soaking time of compacted, lime-modified ($2\%Ca(OH)_2$ or $1.5\%CaO$), mellowed (3 days at 20°C) LOC in (A) an aerated soaking environment at 20°C; or (B) an aerated soaking environment at 5°C.

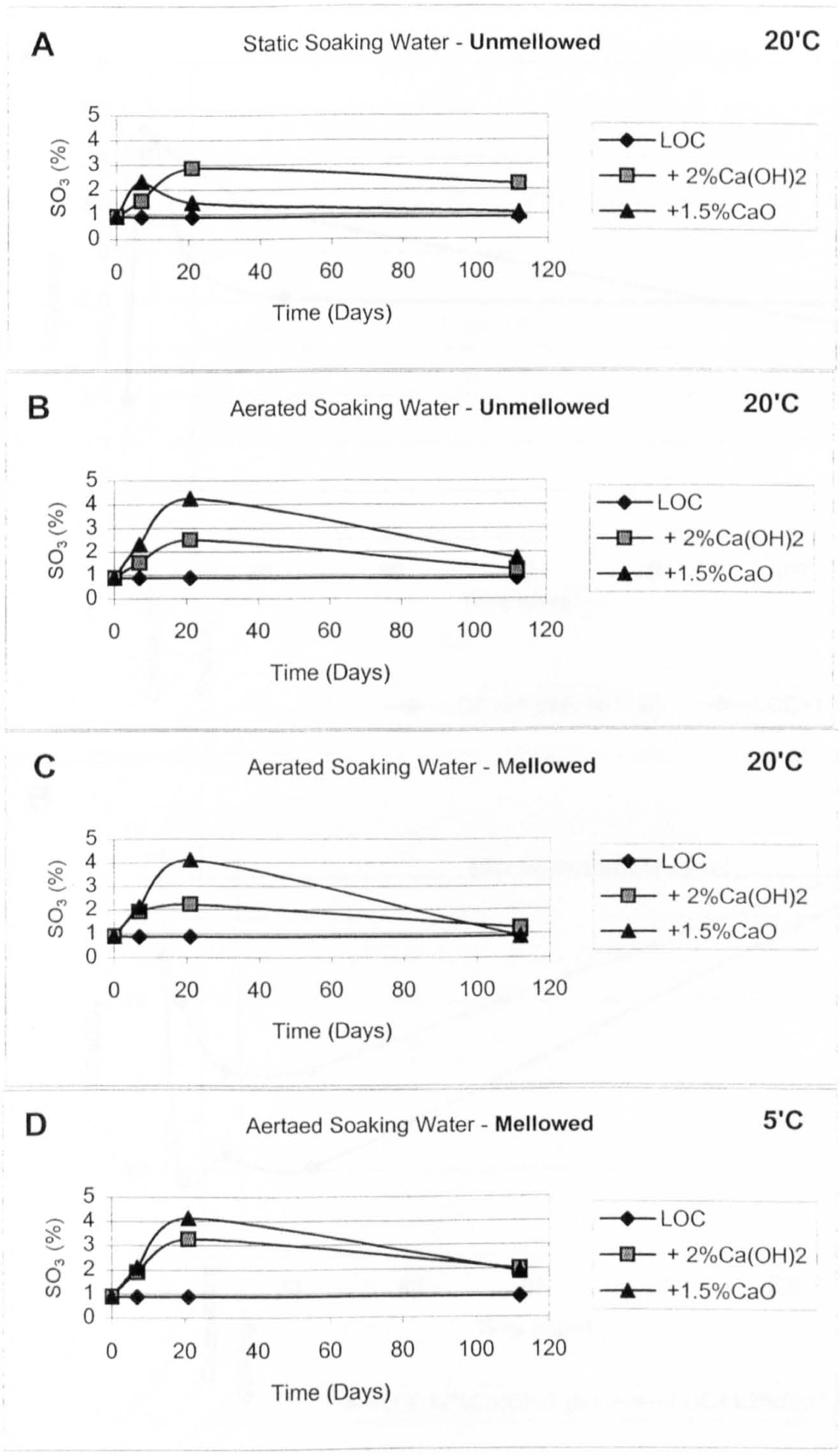


Figure 7.4.3 Sulphate (SO_3) content vs. soaking time of compacted, lime modified (2%$Ca(OH)_2$ or 1.5%CaO) LOC in (A) a static soaking environment at 20°C; (B) an aerated soaking environment at 20°; (C) an aerated soaking environment after mellowing (3 days at 20°C) at 20°C; and (D) an aerated soaking environment after mellowing (3 days at 20°C) at 5°C.

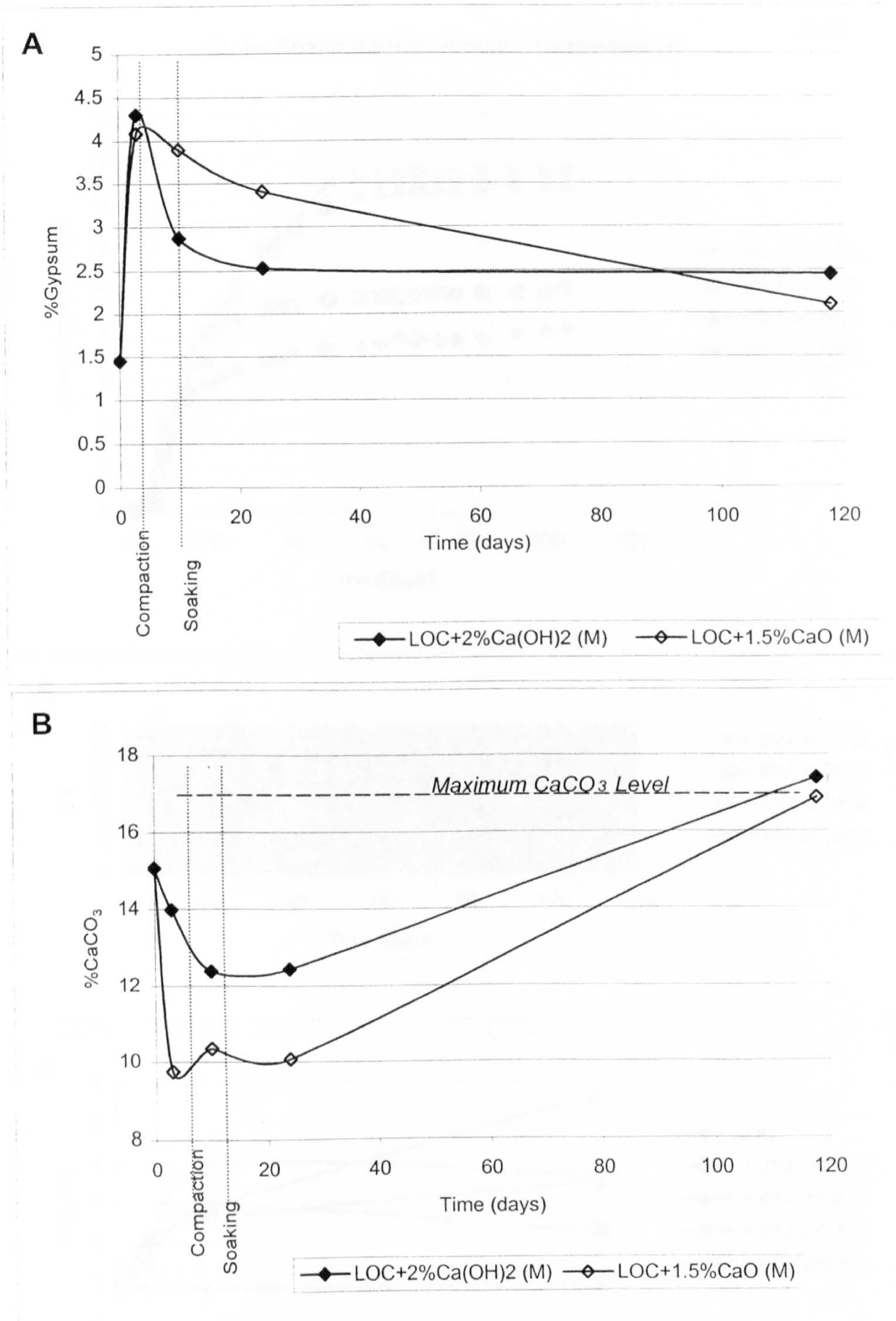


Figure 7.4.4 Graphical representation of thermogravimetric (TGA) data illustrating (A) changes in gypsum content (as a percentage of the LOC) and (B) changes in $CaCO_3$ content (as a percentage of the LOC) of mellowed LOC-2%$Ca(OH)_2$ and LOC-1.5%CaO samples soaked in an aerated environment.

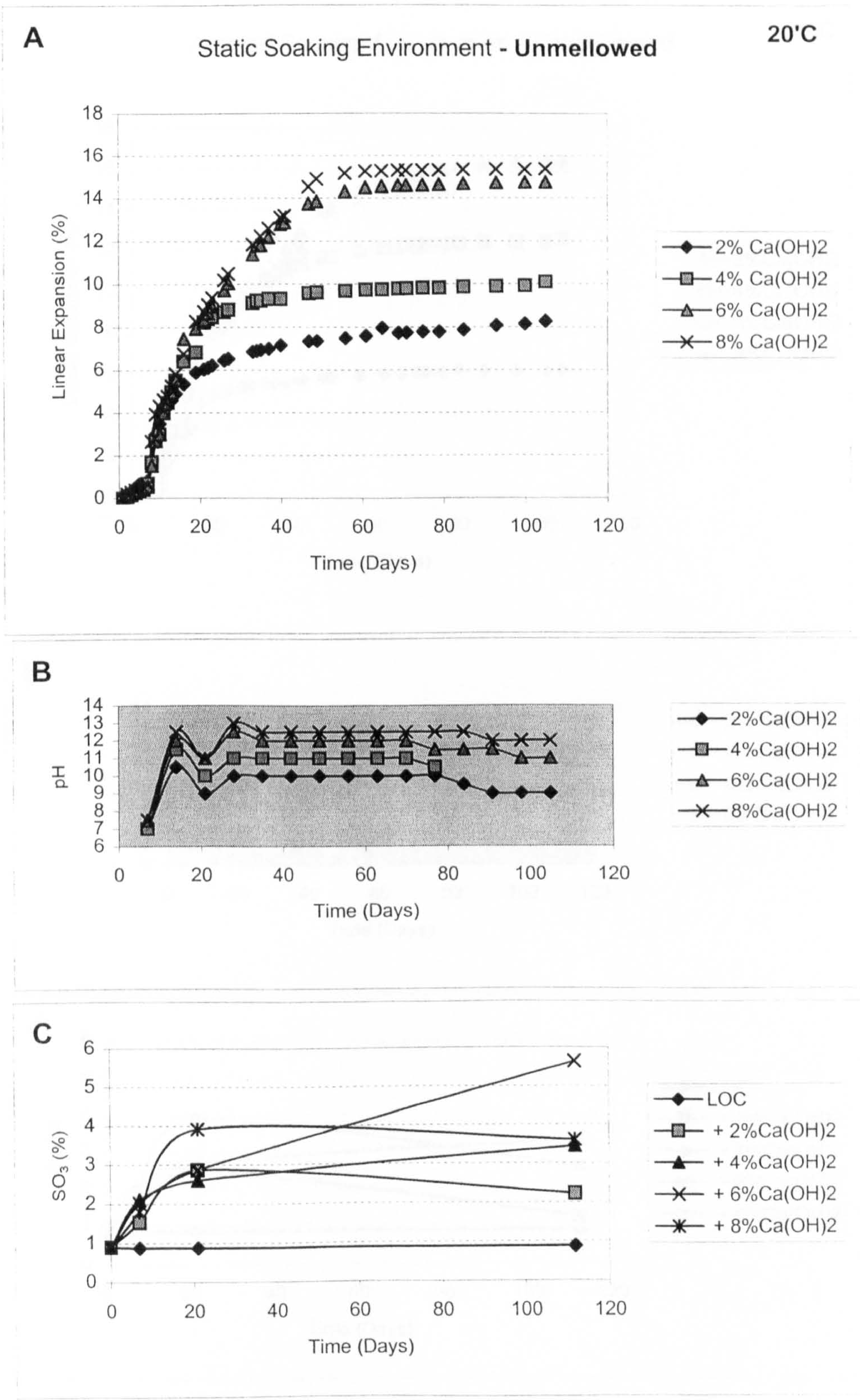


Figure 7.4.5 (A) Linear expansion; (B) pH measurements and (C) sulphate (SO_3) contents of unmellowed, compacted LOC samples with various additions of $Ca(OH)_2$ in a static soaking environment at 20°C.

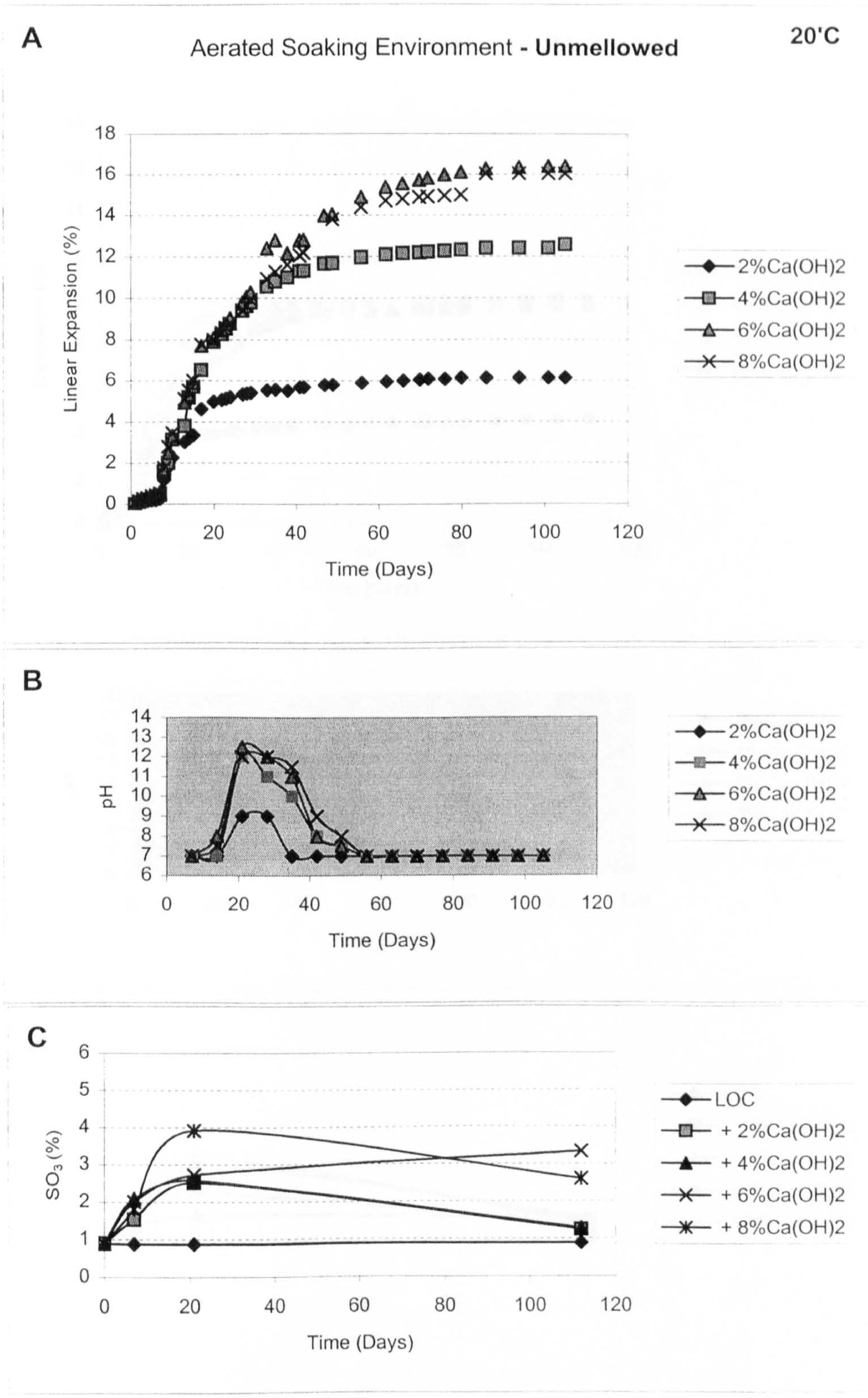


Figure 7.4.6 (A) Linear expansion; (B) pH measurements and (C) sulphate (SO_3) contents of unmellowed, compacted LOC samples with various additions of $Ca(OH)_2$ in an aerated soaking environment at 20°C.

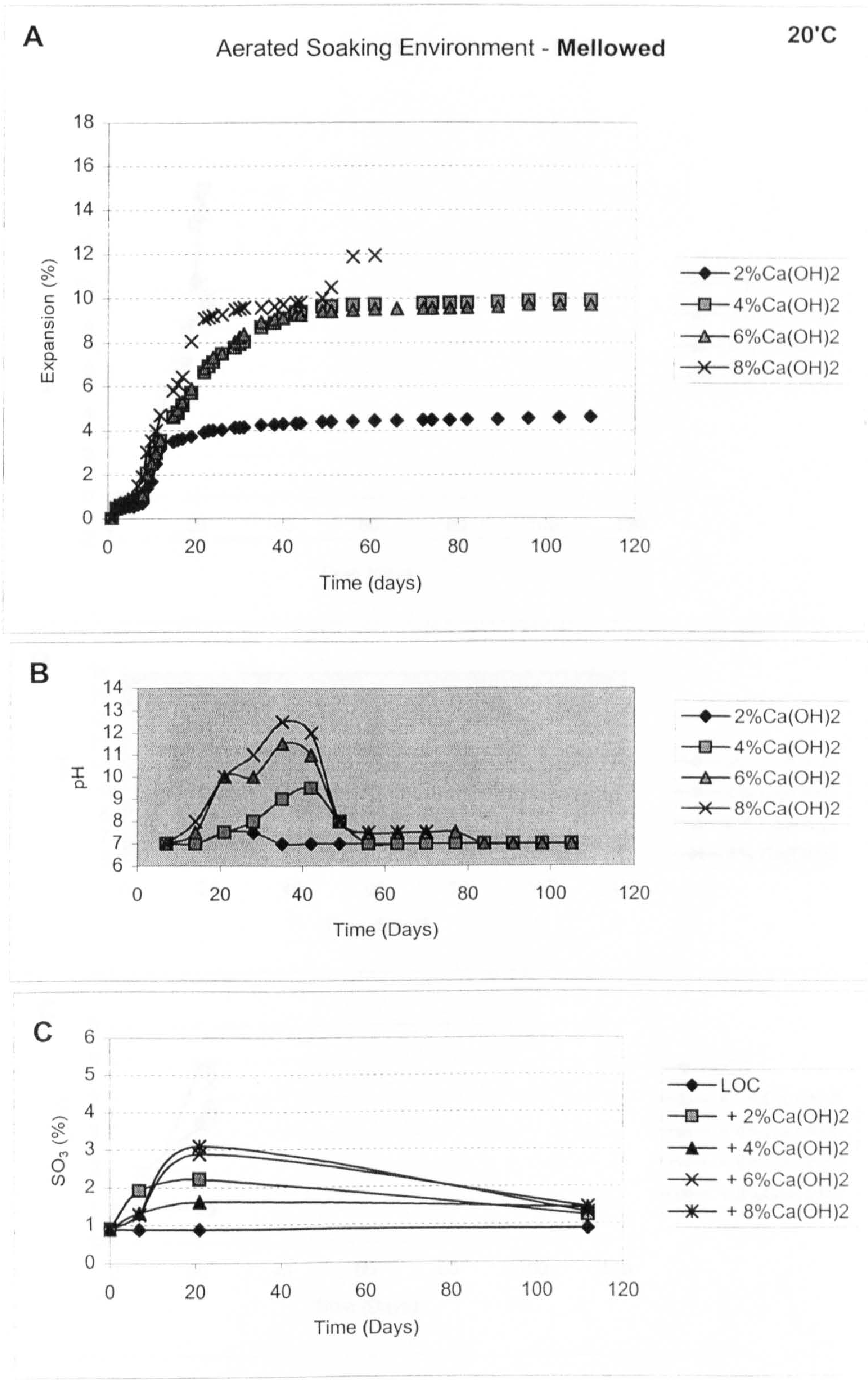


Figure 7.4.7 (A) Linear expansion; (B) pH measurements and (C) sulphate (SO_3) contents of mellowed (3 days at 20°C), compacted LOC samples with various additions of $Ca(OH)_2$ in an aerated soaking environment at 20°C.

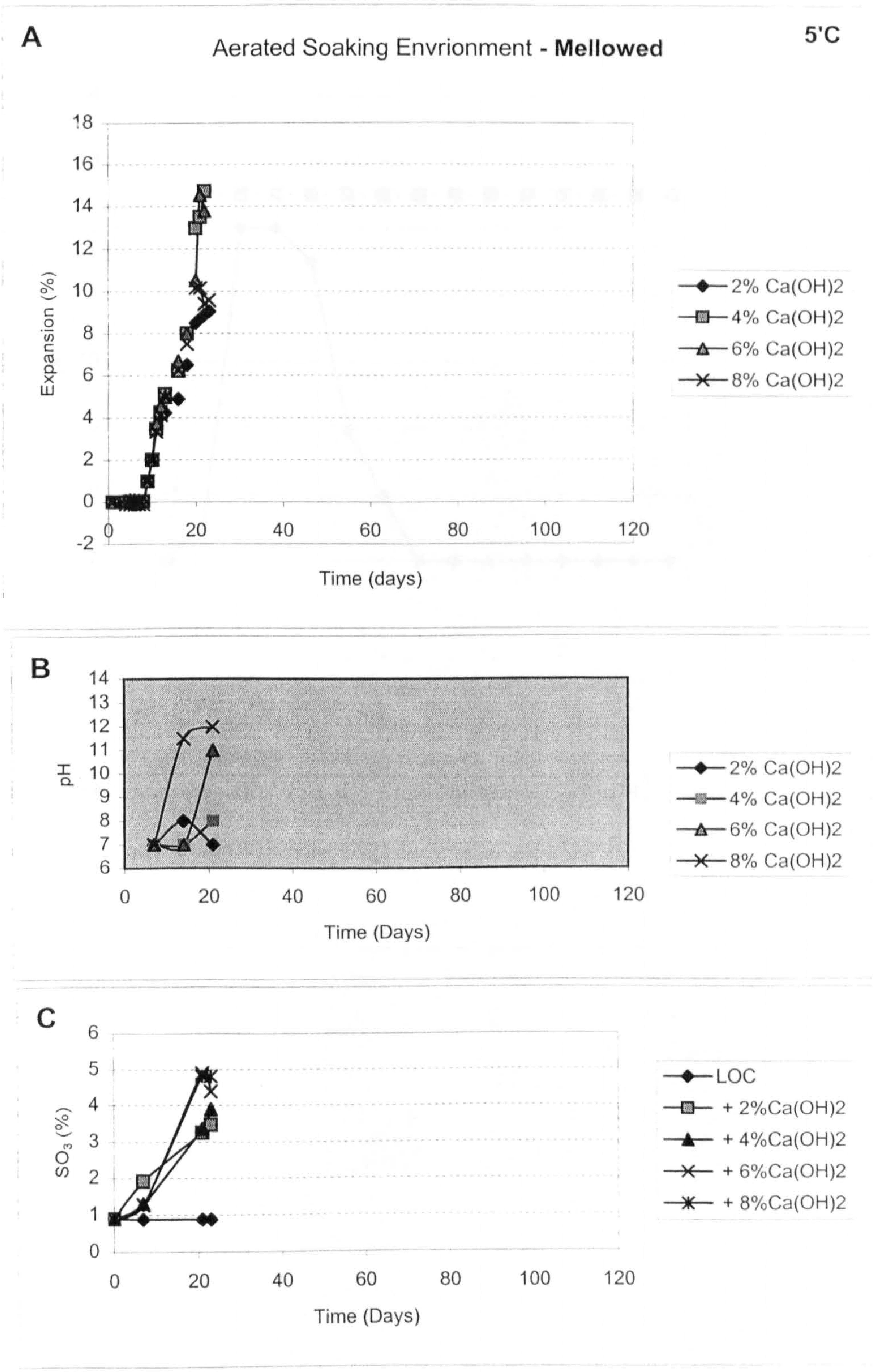


Figure 7.4.8 (A) Linear expansion; (B) pH measurements and (C) sulphate (SO_3) contents of mellowed (3 days at 20°C), compacted LOC samples with various additions of $Ca(OH)_2$ in an aerated soaking environment at 5°C.

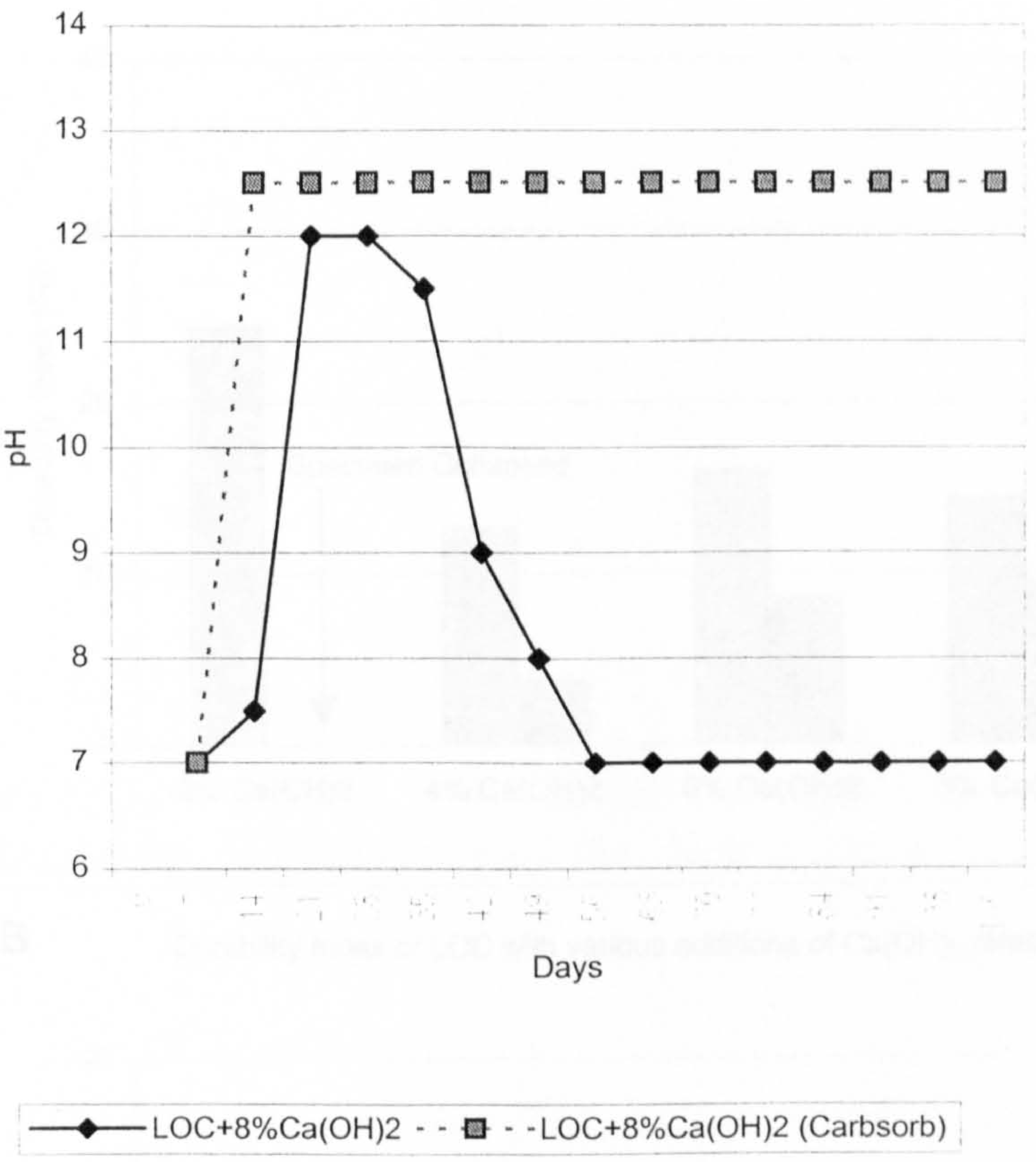


Figure 7.4.9 Comparison of the pH values of aerated soaking waters containing LOC-8%$Ca(OH)_2$ samples. The broken line represents the pH values of CO_2-free air where the air was first passed through soda lime or "carbsorb".

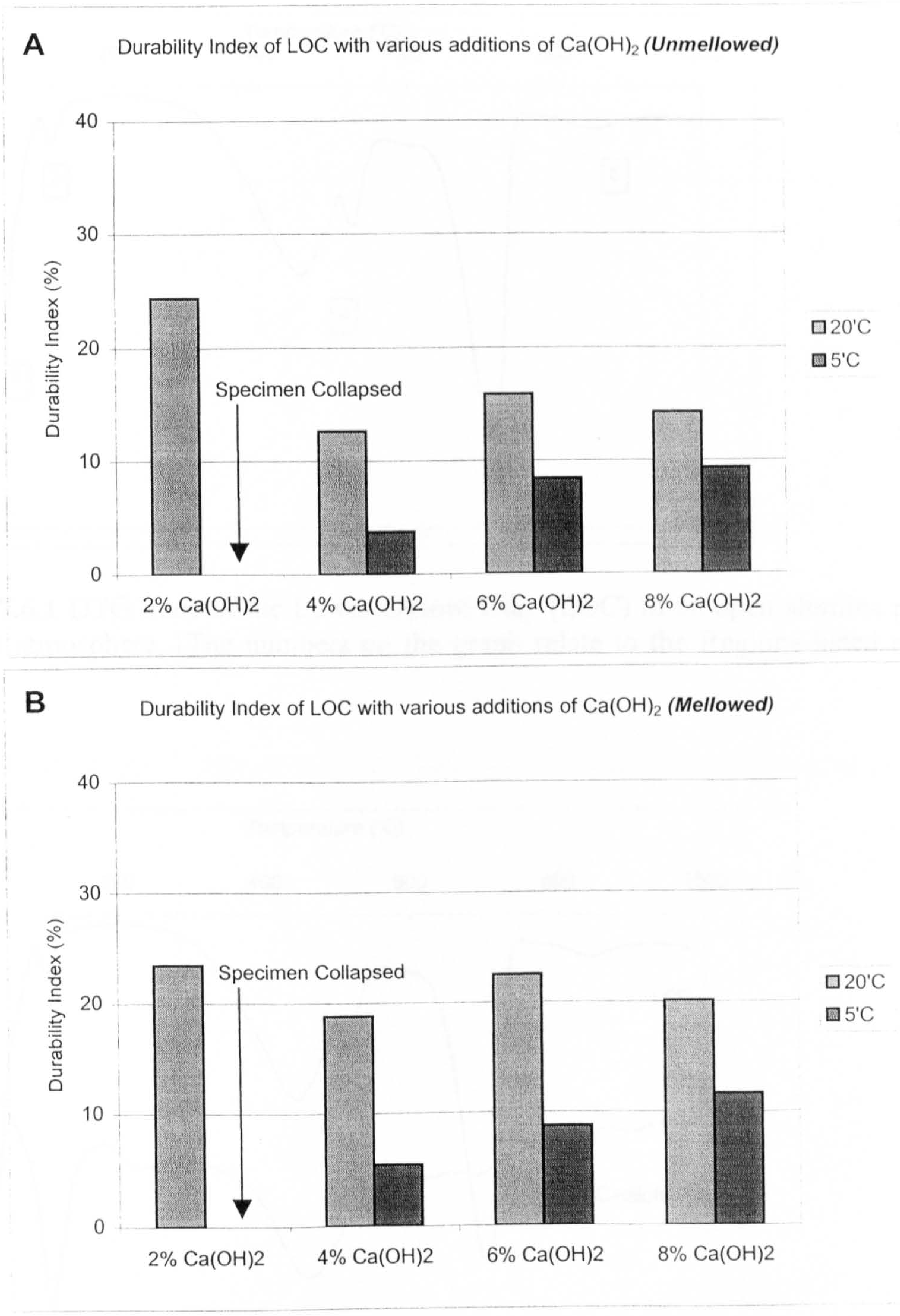


Figure 7.5.1 Durability index (DI) of compacted samples with various additions of $Ca(OH)_2$ tested at 5°C or 20°C, (A) unmellowed or (B) mellowed (for 3 days at 20°C).

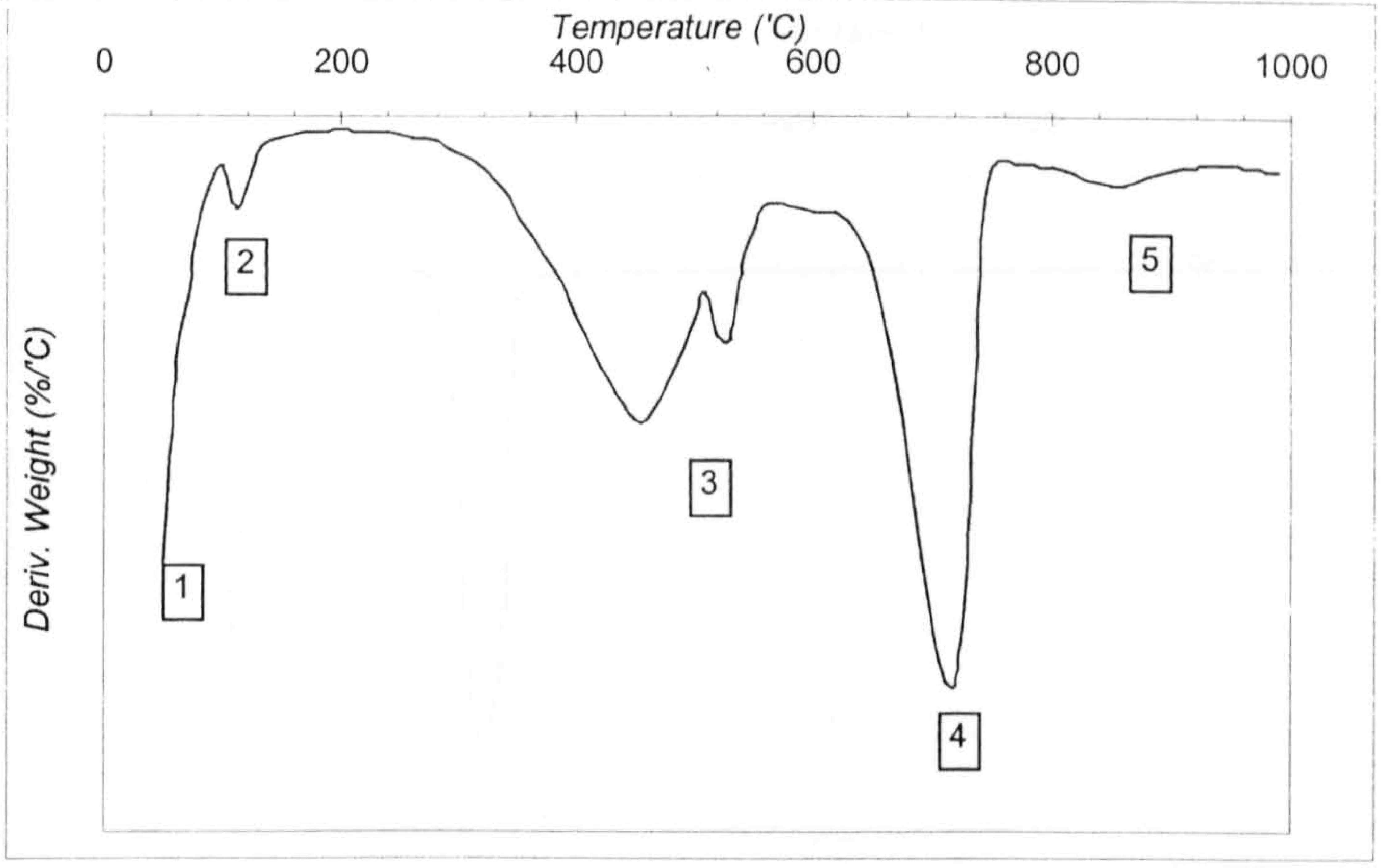


Figure 7.6.1 DTG trace of the Lower Oxford Clay (LOC) in an open alumina pan and nitrogen atmosphere. [The numbers on the graph relate to the Regions listed on page 156].

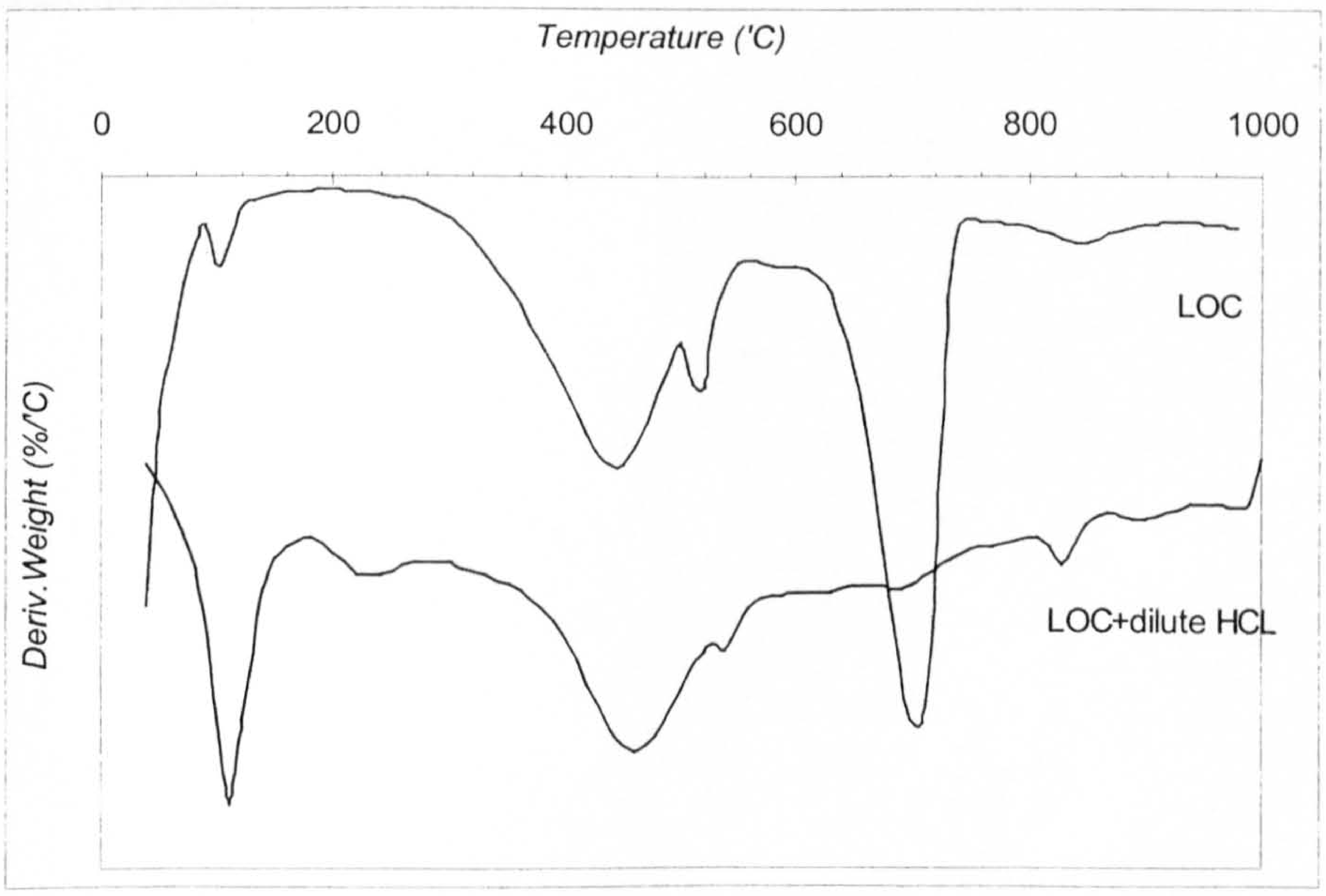


Figure 7.6.2 Comparison of the DTG traces of the LOC with and without treatment with dilute hydrochloric acid (HCl). Both samples were heated in open alumina pans in a nitrogen atmosphere.

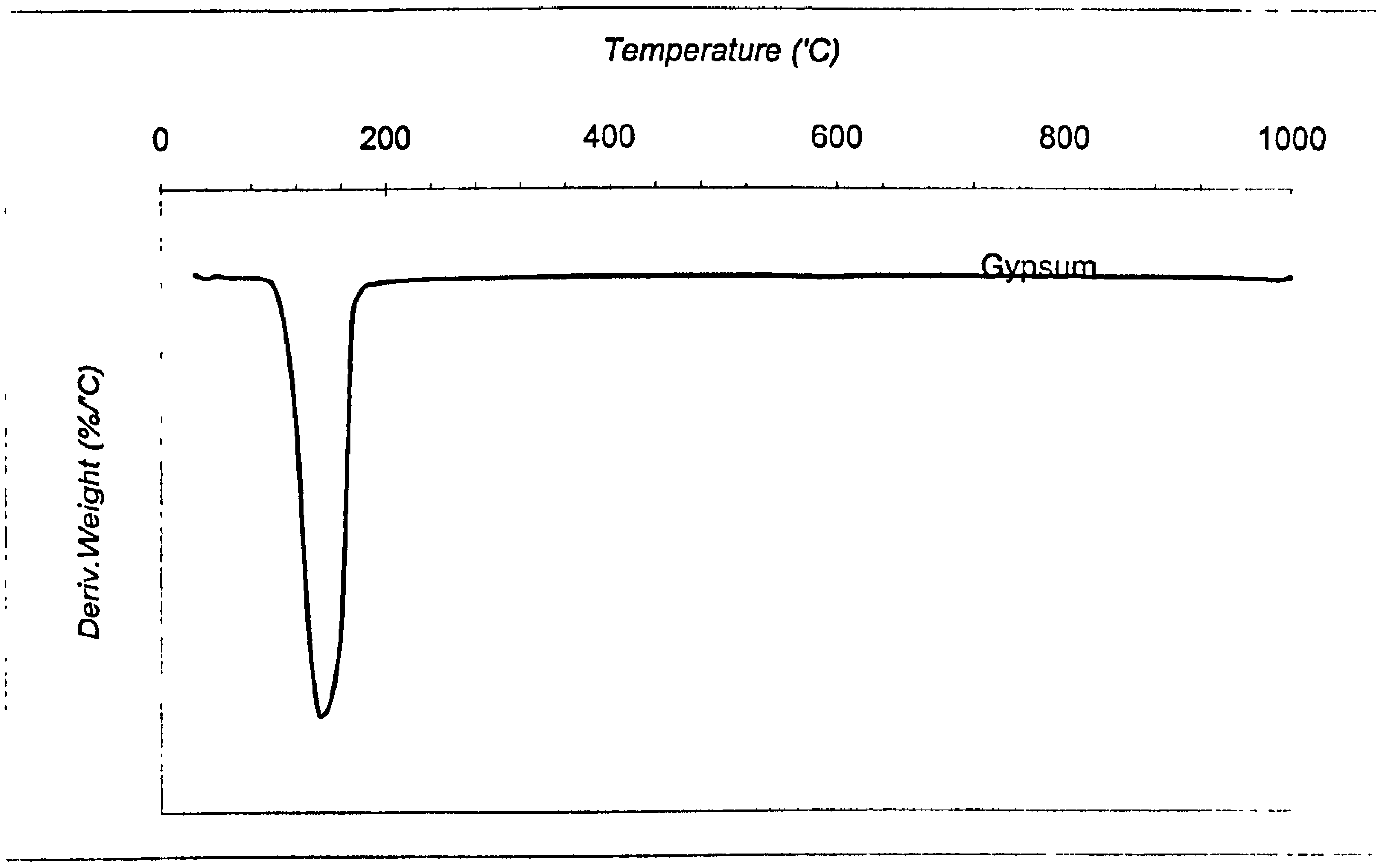


Figure 7.6.3 DTG trace of gypsum ($CaSO_4.2(H_2O)$) in a nitrogen atmosphere in an open alumina pan.

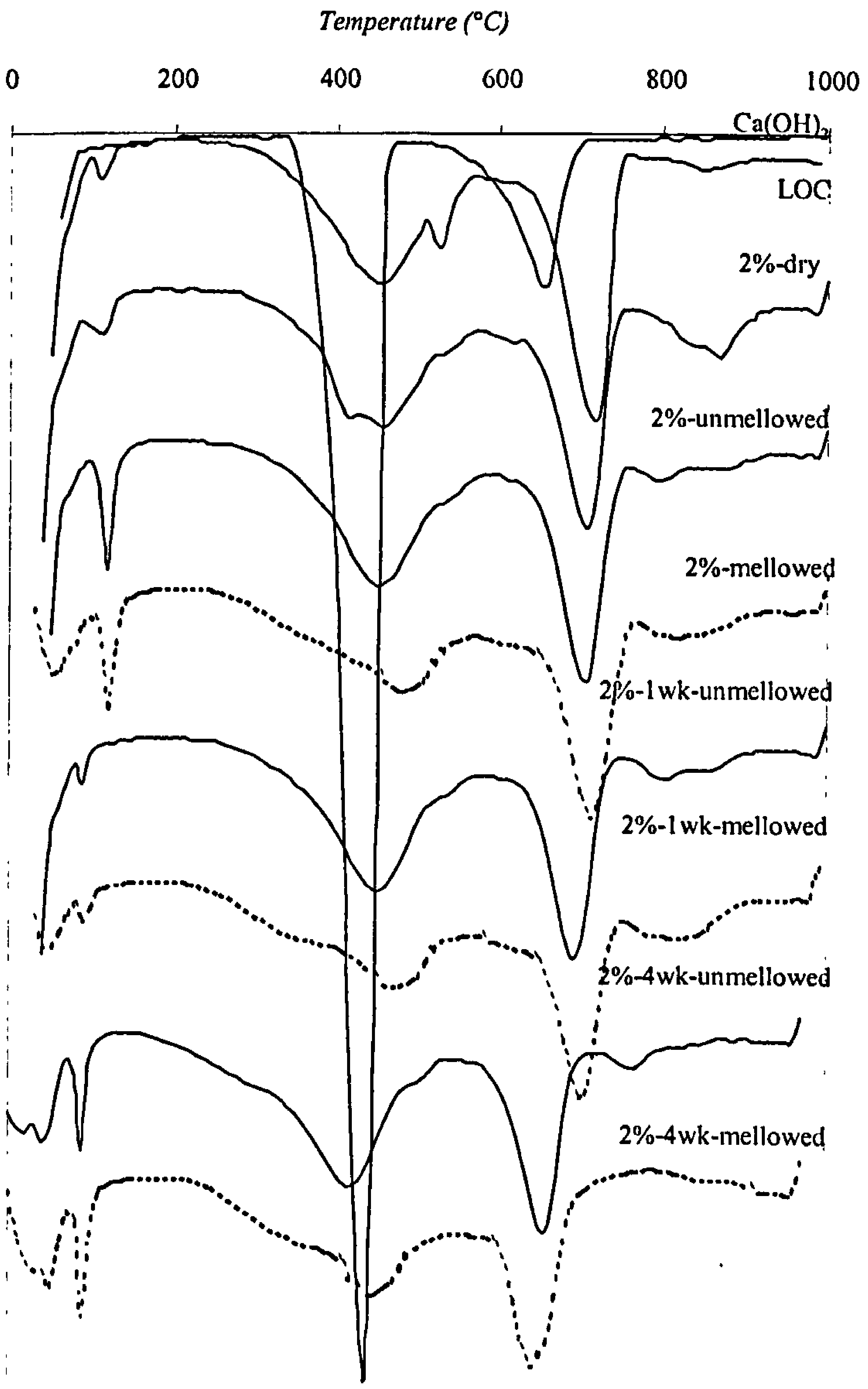


Figure 7.6.4 DTG trace of LOC with an addition of 2%$Ca(OH)_2$ mixed in a dry state; in an unmellowed state; after mellowing (3 days at 20°C); and after 1 and 4 weeks moist curing at 20°C (with or without a period of mellowing prior to compaction).

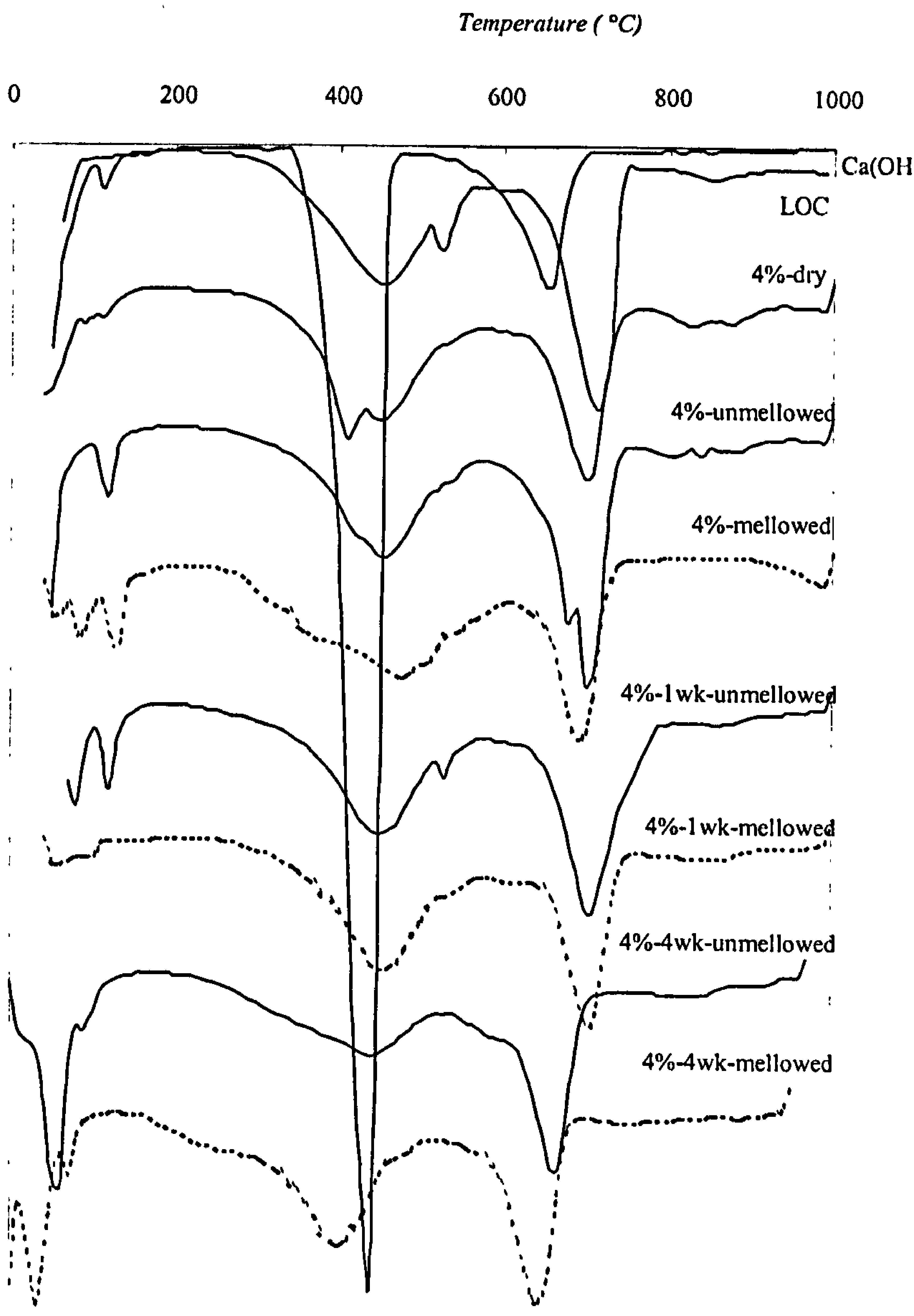


Figure 7.6.5 DTG trace of LOC with an addition of 4%$Ca(OH)_2$ mixed in a dry state; in an unmellowed state; after mellowing (3 days at 20°C); and after 1 and 4 weeks moist curing at 20°C (with or without a period of mellowing prior to compaction).

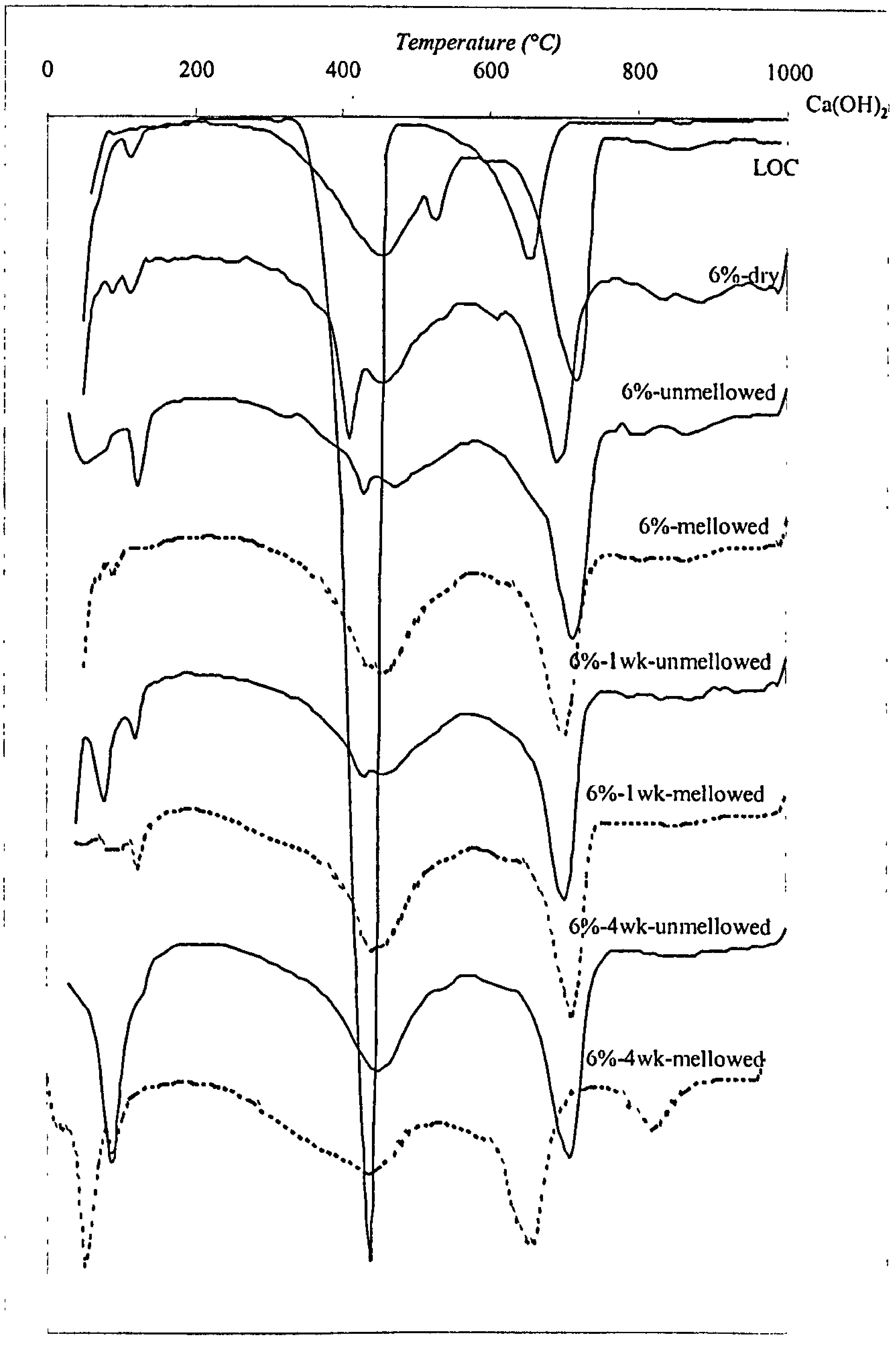


Figure 7.6.6 DTG trace of LOC with an addition of 6%$Ca(OH)_2$ mixed in a dry state; in an unmellowed state; after mellowing (3 days at 20°C); and after 1 and 4 weeks moist curing at 20°C (with or without a period of mellowing prior to compaction).

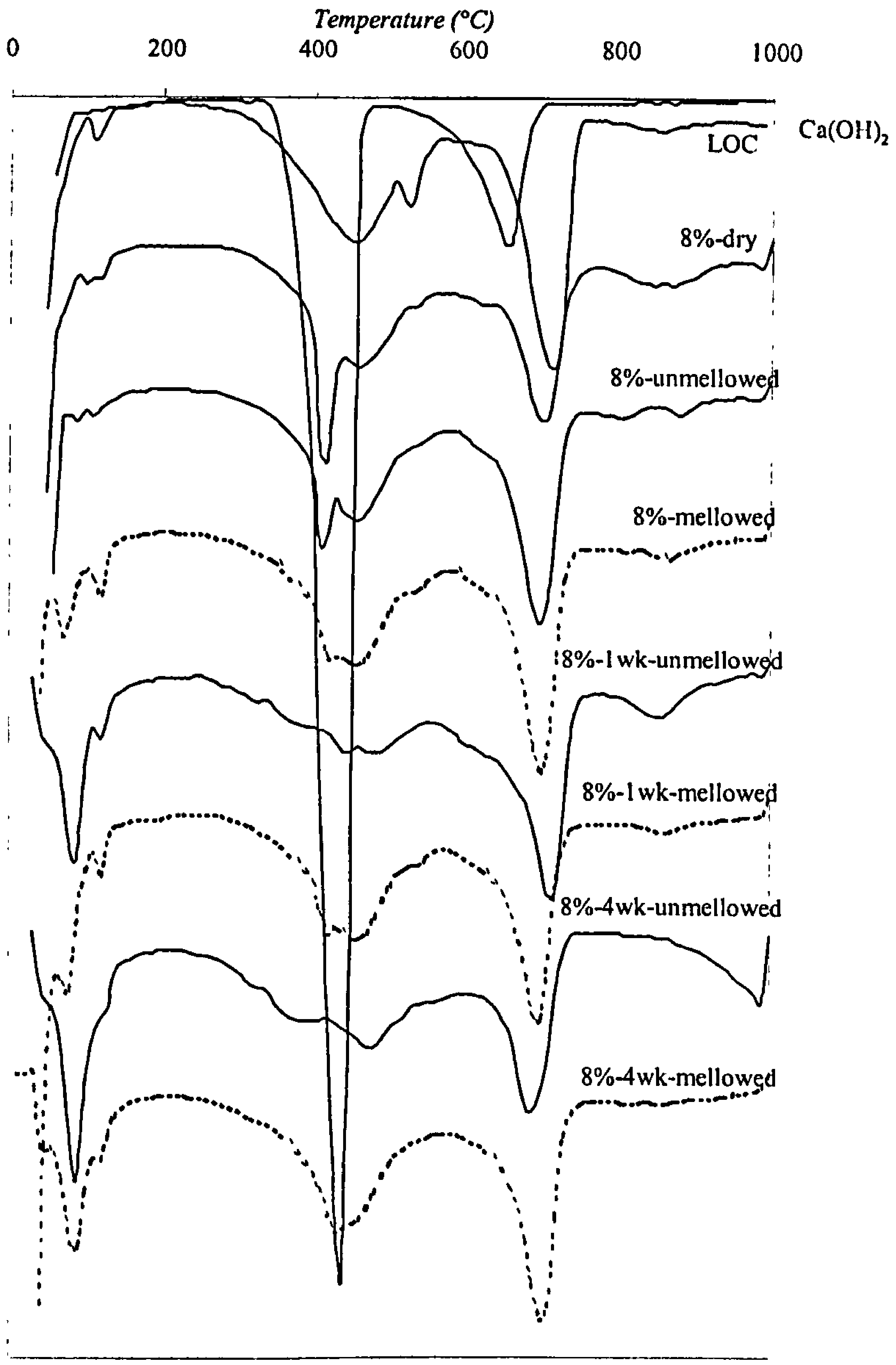


Figure 7.6.7 DTG trace of LOC with an addition of 8%Ca(OH)$_2$ mixed in a dry state; in an unmellowed state; after mellowing (3 days at 20°C); and after 1 and 4 weeks moist curing at 20°C (with or without a period of mellowing prior to compaction).

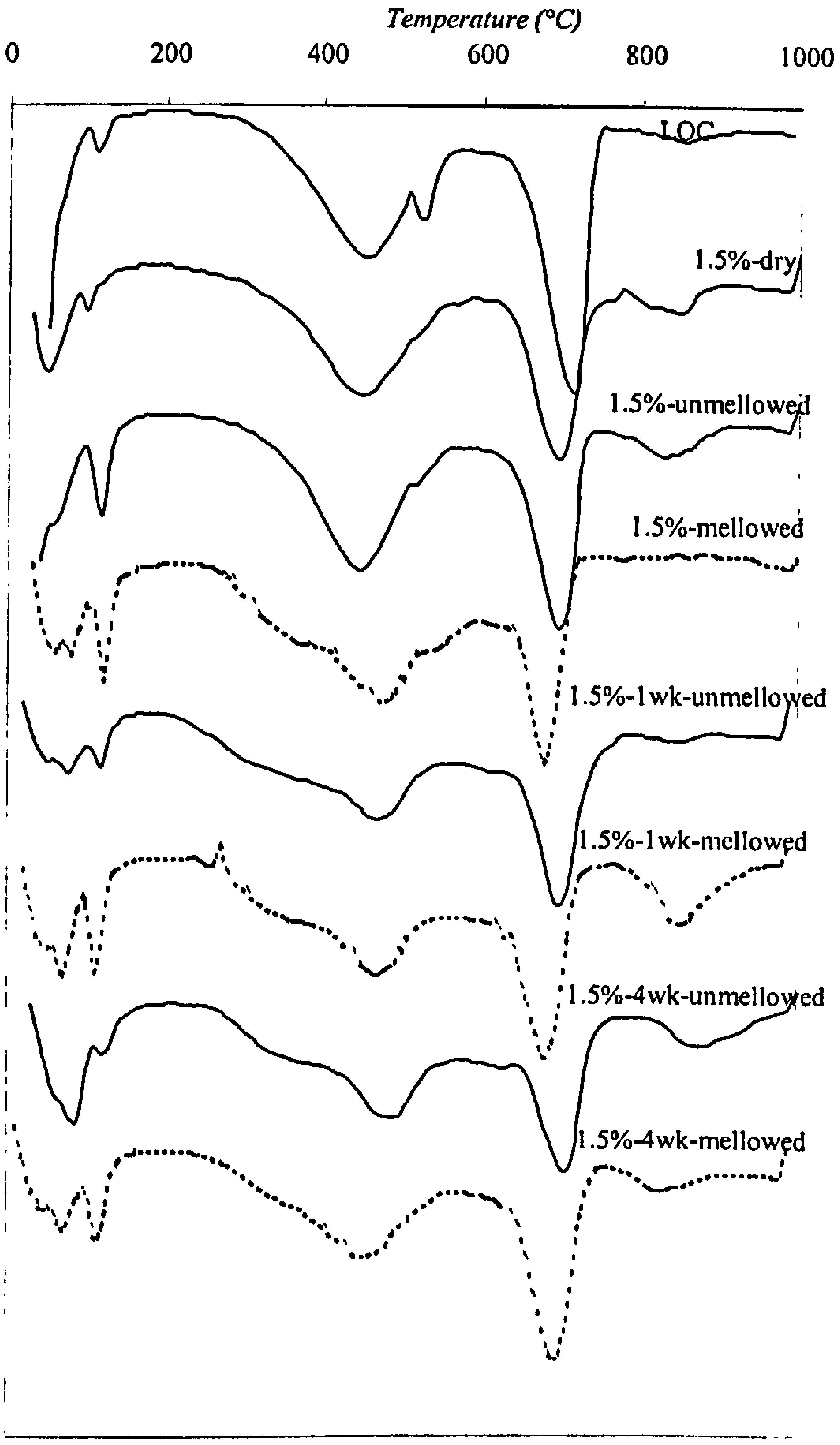


Figure 7.6.8 DTG traces of LOC with an addition of 1.5%CaO mixed in a dry state; in an unmellowed state; after mellowing (3 days at 20°C) and after 1 and 4 weeks moist curing at 20°C (with or without a period of mellowing prior to compaction).

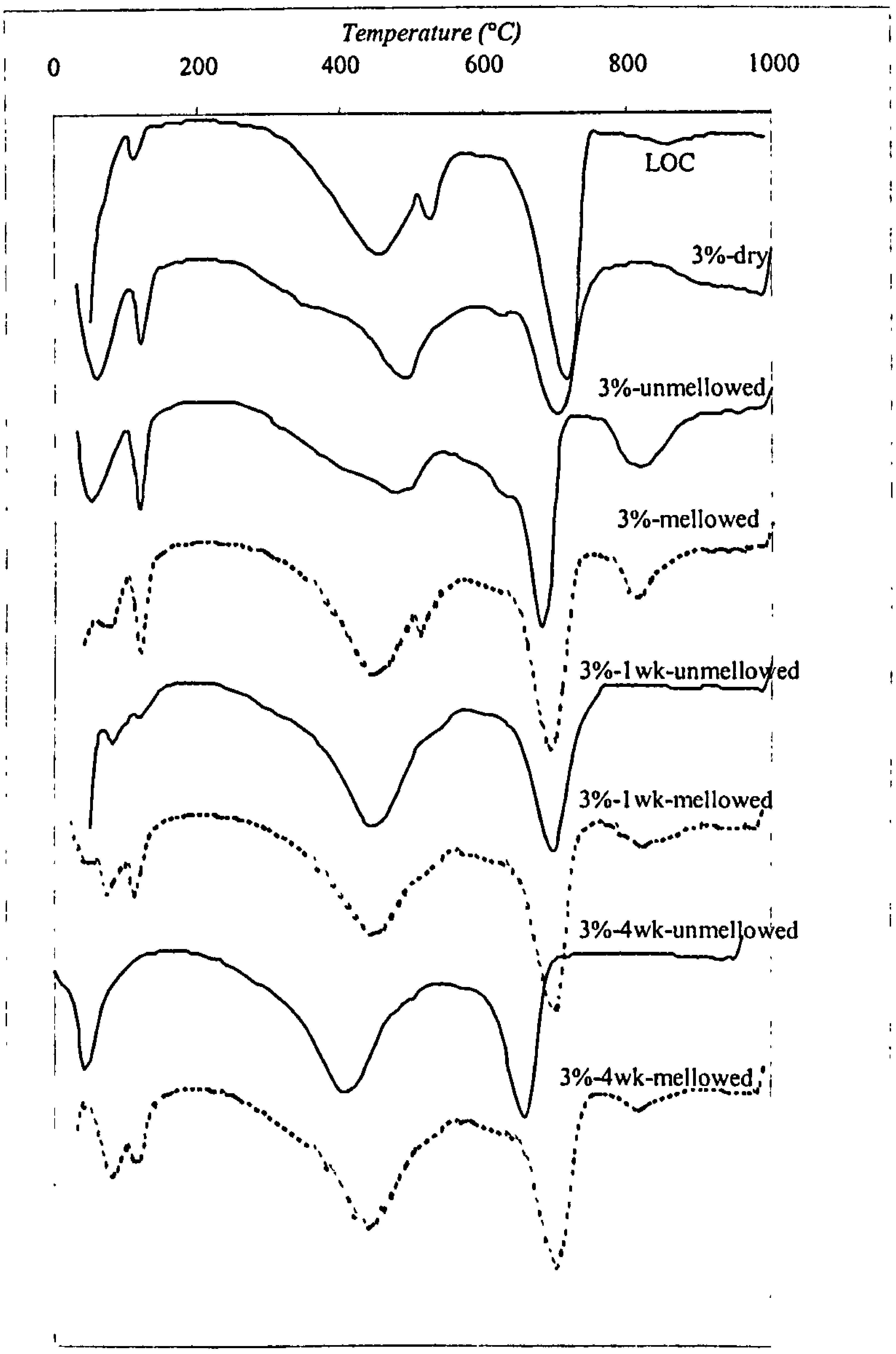


Figure 7.6.9 DTG traces of LOC with an addition of 3%CaO mixed in a dry state; in an unmellowed state; after mellowing (3 days at 20°C) and after 1 and 4 weeks moist curing at 20°C (with or without a period of mellowing prior to compaction).

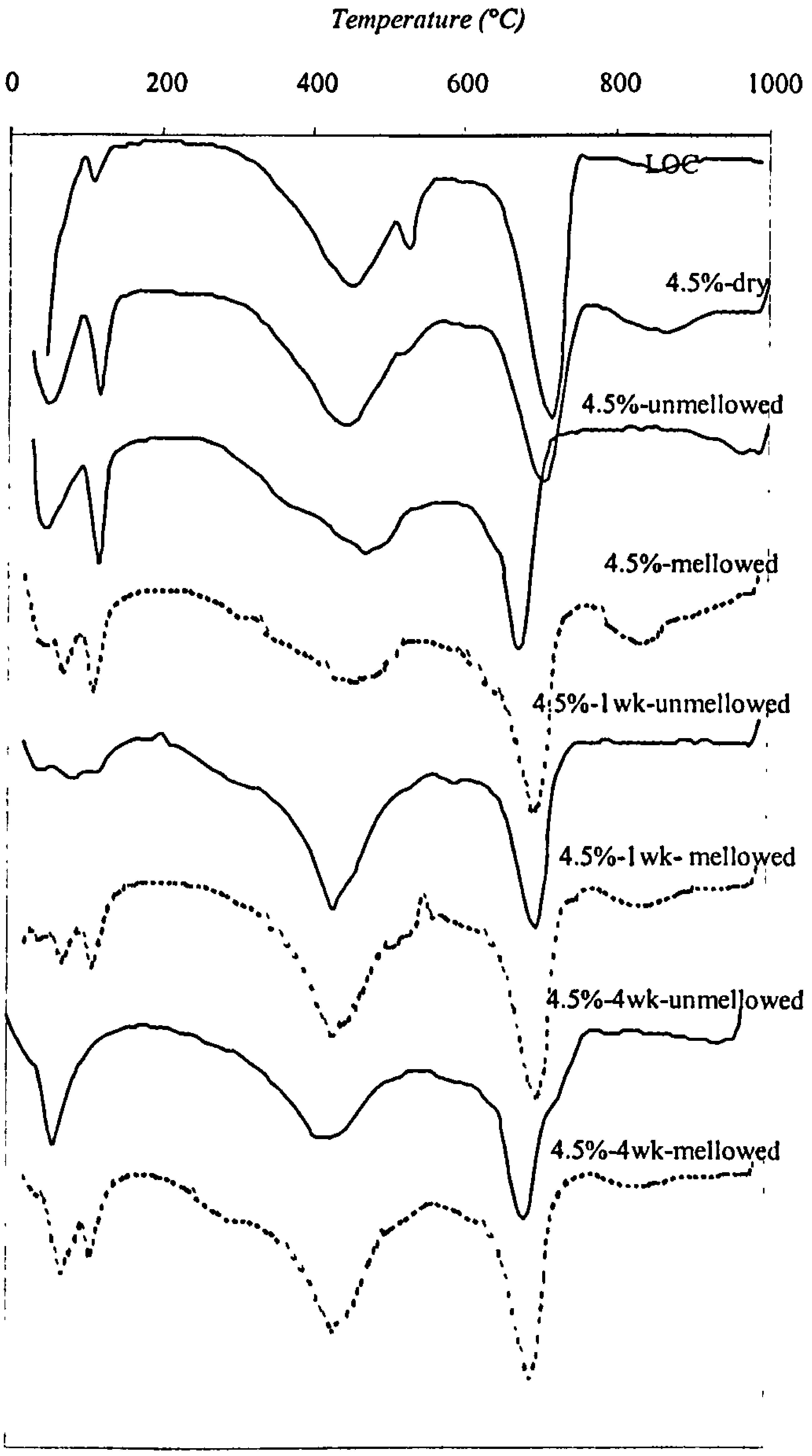


Figure 7.6.10 DTG traces of LOC with an addition of 4.5%CaO mixed in a dry state; in an unmellowed state; after mellowing (3 days at 20°C) and after 1 and 4 weeks moist curing at 20°C (with or without a period of mellowing prior to compaction).

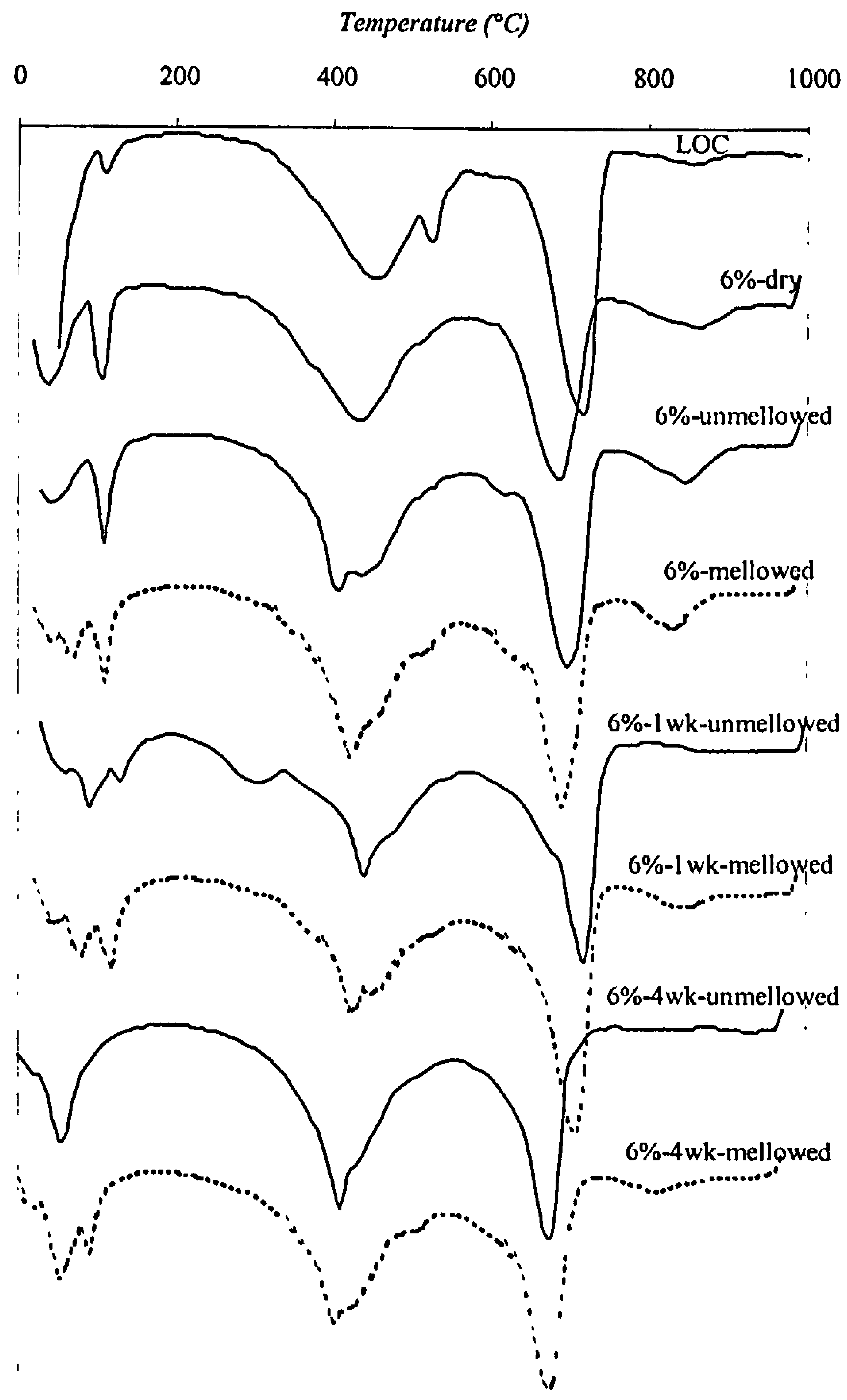
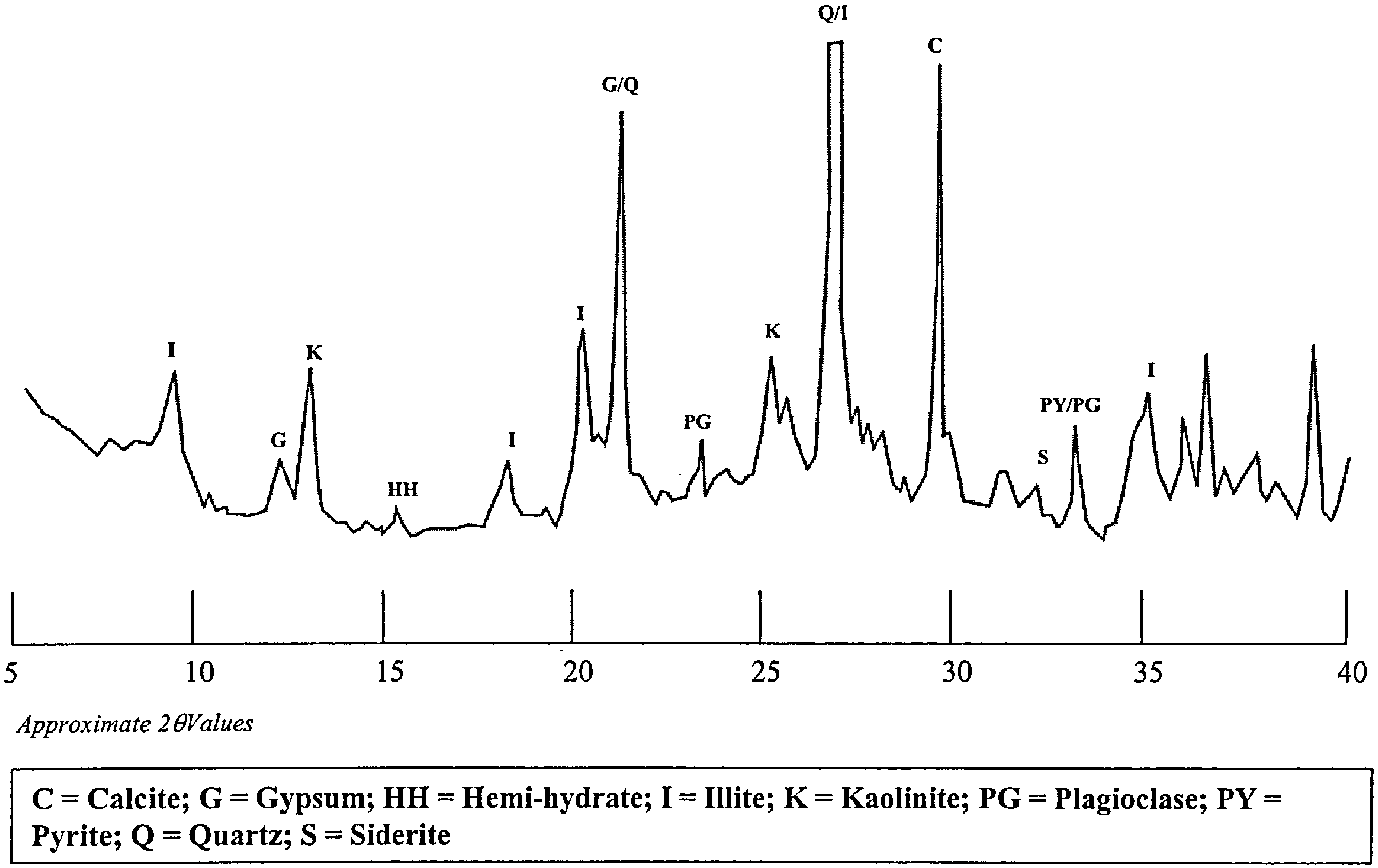
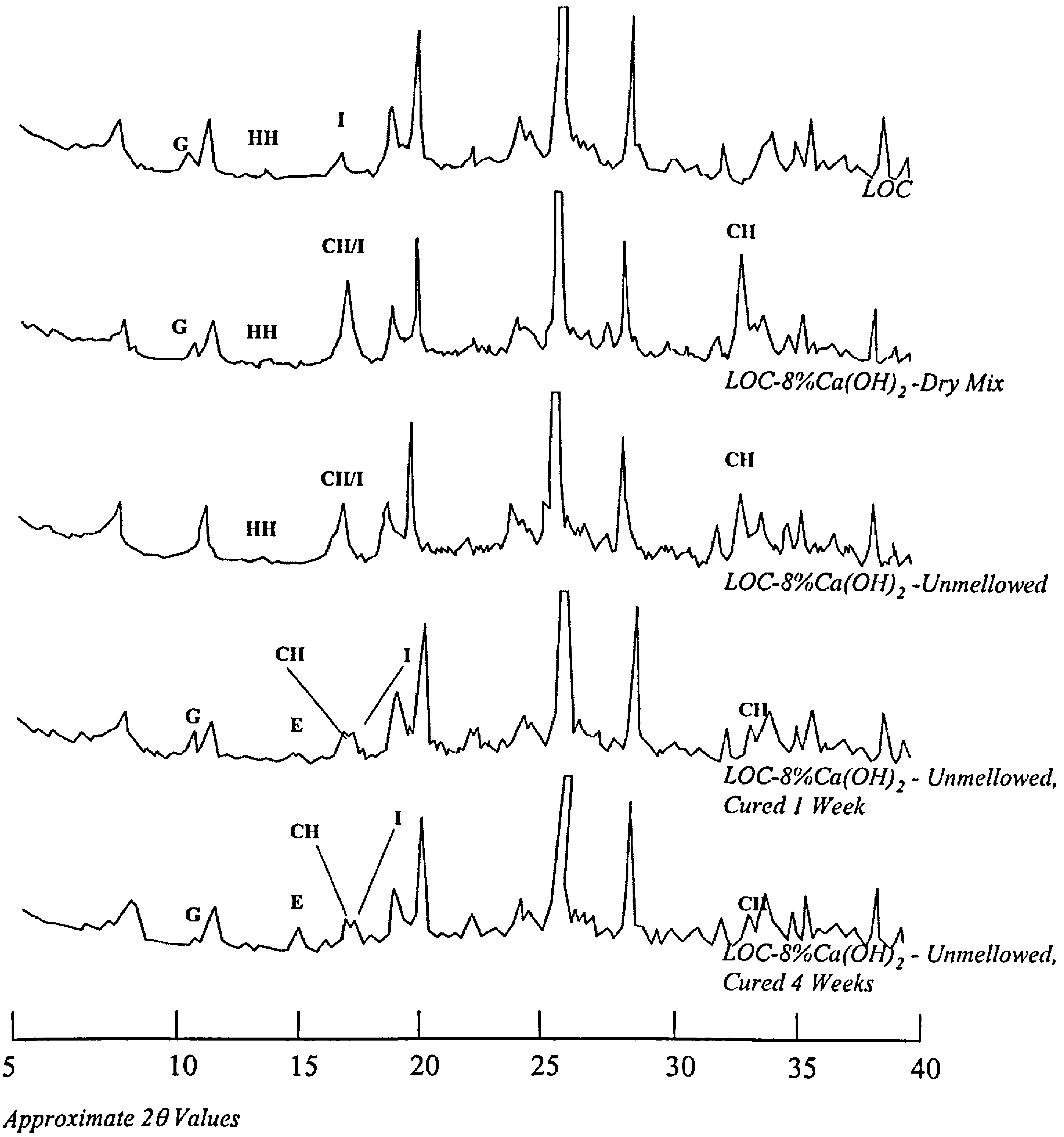


Figure 7.6.11 DTG traces of LOC with an addition of 6%CaO mixed in a dry state; in an unmellowed state; after mellowing (3 days at 20°C) and after 1 and 4 weeks moist curing at 20°C (with or without a period of mellowing prior to compaction).



C = Calcite; G = Gypsum; HH = Hemi-hydrate; I = Illite; K = Kaolinite; PG = Plagioclase; PY = Pyrite; Q = Quartz; S = Siderite

Figure 7.7.1 X-ray diffraction (XRD) trace of the Lower Oxford Clay (LOC) showing only the major peaks.



CH = $Ca(OH)_2$; E = Ettringite; G = Gypsum; HH = Hemi-hydrate; I = Illite

Figure 7.7.2 (A) X-ray diffraction (XRD) traces of LOC-8%$Ca(OH)_2$ samples mixed in a dry state; in an unmellowed state and after compaction and curing at 20°C for 1 and 4 weeks.

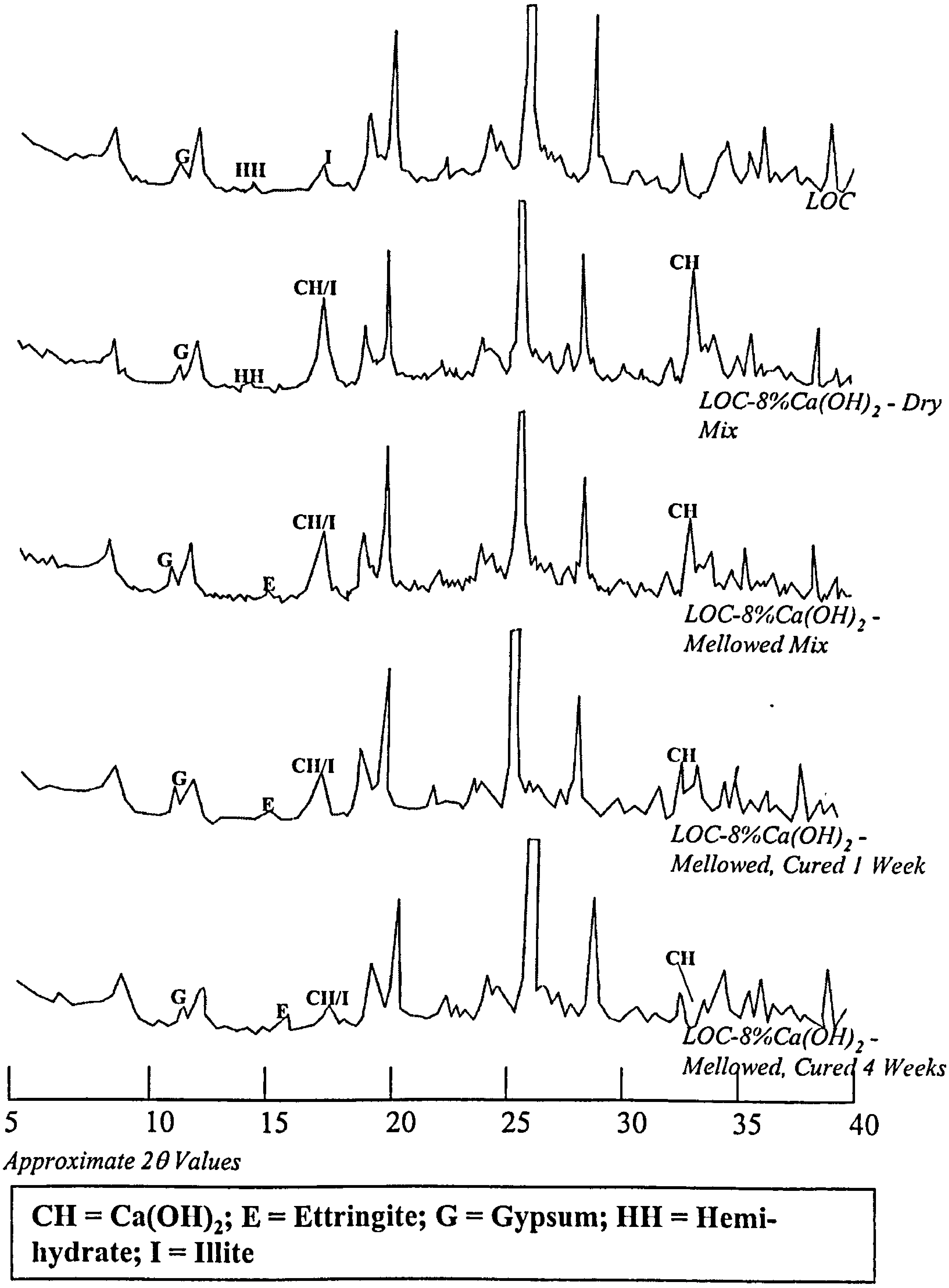
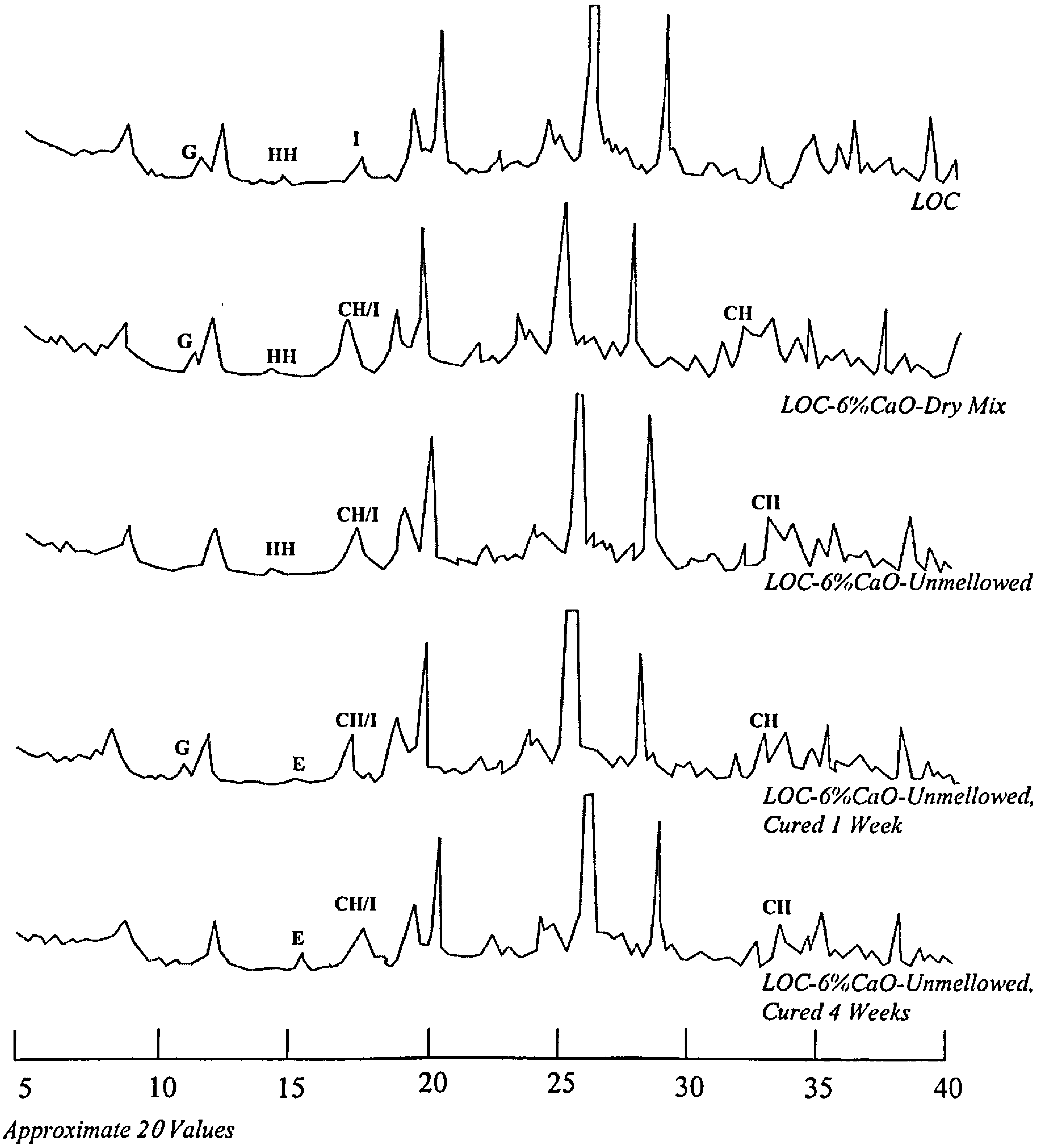


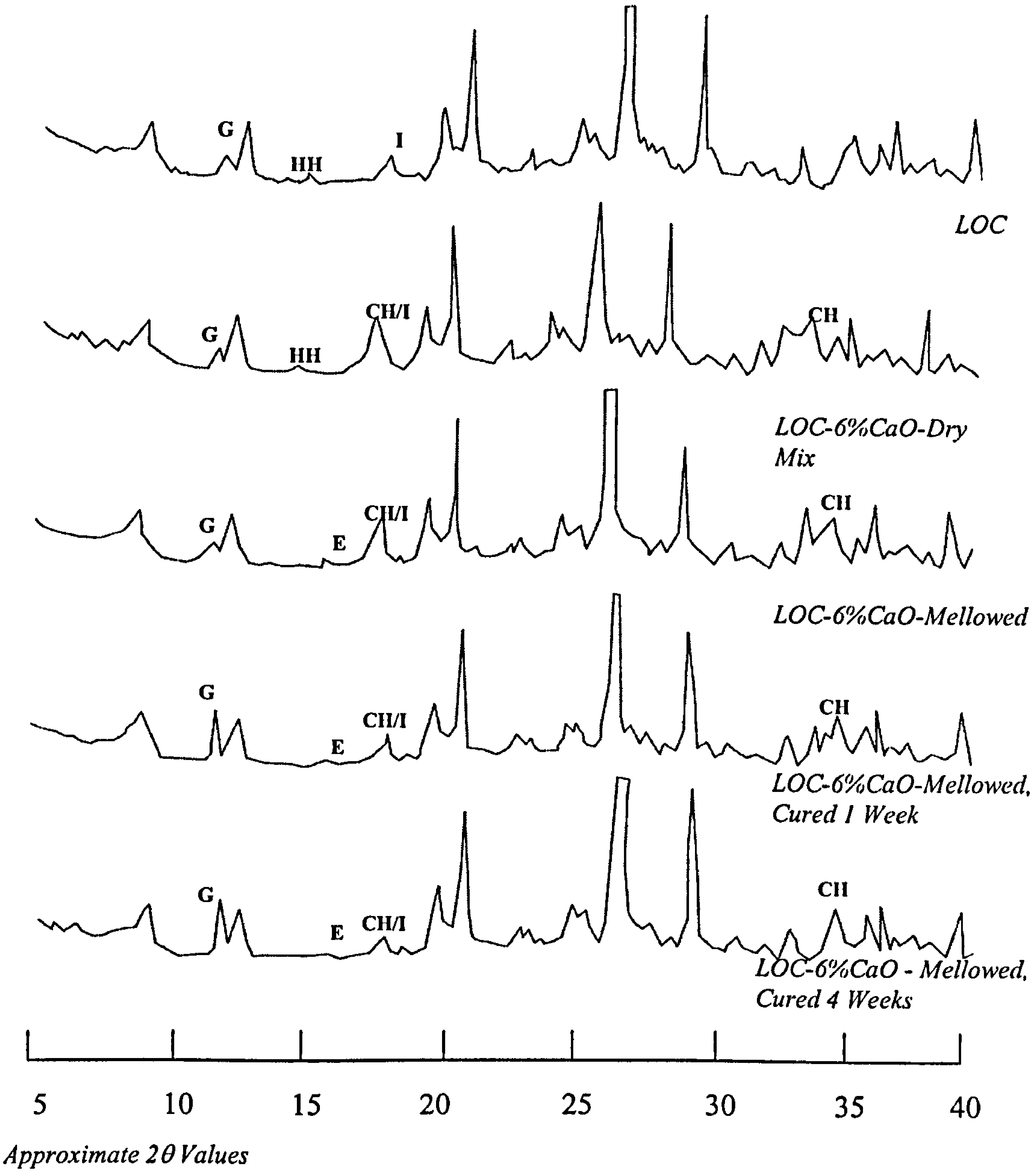
Figure 7.7.2 (B) X-ray diffraction (XRD) traces of LOC-8%$Ca(OH)_2$ samples mixed in a dry state; in a mellowed state (3 days at 20°C) and after compaction and curing at 20°C for 1 and 4 weeks.



CH = $Ca(OH)_2$; E = Ettringite; G = Gypsum; HH = Hemi-hydrate;

I = Illite

Figure 7.7.3 (A) X-ray diffraction (XRD) traces of LOC-6%CaO samples mixed in a dry state; in an unmellowed state and after compaction and curing at 20°C for 1 and 4 weeks.



CH = $Ca(OH)_2$; E = Ettringite; G = Gypsum; HH = Hemi-hydrate; I = Illite

Figure 7.7.3 (B) X-ray diffraction (XRD) traces of LOC-6%CaO samples mixed in a dry state; in a mellowed state (3 days at 20°C) and after compaction and curing at 20°C for 1 and 4 weeks.

8 Experimental Results – Lime Activated GGBS Stabilised, and Lime and PC Stabilised LOC.

8.1 Introduction

As shown in Chapter 7, Section 7.3, the change in UCS values with time and temperature of compacted LOC-2%$Ca(OH)_2$ and LOC-1.5%CaO samples is difficult to interpret because such small additions of lime show modification but little stabilisation as there is insufficient lime to produce significant amounts of cementing reaction products. There is a clear tendency for specimens cured at 5°C to show a decline in strength with increase in curing time, whereas small strength gains can be achieved at 10°C and 20°C. It should however, be noted that strength is influenced by moisture content and as there is clearly little cementation occurring in these samples, the variability in strength values may in part be due to variation in moisture content with curing time (Arabi, 1987). Also the distinction between using CaO or $Ca(OH)_2$ with respect to strength development is not clear although in general strengths are greater at the longer curing periods when CaO is employed. This again may be due to reduced moisture content in specimens containing CaO. The work in Chapter 7 shows that it is possible to achieve higher strengths with increased lime content but this also had the effect of producing increased expansion on soaking, which is unacceptable. One potential route to achieving cementation and strength development without the associated expansion is to use small additions of lime to modify the soil and then incorporate a stabilising agent such as GGBS or PC to provide cementation. The following section describes the strength development of lime modified LOC stabilised with either GGBS or PC. As discussed previously, in temperate regions such as the UK, quicklime (CaO) is generally used in preference to slaked lime ($Ca(OH)_2$) as it has a number of advantages (chapter 3). Also CaO has been utilised as a soil modifier and GGBS activator in stabilisation work in practice in the UK (Higgins and Kennedy, 1999). In addition, much work has already been carried out on the engineering properties of $Ca(OH)_2$-activated GGBS stabilised soils under laboratory conditions (Kinuthia, 1997; Wild et.al, 1998; Veith, 2000). Therefore CaO is used as the principal soil modifier and GGBS activator in the current work, although selected specimen compositions for UCS and durability work will also involve $Ca(OH)_2$ for comparative purposes. As a reference point the strength development of lime-modified LOC was first determined and then subsequently for GGBS stabilised and PC stabilised lime-modified LOC.

8.1.1 Unconfined Compressive Strength - Mellowed, Compacted Lime-Modified LOC

Figure 8.1.1 (A and B) show the UCS development of mellowed (3 days at 20°C) LOC-2%$Ca(OH)_2$ and LOC-1.5%CaO mixes, compacted at MDD and 32% MC. The compacted samples were cured at 5°C, 10°C and 20°C for 1, 4, 12, 24 and 52 weeks.

The mellowed, compacted LOC-2%$Ca(OH)_2$ samples developed little strength regardless of curing time and curing temperature (Figure 8.1.1 (A)). In fact when the samples were cured at 5°C UCS values noticeably diminished with the lowest strength exhibited after 52 weeks when cured at 5°C. The highest UCS value occurred after 52 weeks curing at 10°C. However, apart from the clear decline in strength development in samples cured at 5°C, the pattern of strength development was non-systematic with no sample showing a UCS value above 308 kN/m^2. Similarly the UCS values of mellowed, compacted LOC-1.5%cCaO samples proved to be erratic with the highest strength exhibited by the sample cured for 24 weeks at 10°C (363 kN/m^2) (Figure 8.1.1 (B)).

8.1.2 UCS of LOC-1.5%CaO with Various Percentage Additions of GGBS.

Figure 8.1.2. (A-D) shows the UCS development of mellowed (3 days at 20°C) LOC-1.5%CaO mixes, compacted (at MDD and 32% MC) after additions of 2%, 4%, 6% and 8% GGBS. The compacted samples were cured at 5°C, 10°C and 20°C for 1, 4, 12, 24 and 52 weeks.

An addition of 2%GGBS to the mellowed, compacted LOC-1.5%CaO sample generally resulted in increased UCS values especially when cured at 20°C, with the highest UCS value exhibited after 52 weeks curing (627 kN/m^2) (Figure 8.1.2 (A)). Strength was reduced after 1 weeks curing at 5°C when 2%GGBS was added to the LOC-1.5%CaO sample (from 204 kN/m^2 to 121 kN/m^2). A further addition of GGBS (4%) resulted in enhanced strength development of LOC-1.5%CaO samples, especially after 1 weeks curing at 5°C (Figure 8.1.2 (B)). However, although UCS values were generally slightly higher compared to additions of only 2%GGBS, after 52 weeks curing at 20°C the UCS values for the 2%GGB and 4%GGBS samples were very similar (627 kN/m^2 and 615 kN/m^2 respectively). A further addition of 2%GGBS (i.e. 6%GGBS in total) to the

LOC-1.5%CaO had little effect on the strength development of the compacted material after 1 weeks curing, though further curing did result in increased strength in samples cured at 20°C (Figure 8.1.2 (C)). There was little significant strength gain when a further 2%GGBS was added to the LOC-1.5%CaO-6%GGBS sample (i.e. 8%GGBS). In fact after 52 weeks curing at 20°C the UCS value was less than that exhibited by the LOC-1.5%CaO–6%GGBS sample (987 kN/m^2 compared to 1137 kN/m^2). It is apparent in all LOC-1.5%CaO-GGBS samples that most of the strength development takes place within the first 12 weeks curing at 20°C and further strength development beyond 12 weeks is negligible.

As mentioned earlier (Chapter 4) GGBS hydrates, or is activated, in an alkaline environment (provided in soil stabilisation by the lime), which breaks down the pseudomorphic layer coating individual slag grains. This releases silica and alumina and eventually C-S-H gels and other cementing products form resulting in much improved strength, compared to lime-only stabilised soils. However, in a similar way to pozzolans such as clay minerals in lime-modified soils, the GGBS hydration reaction must compete for available lime with other reactions such as cation exchange (flocculation), ettringite formation, and (if present) pyrites (FeS_2) oxidation in order to proceed. As stated in Chapter 7 it is known that during mellowing (3 days at 20°C) lime is consumed in several reactions resulting in reduced available lime content after mellowing and reduced pH. Therefore it is probable that GGBS hydration, and therefore strength development, may be subdued when a mellowing period is employed beforehand. It can be seen from Figure 8.1.2 (A-D) that, in general, strength is greatest in GGBS stabilised LOC after long curing periods of 12 weeks at 20°C when the samples contain 6%GGBS. This is unsurprising, as it is known that higher curing temperature, increased curing time and high GGBS contents result in increased strength development of lime-activated, GGBS stabilised clay soils (Veith, 2000). After 12 weeks moist curing it is apparent that strength development is not significantly enhanced, especially at 20°C, in all LOC-1.5%CaO samples with added GGBS. It is thought that the relatively small amount of added lime is insufficient to enable further hydration of the GGBS and therefore continued curing does not result in increased strength. It is clear also that increasing the amount of GGBS provides increased strength up to an addition of 6% and that an addition of 8%GGBS yields little further significant increases in strength, which may also be attributed to insufficient lime to provide further activation.

8.1.3 UCS of LOC-1.5%CaO with Various Percentage Additions of PC.

Figure 8.1.3 (A-D) shows the UCS development of mellowed (3 days at 20°C) LOC-1.5%CaO mixes, compacted (at MDD and 32% MC) after additions of 2%, 4%, 6% and 8% PC. The compacted samples were cured at 5°C, 10°C and 20°C for 1, 4, 12, 24 and 52 weeks.

An addition of 2% PC generally improved the strength development of 1.5%CaO-modified LOC (Figure 8.1.3 (A)), although after 1 weeks curing at 5°C the UCS value of the LOC-1.5%CaO-2%PC sample was less than that of the LOC-1.5%CaO sample (165 kN/m^2 and 204 kN/m^2 respectively), which is similar to the behaviour of samples with 2%GGBS. Also after 12 weeks curing at all temperatures a 2%PC addition to the LOC-1.5%CaO resulted in enhanced strength values compared to similar additions of 2%GGBS, with the greatest strength occurring after 24 weeks curing at 20°C (953 kN/m^2). Further additions of PC to the LOC-1.5%CaO generally resulted in increased

UCS, especially after long curing periods at higher temperatures. When compared to similar LOC-1.5%CaO-GGBS samples (Figure 8.1.2 (B-D)), the strengths achieved with PC are higher, and strength development continues to occur beyond 12 weeks, while PC levels above 6% continue to provide strength enhancement.

As previously discussed, the addition of lime to a clay soil before stabilisation with PC and compaction modifies the engineering properties of an otherwise unsuitable material resulting in better workability and ease of mixing and stabilisation. However, unlike GGBS, PC does not require an alkaline environment in order to hydrate and therefore is unaffected by any possible depletion in available lime level after the period of mellowing. PC is also known to hydrate at a faster rate than GGBS producing, in comparison, superior strengths over the early curing period. In addition to producing C-S-H gels and C-A-H phases as cementing products during hydration, PC also produces lime, in the form of $Ca(OH)_2$. It is thought that this extra lime encourages pozzolanic reactions involving clay minerals in PC-stabilised soils adding to long-term strength development. Therefore increasing additions of PC will produce greater strength enhancement than increasing additions of GGBS, as exhibited by the LOC-1.5%CaO-8%PC sample which after 52 weeks curing at 20°C had stabilised at 1775 kN/m^2 whereas the equivalent LOC-1.5%CaO-8%GGBS sample had stabilised at 1000 kN/m^2 and showed little change after 12 weeks. Also when curing PC stabilised material for long periods the UCS values of samples cured at 5°C were significantly better than similar GGBS samples indicating that at such low temperatures PC hydration, although substantially reduced, was not retarded to the same degree as the GGBS stabilised samples.

8.1.4 UCS of LOC-2%$Ca(OH)_2$ with Various Percentage Additions of GGBS or PC.

Figure 8.1.4. (A-D) shows the UCS development of mellowed (3 days at 20°C) LOC-2%$Ca(OH)_2$ mixes, compacted (at MDD and 32% MC) after additions of 4% and 8% GGBS or 4 and 8% PC. The compacted samples were cured at 5°C, 10°C and 20°C for 1, 4, 12, 24 and 52 weeks.

An addition of 4%GGBS significantly enhanced the strength of the mellowed compacted LOC-2%$Ca(OH)_2$ sample, especially when cured at 20°C, with the greatest strength exhibited after 52 weeks curing (Figure 8.1.4 (A)). Further addition of GGBS (8%) further improved the UCS values of the mellowed LOC-2%$Ca(OH)_2$ with the highest strength again exhibited after curing at 20°C for 52 weeks (Figure 8.1.4 (B)). It is again noticeable that strength development was retarded between 12 and 52 weeks curing in the LOC-2%$Ca(OH)_2$-4%GGBS samples, which is explained in terms of insufficient lime being available for continued activation of the GGBS. However, surprisingly at 8%GGBS addition for specimens cured to 10°C and 20°C there was a significant increase in UCS values between 24 and 52 weeks curing, indicating that cementing products were still being formed. It is also apparent that a marked decrease in strength occurs after 12 weeks moist curing at 5°C in both the LOC-2%$Ca(OH)_2$-4%GGBS and 8%GGBS samples and in both samples the UCS value for specimens cured for 52 weeks is less that that of samples cured for 12 weeks.

Similar to an addition of GGBS, an addition of 4%PC improved the UCS of mellowed, compacted LOC-2%$Ca(OH)_2$ samples, with the greatest value being exhibited in the sample cured for 52 weeks at 20°C (1505 kN/m^2) (Figure 8.1.4 (C)). Again a further increase in PC addition (8%) further increased the strength development of the modified LOC especially at higher curing temperatures and extended curing periods (52 weeks at 20°C – 2315 kN/m^2) (Figure 8.1.4 (D)). From Figure 8.1.2 it is apparent that additions of PC prove more effective than equal additions of GGBS with regard to strength development of lime-modified LOC especially after 52 weeks curing. This accelerated strength gain after prolonged curing, when PC hydration is very much retarded, is again indicative of pozzolanic reactions between the $Ca(OH)_2$ provided by the hydrated PC and components in the LOC. It is also apparent that LOC samples initially modified with 2%$Ca(OH)_2$ and subsequently stabilised with either GGBS or PC showed significantly higher UCS values after 52 weeks moist curing at 20°C compared to similar LOC-1.5%CaO samples (Figures 8.1.2-8.1.4). For example, the LOC-1.5%CaO-8%PC sample exhibited a UCS value of 1772 kN/m^2 after 52 weeks curing at 20°C, whereas a similar sample containing 2%$Ca(OH)_2$ showed a value of 2315 kN/m^2. Similarly, samples containing 8%GGBS were significantly stronger when 2%$Ca(OH)_2$ was employed as a modifier compared to 1.5%CaO (1314 kN/m^2 and 987 kN/m^2 respectively). As established in Chapter 7, Section 7.2, although there is no significant difference in strength between compacted LOC-2%$Ca(OH)_2$ and LOC-1.5%CaO samples, the density of the LOC-1.5%CaO is significantly lower than the LOC-2%$Ca(OH)_2$ mix (1.365 Mg/m^3 compared to 1.39 Mg/m^3 respectively). It is thought that the more dense LOC-2%$Ca(OH)_2$ samples may prove stronger when stabilised and cured for long periods as the gel network may be more dense and better formed in the smaller pore matrix resulting in greater strength.

Summary

- The long term strength development (UCS) of mellowed (3 days at 20°C), compacted LOC-2%$Ca(OH)_2$ and 1.5%CaO samples cured at 5°C, 10°C and 20°C for 1, 4, 12, 24 and 52 weeks is insignificant because such small additions of lime show modification but little stabilisation as there is insufficient lime to produce significant amounts of cementing reaction products.
- Increasing additions of GGBS generally increase the strength development of mellowed, compacted and cured LOC-1.5%CaO mixes, especially at 20°C. However additions of >6%GGBS produced little improvement in UCS values. Also after 12 weeks curing little further increases in strength were observed, especially at high curing temperatures.
- Similarly increasing additions of PC generally increase the strength development of mellowed LOC-1.5%CaO mixes after curing, especially at 20°C. It is apparent that additions of PC exhibit greater strength development, especially after 12 weeks curing, than similar samples containing GGBS. As PC does not require an alkaline environment to hydrate (as GGBS does) then the amount of lime consumed during flocculation and mellowing is not significant. PC produces lime on hydration, which is known to react with pozzolanic material (i.e. clay minerals) to further enhance strength.
- Increasing additions of GGBS and PC also generally increase the strength development of mellowed, LOC-2%$Ca(OH)_2$ mixes after curing. When LOC was initially modified with 2%$Ca(OH)_2$ rather than 1.5%CaO before stabilisation and compaction, UCS values were generally higher. This is probably a result of the differing densities produced during compaction when $Ca(OH)_2$ and CaO are used as soil modifiers (see Section 7.2).

Although PC stabilised LOC modified with 2%$Ca(OH)_2$ (or 1.5%CaO) develops greater strength than LOC stabilised with equivalent amounts of GGBS this does not necessarily guarantee lower expansion during soaking and enhanced durability. The following section therefore looks at the effects of soaking on the lime-modified LOC stabilised with differing additions of GGBS or PC.

8.2 Linear Expansion

Chapter 7 of the current work shows that the linear expansion of compacted LOC-lime samples was greatly reduced when a mellowing period (3 days at 20°C) was employed before final compaction. Also in Chapter 7 it was observed that the pattern of linear expansion of compacted samples of LOC modified with 2%$Ca(OH)_2$ or 1.5%CaO was not affected by lime type. In the linear expansion test, 1.5%CaO was used to modify the LOC during mellowing and before the addition of GGBS or PC and subsequent compaction, as it is CaO that is usually employed in GGBS/PC stabilised soils (Higgins and Kennedy, 1999).

8.2.1 LOC-1.5%CaO Stabilised with GGBS and PC

Figure 8.2.1 (A-B) illustrates the linear expansion of mellowed (3 days at 20°C), compacted 1.5%CaO-modified LOC samples with additions of 4% and 8% GGBS or 4% and 8% PC. Before soaking the samples were cured for 7 days. The soaking waters were aerated in order to maximise oxidation of the pyrites present in the LOC at 20°C and 5°C.

Soaking resulted in the immediate expansion of all samples at 20°C, although unlike compacted LOC-$Ca(OH)_2$ samples, the rate of expansion varied dramatically depending on the type and amount of added stabiliser (Figure 8.2.1 (A)). The samples containing GGBS expanded less than the samples containing similar amounts of PC, with the LOC-1.5%CaO-8%GGBS samples showing negligible expansion (<0.3%) throughout the test (140 days). After 40 days of testing, all stabilised samples showed good dimensional stability.

A reduction in soaking temperature from 20°C to 5°C (Figure 8.2.1 (B)) resulted in increased linear expansion in all stabilised compacted samples with the largest increase in expansion occurring in the LOC-1.5%CaO-4%PC sample (an increase of 5.7% at 28 days and 8% after 140 days). Unlike the test carried out at 20°C, expansion was observed in all samples before the soaking water was added (that is, during the 7 days curing period) when the test was carried out at 5°C. Again the samples containing GGBS expanded less than samples containing similar amounts of PC, with the LOC-1.5%CaO-8%GGBS sample again exhibiting the least expansion (2.4% maximum).

Swelling in lime-stabilised sulphate/sulphide bearing soils is common and is known to be associated with the formation of a colloidal product (a precursor to ettringite formation), which forms on the surfaces of clay particles during curing. When, in saturated conditions, ettringite grows and develops from this product, substantial amounts of water are imbibed and significant swelling occurs (Wild et al., 1993). However, the introduction of a stabilising agent such as PC or GGBS modifies the chemical make-up of the clay-lime system, therefore altering the type of reaction products and thus potentially altering any disruptions that the reaction products may cause. As stated in Section 8.1 unlike the pozzolanic reaction of lime with clay, which is very slow, GGBS hydration is much more rapid. This reaction is also known to consume lime. Therefore an explanation for the resistance to the swelling of GGBS-stabilised LOC is twofold. Firstly the strength of the compacted material after 7 days of curing is greatly enhanced with additions of GGBS due to the formation of various strength enhancing reaction products. It is thought that increased strength will confine, at least partially, any swelling caused by ettringite formation. Secondly, as GGBS hydration consumes lime, then the stock of available lime in the system, needed to form the deleterious ettringite will be depleted. Also the stability of ettringite is pH dependent and at pH <10.5 (Gaze and Crammond, 2000; Santhana et al. 2001) ettringite becomes unstable relative to gypsum. As the small amount of added lime (1.5%CaO) is essentially taken up in the process of modification, and also as it is known that during mellowing lime is consumed in the formation of ettringite and gypsum via the oxidation of pyrites (Chapter 7), it is thought that any small excess of available lime will be consumed in GGBS hydration. Therefore the GGBS reaction would become the dominant reaction leaving little or no lime for the precipitation of ettringite (Tasong et al. 1999).

The hydration of PC produces similar cementing products to those of the lime-clay pozzolanic reaction and GGBS hydration, but at a much faster rate. However, Figures 8.1.2 and 8.1.3 show that the strength development of LOC-1.5%CaO-PC and LOC-1.5%CaO-GGBS samples, cured for 1 week at 20°C are very similar (especially with additions of 2% and 4% stabiliser), indicating that strength and therefore confining pressure would be similar in both PC and GGBS systems prior to soaking. As PC does not consume but produces $Ca(OH)_2$ on hydration, it is thought that the increased swelling seen in PC-stabilised samples is a result of ettringite formation due to the more freely available lime and a higher pH in the system.

A reduction in soaking temperature from 20°C to 5°C results in increased expansion in all samples, though again the GGBS stabilised samples showed much greater dimensional stability. The strength development of all stabilised samples is similar prior to soaking. Therefore again, the differences in expansion between PC stabilised and GGBS stabilised LOC must be due to chemical reactions in the system (Figure 8.1.2 and 8.1.3). The hydration reactions described above take place at a much-reduced rate at 5°C as lower temperatures retard both PC hydration and GGBS hydration (Section 8.1). Also, at low temperatures it is known that $Ca(OH)_2$ is more soluble than at higher temperatures. It is possible that this enhanced solubility, together with retarded stabiliser hydration at lower temperatures (and hence reduced lime consumption in the case of GGBS hydration), would result in more freely available lime and hence higher pH during the 7-days curing period at 5°C, resulting in enhanced formation of expansive products both during the curing period (Figure 8.2.1 (B)) and in the presence of excess water on soaking. The situation is also further complicated by the fact that low temperatures favour the formation of thaumasite rather than ettringite, which destroys the cementing C-S-H gel phase.

It is clear that an addition of 8%GGBS to the mellowed LOC-1.5%CaO mix results in excellent dimensional stability when soaked in aerated water at both 5°C and 20°C compared to unstabilised samples (Section 7.4), and displays consistently less expansion than similar samples containing 8%PC. In order to assess the expansion characteristics of LOC-15%CaO-8%GGBS further, linear expansion measurements over a range of soaking environments were carried out. The results are displayed in Section 8.2.2.

8.2.2 Linear expansion of LOC-1.5%CaO-8%GGBS.

Figure 8.2.2 shows the linear expansion of unmellowed LOC-1.5%CaO-8%GGBS in 4 separated soaking environments 1) a static soaking environment at 20°C; 2) in an aerated soaking environment at 20°C; 3) in an aerated soaking environment after mellowing (3 days at 20°C) at 20°C, and 4) in an aerated soaking environment after mellowing (3 days at 20°C) at 5°C. Before soaking the samples were cured for 7 days at their relevant soaking temperatures respectively (20°C or 5°C).

It is clear that regardless of soaking environment, the linear expansion of LOC-1.5%CaO sample containing 8%GGBS was very small when soaked at 20°C (<0.5%) (Figure 8.2.2). However, it is apparent that the least expansion occurred after mellowing had taken place prior to compaction. As explained previously, mellowing not only consumes lime but also results in the oxidation of pyrites to form gypsum, which in turn is known to reduce the pH of the system. Sulphate also enhances GGBS hydration. Therefore, the reduced pH and the increased GGBS hydration results in increased stability.

Summary

- An addition of a stabiliser (i.e. 4% and 8% GGBS, or 4% and 8%PC) results in significantly reduced linear expansion in mellowed LOC-1.5%CaO samples after compaction, curing (7 days) and soaking in aerated water at 20°C.
- Samples containing GGBS show consistently lower expansion than samples containing PC when soaked in aerated water at 20°C, with the LOC-1.5%CaO – 8%GGBS mellowed sample expanding <0.3%. It is thought that as both systems show very similar UCS strength after 1weeks curing (Section 8.1), the enhanced stability shown by the GGBS samples is a result of the GGBS hydration process, which consumes lime and reduces the pH leaving little or no lime for the precipitation of deleterious ettringite. Also the formation of gypsum via pyrites oxidation during mellowing would accelerate the GGBS hydration process.
- A reduction in curing and soaking temperature from 20°C to 5°C results in increased expansion in all samples. It is known that $Ca(OH)_2$ is more soluble at lower temperatures. This enhanced solubility, together with retarded stabiliser hydration at low temperatures (and hence reduced lime consumption in the case of GGBS hydration), is thought to result in more freely available lime and therefore increased expansive ettringite formation. It should be noted that at 5°C thaumasite is also

likely to form, which will break down the C-S-H gel subsequently causing strength loss.

- Expansion is very small when LOC-1.5%CaO-8%GGBS samples are soaked in either a static environment at 20°C; in an aerated environment at 20°C, or in an aerated environment after mellowing at 20°C (<0.5%). However it is apparent that the least expansion is found when a mellowing period is employed prior to compaction, as mellowing not only consumes lime, but also produces gypsum via pyrites oxidation, which is known to encourage GGBS hydration. Therefore, the system will be depleted of lime and have reduced pH, resulting in even less potentially damaging ettringite formation.

After examining the strength (UCS) development and linear expansion characteristics of lime-modified LOC stabilised with various additions of GGBS or PC, the next section deals with both strength and soaking combined in durability tests outlined in Chapter 6.

8.3 Durability Index (DI)

8.3.1 Unmellowed Samples Tested at 20°C

Figure 8.3.1 (A) illustrates the durability indices (DI) of unmellowed, LOC-1.5%CaO with increasing additions of GGBS or PC (2%, 4%, 6% and 8%) cured for 3 weeks and soaked for 1 week at 20°C. Figure 8.3.1 (B) illustrates the DI of unmellowed LOC-2%$Ca(OH)_2$ with additions of GGBS or PC (4% and 8%) cured for 3 weeks and soaked for 1 week at 20°C for comparison.

As expected, the addition of either GGBS or PC to the 1.5%CaO-modified LOC improved the durability of the material (Figure 8.3.1 (A)). However, the performance of the GGBS stabilised LOC was substantially better than the PC stabilised LOC. Increasing additions of GGBS resulted in increased durability, with the best DI value exhibited by the LOC-1.5%CaO-8%GGBS sample (73%). Increasing additions of PC however, did not result in a systematic increase in durability. Instead the DI values of all samples containing PC showed similar durability characteristics (between 35% and 44% DI value). The same trend was apparent when $Ca(OH)_2$ modified LOC was employed where again increasing additions of GGBS resulted in increased durability, with the highest DI value represented by the LOC-2%$Ca(OH)_2$-8%GGBS sample (92%) (Figure 8.3.1 (B)). By contrast, increasing additions of PC showed consistently lower durability compared with similar additions of GGBS. In all cases, an addition of GGBS proved more effective in increasing the DI value than similar additions of PC.

The consistent increase in DI in the LOC-1.5%CaO samples with increasing GGBS content is thought to be due to the GGBS hydration process during the curing period (3 weeks), which is known to consume lime thus reducing the pH leaving little or no calcium for the formation of deleterious ettringite. As PC hydration produces lime rather than consumes it, there is a greater possibility of deterioration in PC-stabilised soils due to deleterious ettringite formation on soaking. It is possible that although the potential for deterioration due to ettringite formation is greater at high PC additions (due to the increased lime content), the levels of confining strength provided by the C-S-H gels and C-A-H phases are sufficient to minimise durability loss. Samples initially modified with 2%$Ca(OH)_2$ rather than 1.5%CaO prior to stabiliser addition and compaction showed consistently higher DI values though the changes were minimal when PC was used as the stabiliser. It is thought that the differing densities exhibited by the LOC-2%$Ca(OH)_2$ and LOC-1.5%CaO mixes (where slightly higher densities were apparent in the LOC-2%$Ca(OH)_2$ mix (Section 7.2)) may produce a differing framework around which the cementing hydration reaction products form, thus resulting in differing durabilities.

8.3.2 Mellowed Samples Tested at 20°C

Figure 8.3.2 (A) illustrates the durability indices (DI) of mellowed (3 days at 20°C), LOC-1.5%CaO with increasing additions of GGBS or PC (2%, 4%, 6% and 8%) cured for 3 weeks and soaked for 1 week at 20°C. Figure 8.3.2 (B) illustrates the DI of mellowed LOC-2%$Ca(OH)_2$ with increasing additions of GGBS or PC (4% and 8%) cured for 3 weeks and soaked for 1 week at 20°C for comparative purposes.

It is evident from comparison of Figure 8.3.1. (A) with Figure 8.3.2 (A) and of Figure 8.3.1 (B) with Figure 8.3.2 (B) that mellowing has a favourable impact upon durability. Mellowing of GGBS-stabilised LOC-1.5CaO samples generally resulted in increased durability values (Figure 8.3.2 (A)). Mellowing improved the DI value of the LOC-1.5%CaO with increasing additions of GGBS up to an addition of 6%GGBS (DI value of 95%), thereafter a small decline occurred. Mellowing had less of an influence on the GGBS stabilised LOC-2%$Ca(OH)_2$ material although durability values were still very high. In contrast mellowing had a substantial influence on PC stabilised material that produced values similar to those of the GGBS stabilised material. For example, mellowing increased the durability of PC stabilised LOC-2%$Ca(OH)_2$ samples by as much as 35% after an addition of 8%PC (Figure 8.3.2 (B)). However, for the CaO modified LOC the durability values of the GGBS-stabilised LOC were still superior to those of the PC-stabilised LOC at high stabiliser levels (6% and 8%).

Section 8.2 shows clearly that on soaking, lime-modified LOC samples stabilised with GGBS expand much less than those stabilised with PC. As the durability index test is effectively a measure of the loss in strength due to soaking (i.e. the ratio of the 21 days moist cured and 7 days soaked strength (kN/m^2) to the 28 days moist cured strength (kN/m^2)), then the fact that PC-stabilised specimens expand more on soaking than do GGBS-stabilised specimens would result, as it does, in a greater strength loss due to soaking for these samples.

8.3.3 Unmellowed Samples Tested at 5°C

Figure 8.3.3 (A) illustrates the durability indices (DI) of unmellowed, LOC-1.5%CaO with increasing additions of GGBS or PC (2%, 4%, 6% and 8%) cured for 3 weeks and soaked for 1 week at 5°C. Figure 8.3.3 (B) illustrates the DI of unmellowed LOC-2%$Ca(OH)_2$ with increasing additions of GGBS or PC (4% and 8%).

A reduction in curing and soaking temperature from 20°C to 5°C generally resulted in reduced DI values for samples containing small additions of stabiliser (i.e. 2%GGBS or PC) in the LOC-1.5%CaO samples (Figure 8.3.3 (A)). However durability remained largely unchanged when greater amounts of GGBS or PC were added, with the largest DI value again being exhibited by the LOC-1.5%CaO-8%GGBS sample (69%). Durabilities of stabilised LOC-2%$Ca(OH)_2$ samples were also reduced when the temperature was lowered to 5°C by a DI value of at least 15% in PC stabilised samples, and by a DI value of at least 35% in GGBS stabilised samples. Again at 5°C GGBS stabilised samples consistently showed better durability than samples with similar additions of PC, with the LOC-lime-8%GGBS sample achieving the highest DI value.

As described in Section 8.1, strength-giving reactions take place at a much-reduced rate at 5°C, and smaller additions of stabiliser were found to be insufficient to confine expansion, resulting in reduced DI values. There is a large difference in DI values when the LOC is modified with 2%$Ca(OH)_2$ rather than 1.5%CaO which again must be a result of differing densities as observed in Section 7.2, as the denser, less porous, stabilised LOC-2%$Ca(OH)_2$ samples showed significantly reduced durability (in fact, the 2%$Ca(OH)_2$ modified LOC sample collapsed whereas the LOC-1.5%CaO sample showed a DI of 12%).

8.3.4 Mellowed Samples Tested at 5°C

Figure 8.3.4 (A) illustrates the durability indices (DI) of mellowed, LOC-1.5%CaO with increasing additions of GGBS or PC (2%, 4%, 6% and 8%) cured for 3 weeks and soaked for 1 week at 5°C. Similarly, Figure 8.3.4 (B) illustrates the DI of mellowed LOC-2%$Ca(OH)_2$ with increasing additions of GGBS or PC (4% and 8%).

Mellowing of 1.5%CaO-modified LOC-GGBS stabilised samples resulted in increased DI values at high GGBS additions (i.e. 6% and 8% GGBS), though samples containing <6%GGBS show reduced durability at 5°C, probably due to slower hydration and therefore reduced strength (Figure 8.3.4 (A)). However the opposite occurred in samples stabilised by PC where an average reduction of 21.5% DI value was observed after mellowing. Again the LOC-1.5%CaO-8%GGBS sample proved to be most durable as it had a DI value of 100%, indicating that the sample had lost no strength after soaking compared to a similar sample that had been cured for 4 weeks without soaking. Mellowing of 2%$Ca(OH)_2$-modified LOC stabilised with PC improved the durability by an average increase in DI value of 14% (Figure 8.3.4 (B)). An increase in durability after mellowing was also recorded when 8%GGBS was used to stabilise the LOC-2%$Ca(OH)_2$ mix (20% DI value), however an addition of only 4%GGBS resulted in a loss of durability (12% DI value).

The obvious reduction in durability index values when curing and soaking is carried out at 5°C is primarily a result of reduced strength development due to retarded GGBS and PC hydration, as shown in Section 8.1, but also as a consequence of the formation of deleterious reaction products such as ettringite or (more probably at this low temperature) thaumasite.

Summary

- The addition of either GGBS or PC improves the durability of LOC-1.5%CaO and LOC-2%$Ca(OH)_2$ samples, regardless of mellowing and curing time. Throughout the tests, samples containing GGBS showed greater DI values than samples containing PC, especially at high stabiliser contents.
- After curing and soaking at 20°C the lime-modified, GGBS-stabilised samples showed better DI values than similar samples containing PC as the GGBS hydration process consumes lime, which is needed in the formation of deleterious ettringite formation in the presence of water, and reduces pH whereas PC hydration produces lime and enhances pH.

- A period of mellowing (3 days at 20°C) increases the durability indices in all samples tested at 20°C. This is considered to be a result of the reduced available lime and gypsum levels as both are consumed in pre-compaction reactions prior to curing and soaking. Again large additions of GGBS to the lime-modified LOC show greater DI values than similar additions of PC.
- A reduction in curing and soaking temperature from 20°C to 5°C results in reduced DI values at low stabiliser additions, but durability is either unchanged or reduced with greater additions. Again, additions of more than 2%GGBS to the lime-modified LOC showed better durability than samples containing additions of PC.
- The introduction of a mellowing period prior to compaction, curing and soaking at 5°C significantly reduced the durability values of 1.5%CaO modified LOC stabilised with PC. It is thought that the increased gypsum content as a consequence of mellowing, coupled with the available lime (which is known to be more soluble at lower temperatures) would combine to form deleterious products, such as thaumasite, in the presence of excess water. Samples containing >6%GGBS show improved durability after mellowing, though the opposite is apparent with smaller additions.
- Throughout the tests, samples modified by 1.5%CaO exhibited differing DI values than similar samples modified by 2%$Ca(OH)_2$. It is apparent that at 20°C DI values of samples were higher when 2%$Ca(OH)_2$ was utilised as the modifying agent. However, after a period of mellowing DI values were greater when 1.5%CaO was employed. It is possible that the differing densities of the two mixed materials, especially after curing (Section 7.2), may produce a differing framework around which the various hydration reaction products form resulting in varied durability values.

- The most significant observation from the durability study is that for GGBS stabilised LOC at stabiliser contents of either 6% or 8% the durability index is consistently greater than equivalent PC stabilised LOC regardless of temperature (20°C or 5°C), lime type (CaO or $Ca(OH)_2$) or preconditioning (mellowed or unmellowed).

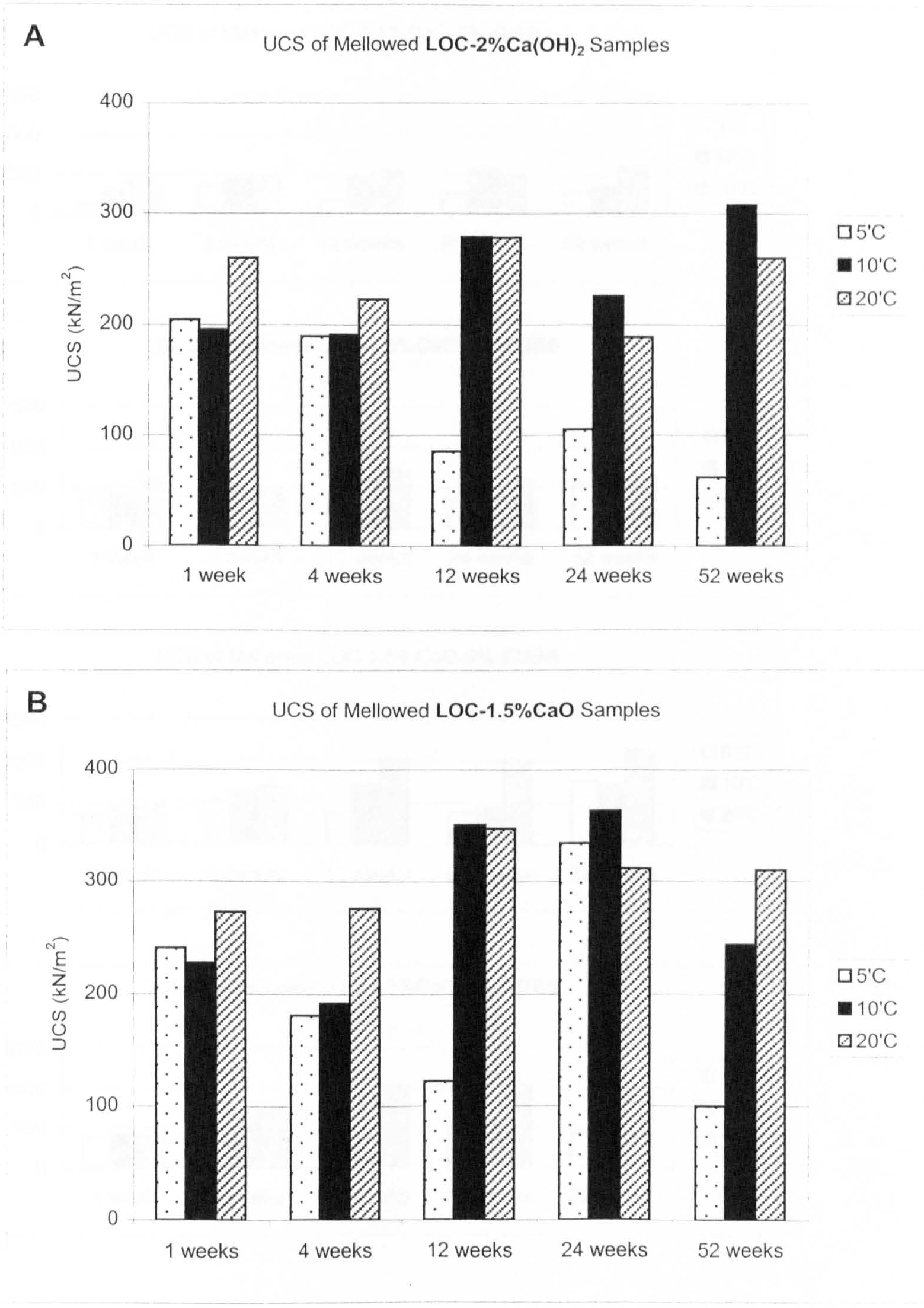


Figure 8.1.1 Unconfined compressive strength (UCS) vs. curing time (weeks) for mellowed (3 days at 20°C) (A) LOC-2%$Ca(OH)_2$ and (B) LOC-1.5%CaO samples, after curing at 5°C, 10°C and 20°C

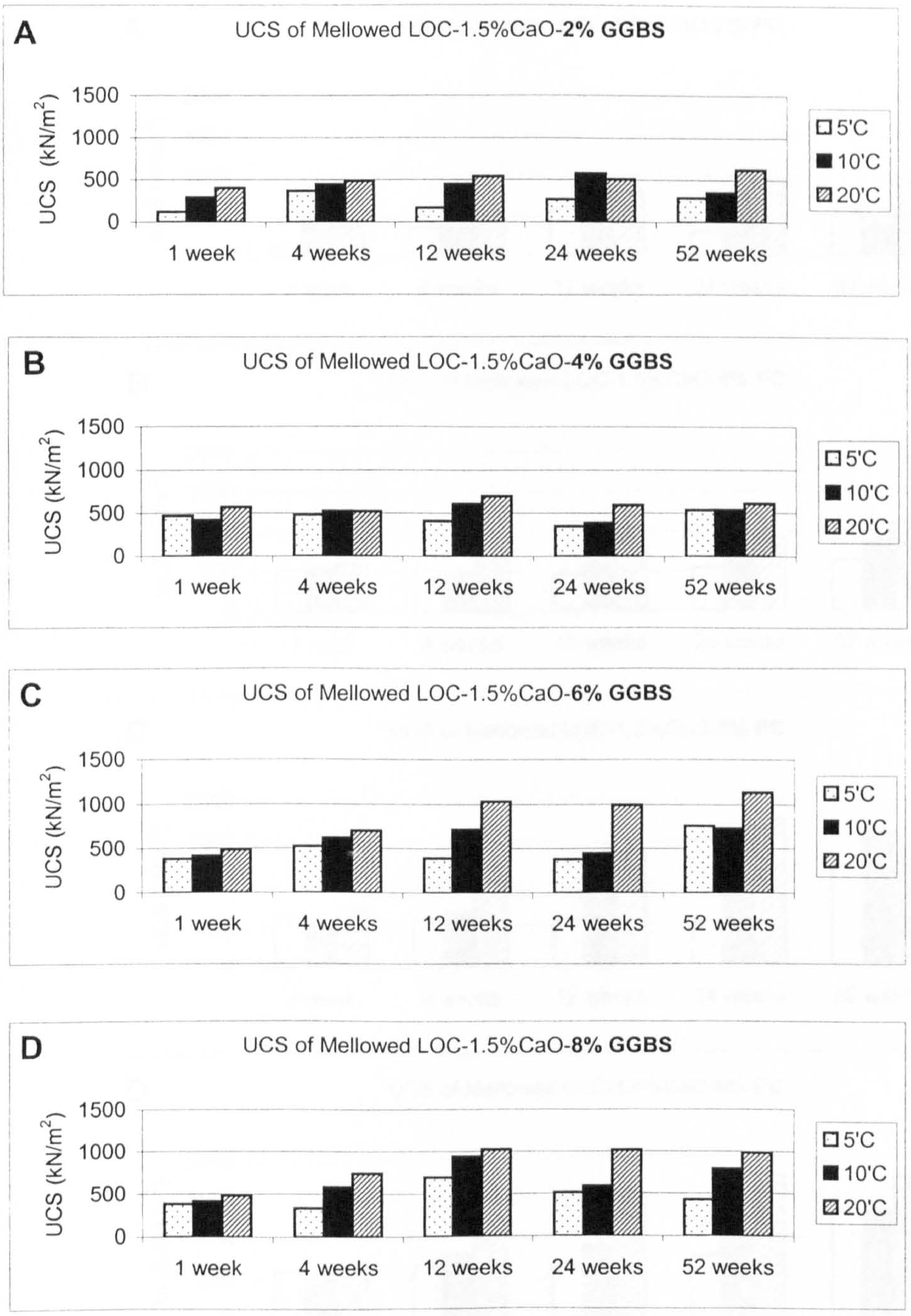


Figure 8.1.2 Unconfined compressive strength (UCS) vs. curing time (weeks) after curing at 5°C, 10°C and 20°C for mellowed (3 days at 20°C) LOC-1.5%CaO samples with additions of
(A) 2%GGBS (B) 4% GGBS
(C) 6%GGBS (D) 8%GGBS

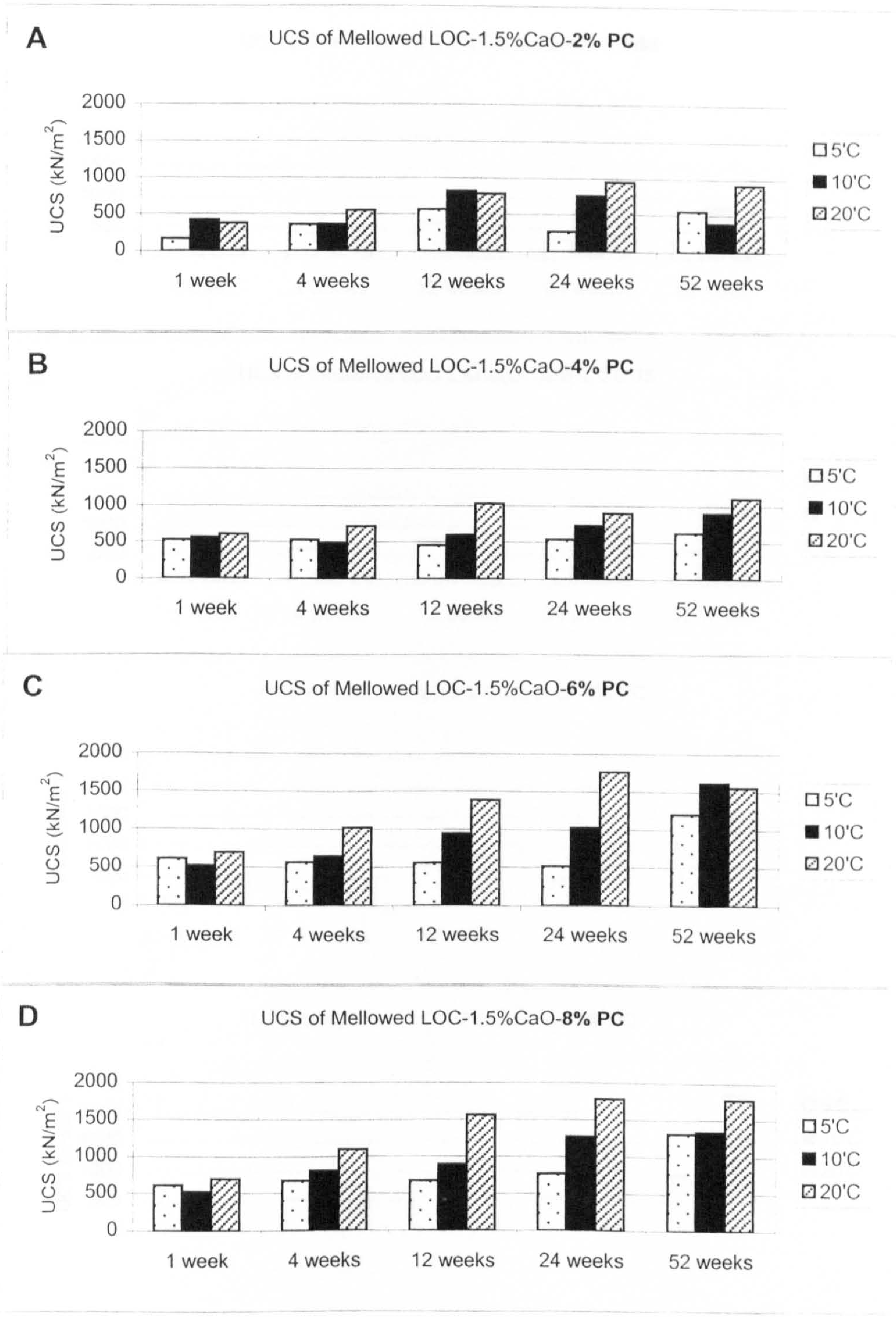


Figure 8.1.3 Unconfined compressive strength (UCS) vs. curing time (weeks) after curing at 5°C, 10°C and 20°C for mellowed (3 days at 20°C) LOC-1.5%CaO samples with additions of
(A) 2%PC (B) 4% PC
(C) 6% PC (D) 8% PC

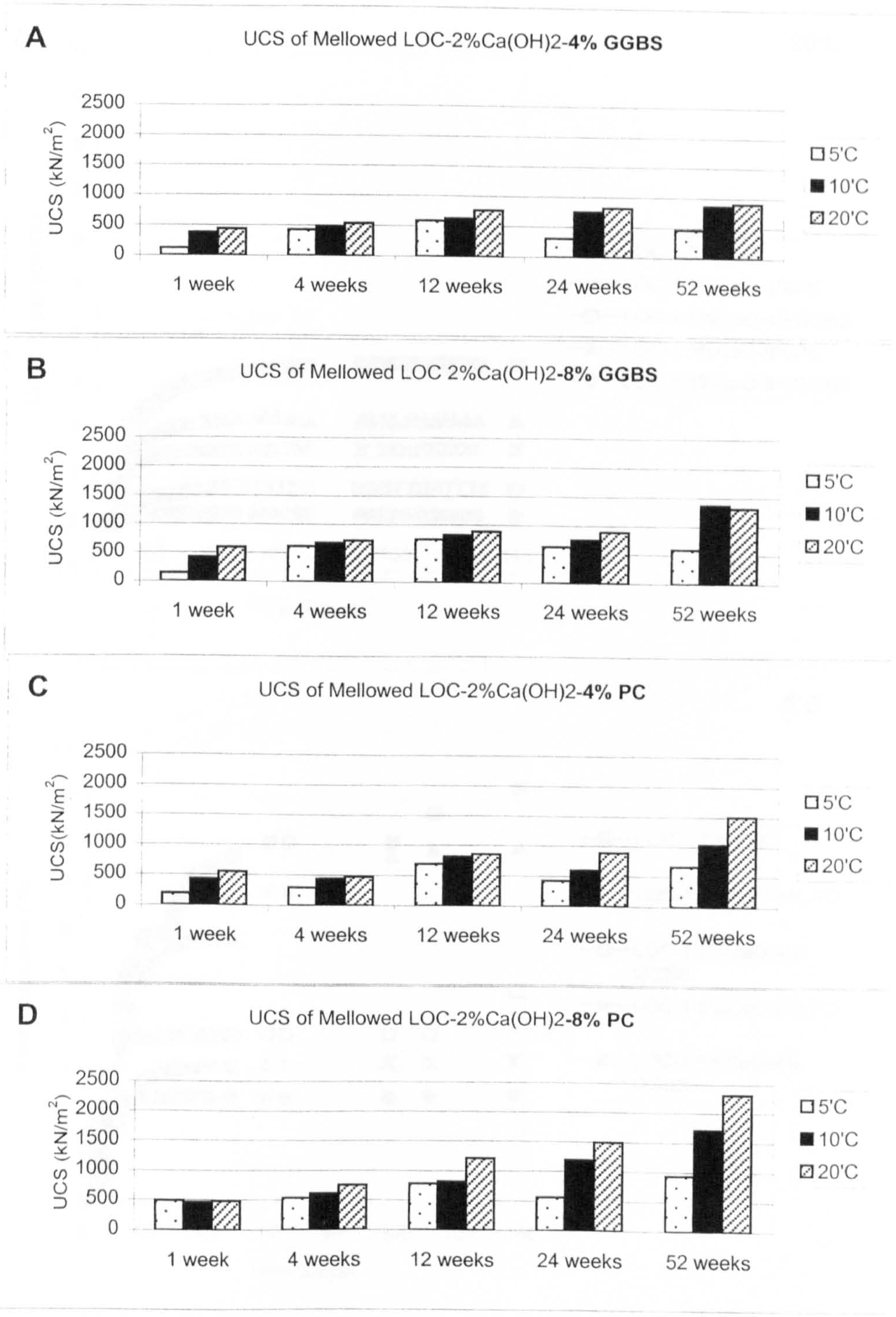


Figure 8.1.4 Unconfined compressive strength (UCS) vs. curing time (weeks) after curing at 5°C, 10°C and 20°C for mellowed (3 days at 20°C) LOC-2%$Ca(OH)_2$ samples with additions of
(A) 2%GGBS (B) 8% GGBS
(C) 4%PC (D) 8%PC

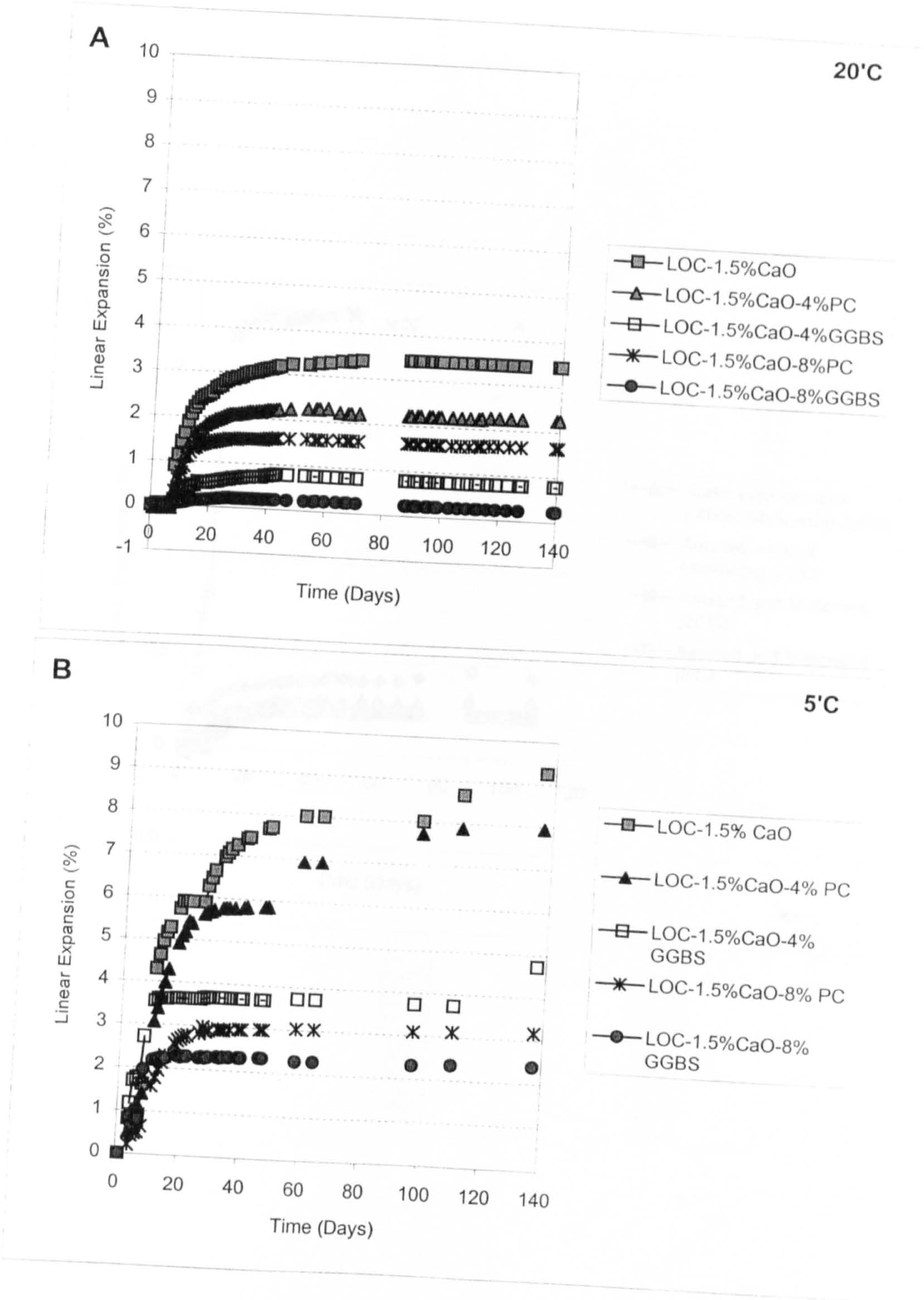


Figure 8.2.1 Linear expansion (%) vs. soaking time (days) for mellowed (3 days at 20°C) LOC-1.5%CaO samples containing 4% or 8% PC or GGBS subjected to soaking in an aerated environment at (A) 20°C and (B) 5°C.

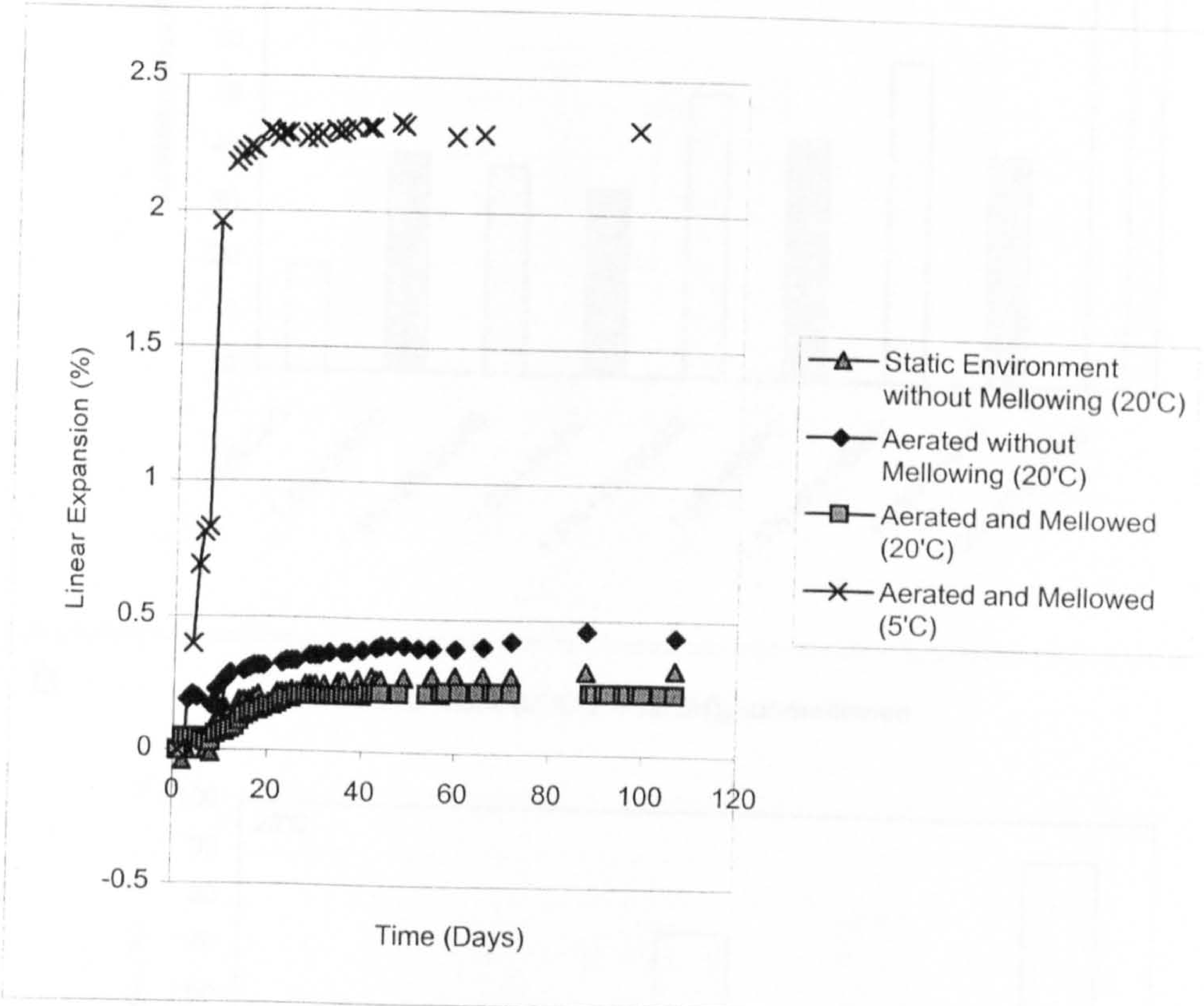


Figure 8.2.2 Linear expansion (%) vs. soaking time (days) LOC-1.5%CaO-8%GGBS samples soaked in a number of soaking environments and temperatures, with and without a period of mellowing (3 days at 20°C) prior to compaction.

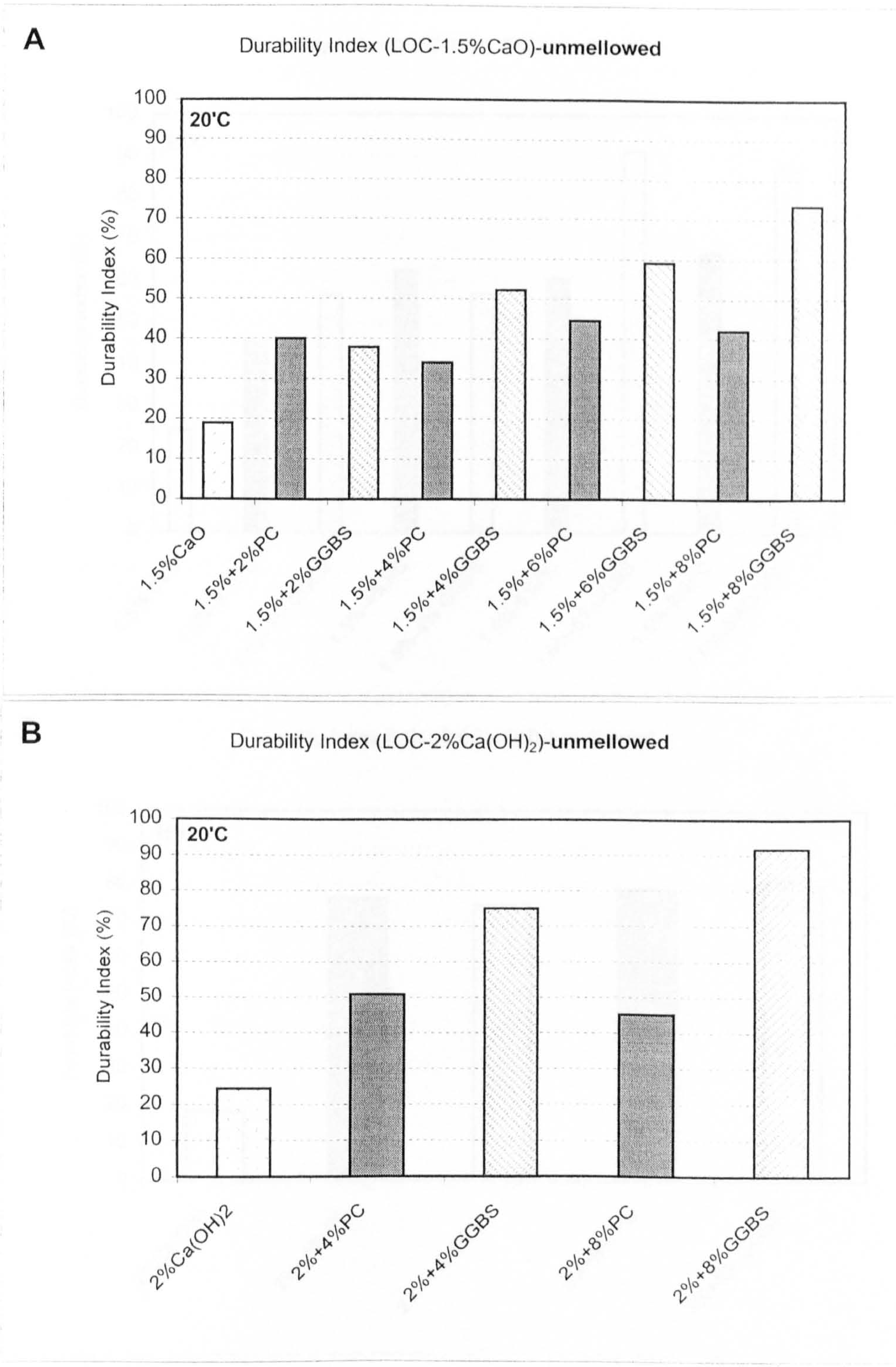


Figure 8.3.1 Durability indices (%) of (A) unmellowed, LOC-1.5%CaO and (B) unmellowed LOC-2%$Ca(OH)_2$ samples with increasing additions of GGBS and PC at 20°C.

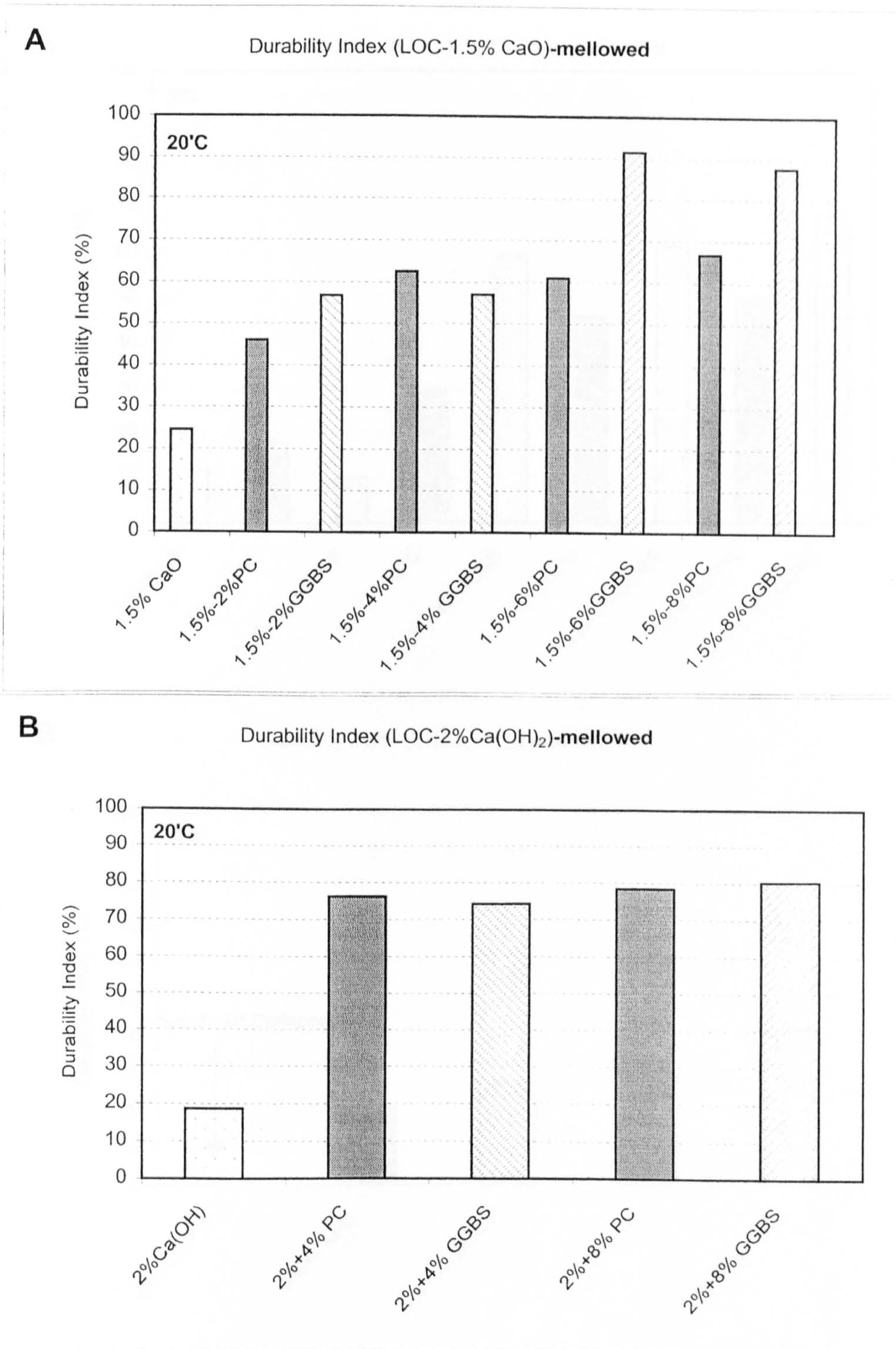


Figure 8.3.2 Durability indices (%) of (A) mellowed (3 days at 20°C), LOC-1.5%CaO and (B) mellowed (3 days at 20°C) LOC-2%$Ca(OH)_2$ samples with increasing additions of GGBS and PC at 20°C.

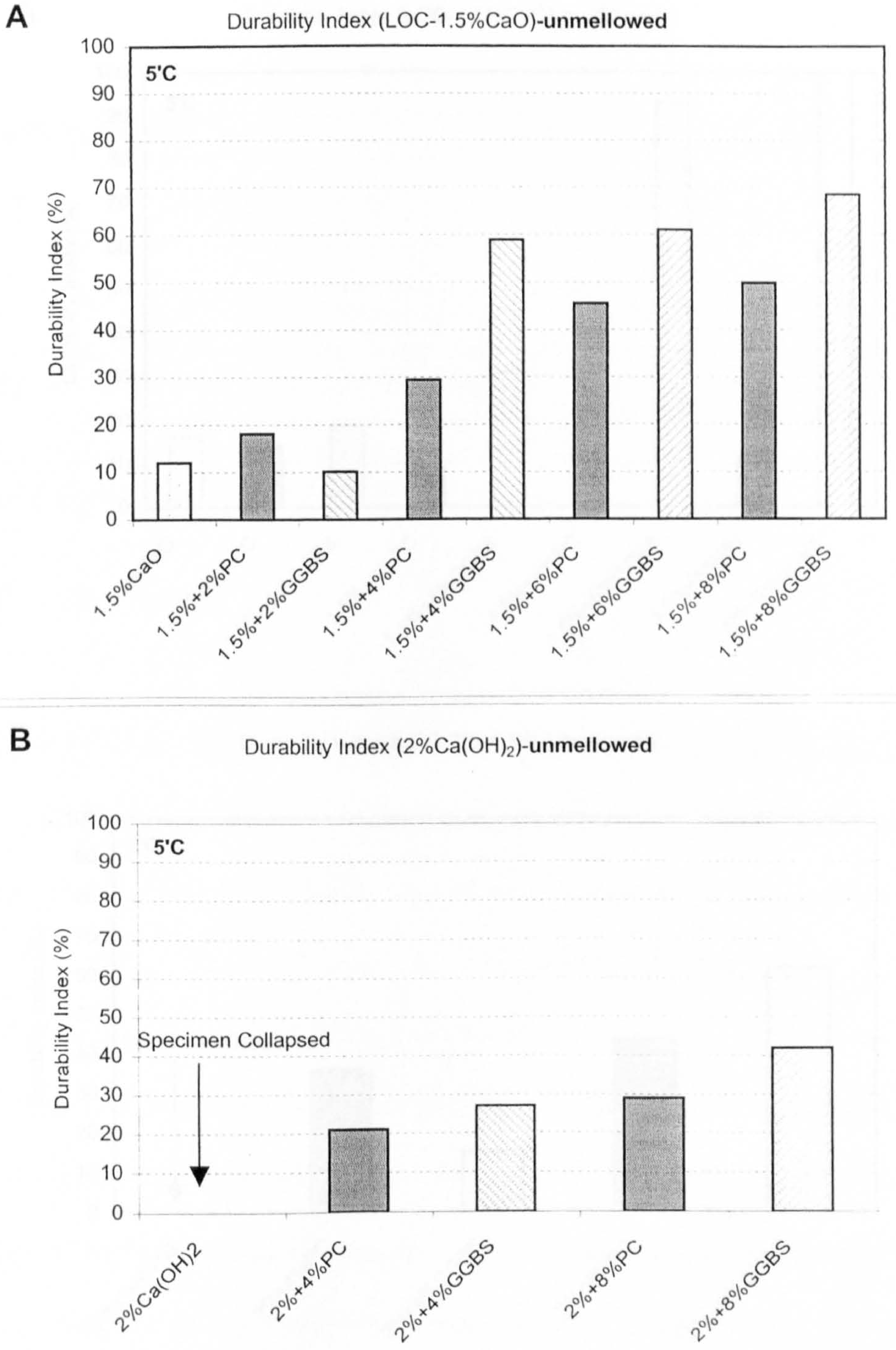


Figure 8.3.3 Durability indices (%) of (A) unmellowed, LOC-1.5%CaO and (B) unmellowed LOC-2%Ca(OH)$_2$ samples with increasing additions of GGBS and PC at 5°C.

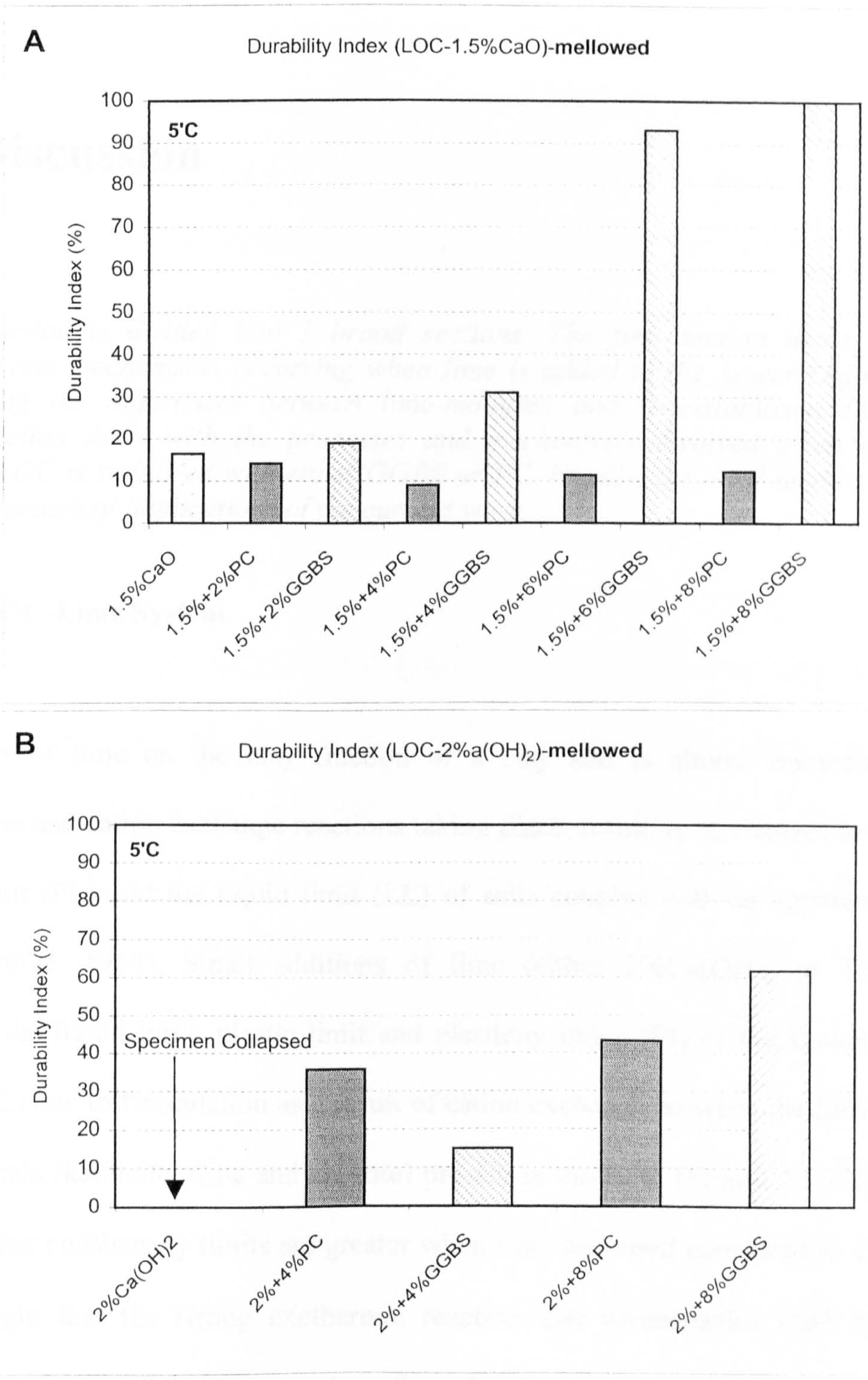


Figure 8.3.4 Durability indices (%) of (A) mellowed (3 days at 20°C), LOC-1.5%CaO and (B) mellowed (3 days at 20°C) LOC-2%Ca(OH)$_2$ samples with increasing additions of GGBS and PC at 5°C.

9 Discussion

The discussion is divided into 3 broad sections. The first section deals with the processes and mechanisms occurring when lime is added to the Lower Oxford Clay, highlighting the differences between lime-modified and lime-stabilised LOC. The second section deals with the processes and mechanisms involved when the lime-modified LOC is stabilised with either GGBS or PC. Finally, the third section explores the major practical implications of the current work.

9.1 LOC-Lime System

The effect of lime on the clay fraction of a clay soil is almost immediate with flocculation and cation exchange reactions taking place, resulting in changes to both the plastic limit (PL) and the liquid limit (LL) of soils coupled with an apparent drying effect (Cobbe, 1988). Small additions of lime (either 2%$Ca(OH)_2$ or 1.5%CaO) increased the liquid limit, plastic limit and plasticity index (PI) of the Lower Oxford Clay (LOC) due to flocculation as a result of cation exchange between the lime and the clay minerals (kaolinite, illite and chlorite) present in the LOC (Figure 7.1.1-2). It was apparent that consistency limits are greater when CaO was used compared to $Ca(OH)_2$. It is thought that the strong exothermic reaction that accompanies CaO hydration produces a slightly stronger, more robust flocculated material matrix capable of holding a greater volume of moisture.

Increasing additions of lime (6%$Ca(OH)_2$ or 4.5%CaO) further increased the PL and LL of the LOC due to increased flocculation. However additions of lime in excess of 6%$Ca(OH)_2$ or 4.5%CaO resulted in a slight decline in consistency limits. Hilt and

Davidson (1960) postulated that at some percentage of lime additive saturation of the calcium ions that can adsorb onto the clay particles occurs and further increases in lime addition result only in supplying to the soil an excess of calcium, which is not effective in flocculation. If the calcium that increases the plastic limit is so fixed in the soil, then the percentage of lime present at the point where the plastic limit reaches its maximum will reliably indicate the percentage of lime fixation in the soil. Therefore, it is thought that the lime fixation point of LOC is 6%$Ca(OH)_2$ or 4.5%CaO as no further increase in PL occurs with further lime additions.

Mellowing (3 days at 20°C) of the LOC-2%$Ca(OH)_2$ mix had little effect on consistency limits probably because the small amount of added lime would have quickly reacted with the LOC on mixing. However, mellowing of the LOC-1.5%CaO mix prior to testing resulted in increased LL and PL. It is thought that these differences are due to the stronger flocculated material matrix of the LOC-1.5%CaO mix due to increased flocculation during mellowing as a result of increased reactivity, attributed to the strong exothermic hydration reaction. Mellowing (3 days at 20°C) of LOC with increasing additions of lime resulted in increased LL and PL as it is thought that the extra reaction time afforded to the extra lime and clay mixture leads to increased flocculation (up to an addition of 6%$Ca(OH)_2$-4.5%CaO) and therefore an increased ability to hold moisture.

It is generally accepted that the addition of lime to all clays increases the optimum moisture content (OMC) and reduces the maximum dry density (MDD), for the same compactive effort, again due to flocculation caused by cation exchange between lime and clay particles. Small additions of lime (2%$Ca(OH)_2$ or 1.5%CaO) to the LOC resulted in increased OMC and decreased MDD values, with the LOC-1.5%CaO mix showing slightly higher OMC and lower MDD values than LOC-2%Ca(OH)$_2$ mixes (Figures 7.2.3-4). Similar to the Atterberg limits, it is thought that the strong exothermic reaction accompanying CaO hydration caused increased flocculation (in comparison to the LOC-2%Ca(OH)$_2$ material) and possibly moisture loss due to evaporation on mixing. Therefore, the material was found to be comparatively drier and, as explained above, possessed a more rigid material matrix, thus explaining the slightly higher OMC and lower MDD values. Bell and Coulthard (1990) maintained that the more lime added to a soil, then the lower the MDD and the higher the OMC. Hence, similar to the Atterberg limits, increases of lime up to 6%Ca(OH)$_2$ or 4.5%CaO to the LOC resulted in further increases and decreases in OMC and MDD respectively, whereas lime additions in excess of lime fixation exhibited either no change or an inverse in the compaction value trend. This, coupled with the Atterberg limits data, strongly indicates that an addition of lime to the LOC in excess of the "lime fixation" point (i.e. 6%Ca(OH)$_2$ or 4.5%CaO) results only in supplying to the soil an excess of calcium.

Mellowing (3 days at 20°C) of lime-modified LOC mixtures prior to testing further lowered MDD and increased OMC due to increased flocculation. However, there is little difference when mellowing was carried out for 6 hours or 3 days as the relatively small amount of added lime (2%Ca(OH)$_2$ or 1.5%CaO) is consumed almost immediately on mixing. Also, the changes in OMC and MDD after mellowing in lime-modified LOC are greater when mellowing takes place at 10°C compared to mellowing at 20°C. It has been suggested that cementitious products and, in the presence of sulphate, ettringite forms immediately on mixing lime with clay soil (Croft, 1964; Lees et al. 1982; Kinuthia, 1997). As these reactions are known to occur at an accelerated rate at higher temperatures (Arabi and Wild, 1989) and are also thought to reduce the compactibility of lime treated soils (Lees et al., 1982) it is suggested that a slightly higher mellowing temperature encourages the formation of reaction products in the lime-modified LOC, explaining the slightly increased density MDD and reduced OMC values relative to samples mellowed at lower temperatures.

Mellowing (either 6 hours or 3 days at 20°C) of LOC with increasing additions of $Ca(OH)_2$ and CaO resulted in further reduced MDD and increased OMC up to a lime addition of 6%$Ca(OH)_2$ or 3-4.5%CaO, with increased mellowing time resulting in greater changes in compaction values. Mitchell and Hooper (1961) demonstrated that a pronounced decrease in density occurs with increasing time intervals between mixing and compaction, so that MDD occurs at a somewhat higher OMC, suggesting that the main factor responsible for this behaviour is the flocculation of the soil structure, which increases with time of exposure of the soil to water and lime. Also, Bell and Coulthard (1990) suggested that if a soil-lime mixture remains uncompacted, it undergoes carbonation with the cemented particles then behaving like sand grains, making subsequent compaction more difficult, and as a consequence, reducing the pH of the mix (an important feature with respect to the relative stability of reaction products such as gypsum and ettringite). However, lime addition in excess of the lime fixation point of the LOC resulted in either no further change or in some cases a reversal of the established trends. As mentioned above, excess lime only results in supplying to the soil an excess of calcium. Therefore it is thought the excess lime inhabits the inter-particle spaces, resulting in better packing and a reversal of the expected and established trends.

After compaction of lime-modified LOC in 100mmx50ϕmm cylinder moulds (with or without an initial mellowing period of 3 days at 20°C), and subsequent curing for 1 or 4 weeks at 5°C, 10°C or 20°C, it is clear that higher strengths were achieved after longer curing periods at higher temperatures (Figure 7.3.1). As reported earlier (Chapter 3, Section 3.6.3) the amount of strength increase in a soil that can be produced by adding lime is dependent on several factors including pozzolanic content of the soil, percentage lime addition and curing time and temperature (Arabi and Wild, 1989; Bell and Coulthard, 1990; Sherwood, 1993). However, the trends with respect to mellowing, curing time and temperature observed in the lime-modified LOC were non-linear and difficult to interpret. It is thought that the small amount of added lime, although suitable for modification, was insufficient to produce significant amounts of cementing products (Bell, 1988). Also in the absence of significant cementation, small variations in moisture content would have a disproportionate effect on strength.

Increasing additions of $Ca(OH)_2$ to the LOC resulted in increased strength after extended curing periods at higher temperatures due to increased pozzolanic reactions between the lime and the clay fraction. It is generally recognised (Diamond et al., 1964; Brandl, 1981; Lees et al. 1982; Bell and Coulthard, 1990) that the principal cementitious product of pozzolanic reactions is calcium silicate hydrate (C-S-H) gel and that strength development of clay-lime material may be attributed to either (a) the gradual crystallisation of this gel (Bell, 1988), or (b) to its continued formation with no crystalline structure, blocking pores and providing strength as it develops (Wild et al., 1989). In addition, small amounts of calcium aluminate hydrate phases (such as C_4AH_6) and calcium silicate aluminate hydrate phases (such as C_2ASH_8) may form especially in high alumina clays containing kaolinite (Arabi and Wild, 1989), and when (as in the current work) sulphates are present these aluminate phases are replaced by sulphoaluminate phases (principally ettringite) which also contribute to strength development. Wild and co-workers (1989) postulated that when very limited pozzolanic activity was occurring (e.g. when curing is at low temperatures) there is insufficient gel formed to reduce the void space between particles, resulting in increased permeability with curing time. This fact, in conjunction with reports from other workers (Bell and Coulthard, 1990; Sherwood, 1993; Waswa et al., 1993) that reduced curing temperatures retard and may even terminate pozzolanic reactions, explains the reduced UCS values attained by samples cured at lower temperatures.

After 1 weeks curing the samples containing >2%$Ca(OH)_2$ which had undergone a period of mellowing (3 days at 20°C) prior to compaction showed consistently higher strengths compared to similar unmellowed samples (Figure 7.3.2 (A-D)). However, when similar samples were cured for 4 weeks, the unmellowed samples were generally stronger (Figure 7.3.3 (A-D)). As mentioned above mellowing increased Atterberg limits and increased OMC and decreased MDD of LOC with various additions of lime due to increased flocculation and the formation of reaction products including ettringite. Although ettringite is known to contribute to the early strength development of Portland cement (PC) (Neville, 1995) mortars and is the principal strength-giving phase in super-sulphated cement (SSC) (Stark and Frohburg, **date**), it also produces expansion. After 1 weeks curing, ettringite forms in both mellowed and unmellowed LOC-lime samples. However, as ettringite is formed during mellowing not only is the system subsequently depleted in sulphate and calcium, but also reduced expansion is experienced during the early curing period after compaction. In unmellowed samples ettringite forms during curing after compaction and as a consequence reduces early strength due to greater expansion. Because early reactions depleted the mellowed samples of calcium during the mellowing period and contributed little to early strength there is less calcium available to participate in strength enhancement at extended curing periods (4 weeks). The opposite apparent in unmellowed samples as there is sufficient calcium available to further enhance strength.

Soaking of either mellowed or unmellowed, lime-modified LOC samples (containing 2%Ca(OH)2 or 1.5%CaO) after 1weeks curing at either 20°C or 5°C resulted in immediate linear expansion, with figures 7.4.1-2 clearly showing that lime type had no bearing on expansion trends. Similarly, compacted lime-stabilised LOC samples (containing 4%, 6% and 8% $Ca(OH)_2$) expanded immediately on soaking, with the samples containing larger amounts of lime generally showing the greatest expansion (Figures 7.4.5-8 (A)). In all tests expansion was found to be consistently less in mellowed samples compared to unmellowed samples, and far greater at lower temperatures (5°C). Wild et al. (1993) postulated that swelling in lime-stabilised kaolinite specimens with added sulphate, is a result of the formation of a colloidal product (a precursor to ettringite formation), which forms on the surfaces of clay particles during curing. If this colloidal product continues to precipitate in an unsaturated environment, then ettringite will be stable and will not swell even if subsequently soaked. However in saturated conditions if ettringite grows and develops from this product substantial amounts of water are imbibed and significant swelling occurs. As mentioned above, and confirmed by current observations ettringite develops during the mellowing period LOC (Section 7.3). Therefore the system is depleted in both calcium and sulphate inhibiting the formation of ettringite in the saturated environment and thus reducing expansion, which itself degrades strength. Furthermore, as mellowed LOC-lime mixes are less dense than unmellowed mixes (Section 7.2) then it is thought that if expansive ettringite forms then swelling can be partially accommodated due to the wider, more open pore structure.

The formation of expansive products (and thus linear expansion) in the presence of moisture in the lime-stabilised LOC is further complicated by the oxidation of pyrites (FeS_2) in LOC, which, according to Russell and Parker (1979), is known to produce gypsum ($CaSO_4.2H_2O$). In fact, the precipitation of gypsum itself is known to cause significant heave in calcareous pyritic mudstones. It is thought that access of the weathering agents (i.e. oxygen and water) alter the pyrites to iron sulphates and sulphuric acid, which in turn attack other minerals present, particularly calcite. With the altered chemistry of the pore fluids crystallisation takes place, commencing with the growth of thin calcium sulphate crystals in naturally weak zones, such as large pores (Hawkins and Pinches, 1987).

This work has shown that the addition of lime (between 2% and 8%$Ca(OH)_2$) to the LOC increased the SO_3 content from 0.88-0.91%SO_3 to 1.53-2.32%SO_3, after compaction and 7 days curing at 20°C (Section 7.4.2). This is clearly a result of pyrites oxidation (which is enhanced in an alkaline environment) producing sulphates such as gypsum. As soaking time is increased so therefore (in the presence of oxygen) is oxidation and SO_3 content. Hawkins and Pinches (1987) reported that sulphate tests (using BS 1377:1975) on a pyrites rich mudstone which was exposed to the atmosphere indicated a three to four fold increase in total sulphate values over 74 days which occurred in a linear manner. Similarly, Snedker (1996), reporting on the heave observed in lime-stabilised pavements at the Banbury IV Contract, Bucks, UK, showed (using

XRD data) that stabilised areas displaying little heave had high pyrite levels (4.7-6.6%) and low gypsum (0%) and ettringite (2.2-3.0%) levels, whereas areas showing significant heave showed a complete lack of pyrites but gypsum and ettringite contents of 0.2-1.1% and 16.5-20.2% respectively.

After 14 days soaking SO_3 contents in all LOC-lime samples had increased, with the samples containing the greater lime additions exhibiting greatest increases. However, continued soaking (105 days) resulted in marked reductions in sulphate levels when the soaking waters were aerated (Figures 7.4.4 and 7.4.9). It is suggested that the aeration process, originally intended to oxidise the FeS_2 in the LOC, introduced a continuous supply of CO_2 into the soaking waters, which carbonated lime that had not yet reacted with other components in the LOC. Carbonation of lime is common but not desirable as it leads to a decrease in availability of calcium ions and a reduction in pH value, and it is this process that ultimately reduced the pH of the soaking waters (Figure 7.4.6-7.4.7) Continued carbonation of the available lime reduced the pH of the system below the point where ettringite is stable (between 10.5 and 11.5 pH) (Gaze and Crammond, 2000; Santhanam et al. 2001), eventually resulting in ettringite carbonation and decomposition, primarily to calcite ($CaCO_3$), thus explaining the reduction in pH of the aerated soaking waters, compared to the relatively consistent pH values of the static/non-aerated soaking waters (Figure 7.4.5). Nishikawa et al. (1992) proposed a mechanism by which ettringite carbonation occurs when ettringite is in contact with water which contains carbonated ions and shows a low pH. Calcium and sulphate ions immediately dissolve in the water leaving the ettringite crystals coated in alumina gel. The dissolved ions released into the liquid are consumed to form calcium carbonate and calcium sulphate. The proposed reaction is:

$3CaO.Al_2O_3.3CaSO_4.26H_2O + 3CO_2 + 3H_2O \rightarrow$

$2Al(OH)_3 + 6Ca^{2+} + 3HCO_3^- + 3SO_4 \rightarrow 3CaSO_4.2H_2O + 3CaCO_3 + 2Al(OH)_3 + 24H_2O$

($Al(OH)_3$ = alumina gel; $CaCO_3$ = calcium carbonate ; $CaSO_4.2H_2O$ = gypsum.)

A fine, white salt was observed both on the exterior of the cylindrical sample and on the sides of the confining plastic cell in specimens subjected to aerated water in the current work after long soaking periods. This is almost certainly a mixture of calcite and gypsum, indicated by the above reaction. This explains the greatly reduced SO_3 contents of LOC-lime samples soaked for 105 days and the finalm pH value of 7 - the pH of a solution containing gypsum (Figure 5.1). Figure 9.1 (A-D) explains the changes in pH level and SO_3 content due to carbonation of the unmellowed LOC-8%Ca(OH)2 sample soaked in aerated water.

The reduced SO_3 content of mellowed LOC-lime material, compared to unmellowed material, after 105 days soaking, are again thought to be a consequence of differing densities and porosities. It is suggested that leaching of the various ions from the sample (due to ettringite decomposition) was more effective in the more porous mellowed samples, resulting in less detectable SO_3 after 105 days soaking. Also, the different pH characteristics exhibited by the mellowed LOC-samples where pH slowly rose to 12.5 (maximum) after 35 days and fell rapidly to 7.5 after 56 days, compared to a comparably sharp rise in pH (to 12 after 21 days - maximum) and then a constant decline to pH 7 (after 56 days) in unmellowed samples is a result of the amount of free lime in the compacted samples. Unmellowed samples contain lime that has not been consumed, during mellowing, in extended flocculation and ettringite formation and therefore exhibited a much higher pH level on soaking. The mellowed samples however are depleted in available lime (especially at low lime additions) and therefore when soaked, showed lower pH values compared to unmellowed samples. Also, as stated earlier, a period of delay between mixing and compaction (i.e. mellowing) results in carbonation and consequently reduced pH levels compared to unmellowed samples.

Similar to the UCS results, the durability indices showed that, at low lime contents, strength loss is greater at 5°C than at 20°C (Figure 7.5.1 - Figure 8.3.1-4). Also, at 20°C there is little difference between the DI values of samples containing 2%$Ca(OH)_2$ or 1.5%CaO, although at 5°C the LOC-2%$Ca(OH)_2$ sample showed a complete lack of cementitious bonding whereas the LOC-1.5%CaO showed strength losses of only 88% in the unmellowed sample. However with such a small initial addition of lime there is little cementation, strength development is negligible and moisture content has a disproportionate influence on strength, and therefore it is difficult to interpret specific individual results.

Further additions of lime (4%, 6% and 8%$Ca(OH)_2$) resulted in an overall reduction in DI values, compared to the LOC-2%$Ca(OH)_2$ sample, at both 20°C and 5°C (Figure 7.5.1). As on soaking LOC-lime samples show higher expansion with higher lime levels, due to the formation of deleterious phases such as ettringite, it is unsurprising that substantial strength loss occurred on soaking resulting in loss of durability. From Atterberg (consistency) limits and Proctor compaction data it is thought that an addition of greater than 6%$Ca(OH)_2$ to the LOC results only in supplying an excess of lime to the system. The excess lime in still apparent on the DTG traces after 4 weeks curing (Figure 7.6.7 and 7.6.11). Hence there is little difference in expansion between additions of 6% and 8% lime (Figure 7.4.5-7.4.7). Mellowing resulted in slightly better DI values as both lime and sulphate are consumed, depleting the systems of the necessary ingredients in ettringite formation. Similar to UCS development, the DI of LOC-lime samples tested at 5°C exhibited lower values than at 20°C due to inefficient bonding, although, as expected, mellowing led to improved durability.

The differential thermogravimetric (DTG) analysis of LOC with either 2%$Ca(OH)_2$ or 1.5%CaO, mixed in the dry state, clearly showed that the addition of lime increased the gypsum content due to the oxidation of pyrites (Figures 7.6.4. and 7.6.8) As the oxidation reaction must involve water, it is thought that even after extensive oven drying, adsorbed water was still present in the LOC allowing Eq.3.8 to proceed.

$$2Ca(OH)_2 + 7.5/2\ O_2 + FeS_2 + 2.5H_2O \rightarrow 2CaSO_4.2H_2O + FeOHO \quad \textbf{Eq.3.8}$$

The intentional introduction of water to both mixes further increased immediately the gypsum content to 4.42% (2%$Ca(OH)_2$) and 4.59% (1.5%CaO) (compared to the maximum potential gypsum content of 6.10%) as a result of pyrites oxidation. Many reports on pyrites oxidation and its consequences with specific regard to stabilised soils describe long, dormant periods where disruption is not noticeable, followed by sudden failure and heave attributed to pyrites oxidation and subsequent sulphate generation over time (Thomas et al. 1981; Hawkins and Pinches 1987; Snedker, 1996). However, the DTG traces presented in the current work clearly show that in a highly alkaline environment pyrites oxidation, and subsequent gypsum formation by reaction with available calcium, is comparatively instantaneous. After, compaction and 1 weeks curing ettringite had formed at the expense of gypsum, although after further curing and a drop in pH levels, as all available $Ca(OH)_2$ was consumed, the gypsum content increased once again. However, it is thought that this increase was a result of ettringite decomposition due to reduced pH levels, rather than further pyrites oxidation.

A period of mellowing (3 days at 20°C) prior to compaction modified the type and amount of reaction products in the LOC-2%$Ca(OH)_2$/1.5%CaO system. During mellowing ettringite was produced at the expense of the lime and gypsum. Although water is present in the mellowed material the ettringite formed during mellowing is thought to be crystalline, as opposed to colloidal in nature, and will therefore not imbibe large quantities of water. After compaction and 1 weeks curing of the mellowed samples, ettringite continued to form at the expense of gypsum indicating that the pH of the system was sufficiently high to allow ettringite formation. However, further curing (4 weeks) resulted in increased gypsum contents. As there was no lime present in the system at this time it is thought that the pH level had reduced, and ettringite subsequently became unstable decomposed, thus forming new gypsum.

In both the mellowed and unmellowed lime-modified LOC systems it is thought that the pH levels of the systems rapidly reach 12.4 (the pH of lime in solution) encouraging the formation of ettringite. However with increased curing time it is suggested that eventually the pH levels of the lime-modified LOC samples reduce as the small amount of added lime is consumed during mixing in the presence of water, ultimately leading to ettringite decomposition to gypsum and alumina gel. Carbonation will clearly accelerate this process and the mellowed material is more susceptible to early carbonation than the unmellowed material.

Similar to lime-modified LOC, additions of $Ca(OH)_2$ or CaO resulted in increased gypsum contents immediately on mixing in the dry state (Figures 7.6.5-7 and 7.6.9-11). Also, additions of CaO not only resulted in higher gypsum contents with increasing lime addition, but were also consistently higher than similar additions of $Ca(OH)_2$ confirming that CaO is more reactive than $Ca(OH)_2$. The intentional addition of water and mixing further increased the gypsum contents via the oxidation of pyrites and also reduced the $Ca(OH)_2$ content of the samples. Gypsum contents were higher in LOC-CaO systems as the addition of water to CaO leads to a substantial heat increase due to the exothermic hydration reaction, thus encouraging pyrites oxidation, release of calcium and ultimately gypsum precipitation at a faster rate compared to $Ca(OH)_2$. Compaction and curing generally resulted in a reduction in gypsum content primarily due to the formation of ettringite. At high lime additions (i.e. 8%$Ca(OH)_2$ and 6%CaO) it is clear that ettringite is the principal reaction product because instead of an increase in gypsum content with further curing (4 weeks) (as there was in the LOC-2%$Ca(OH)_2$ sample), a reduction is apparent (in fact no gypsum was found in the LOC-4.5% and 6%CaO samples). Also, as there was available unreacted lime in the system, a high pH was maintained. The presence of gypsum in the LOC-8%$Ca(OH)_2$ sample after 4 weeks curing, although less than the lime-modified samples, is further evidence to suggest that CaO is more effective in oxidising the pyrites. It is thought that with further curing time, the gypsum content of the LOC-8%$Ca(OH)_2$ would be minimal due to its consumption via ettringite formation.

Mellowing (3 days at 20°C) of lime-stabilised LOC samples allowed extra time for pyrites oxidation (and therefore gypsum precipitation) and ettringite formation prior to compaction. As shown in the Atterberg limit values and Proctor compaction data, at high lime additions, a percentage of lime does not immediately react with the components of the soil. This allows the pH of the system to remain continuously high during mellowing, encouraging pyrites oxidation and subsequently ettringite formation. However, it is thought that lime is also consumed in increased flocculation during mellowing and therefore compacted mellowed samples are depleted in available lime compared to compacted unmellowed samples and, it is possible that carbonation of lime, which is known to reduce pH levels, may also occur. After compaction and 4 weeks curing, both gypsum and ettringite were present in mellowed samples. Lime is also present, indicating a high pH, though it is probable that the pH level in the mellowed samples is less compared to unmellowed samples. Increased curing time reduced the gypsum content indicating that with further curing all gypsum will be consumed in ettringite formation.

Unlike the lime-modified LOC samples (2%$Ca(OH)_2$ or 1.5%CaO), where the pH of the systems were initially sufficiently elevated so that ettringite was the principal reaction product and then subsequently declined during curing so that gypsum was more stable, the lime-stabilised LOC (4-8%$Ca(OH)_2$ or 3-6%CaO) samples attained a high pH which was maintained throughout curing, favouring the formation of ettringite at the expense of gypsum. Similar patterns were observed in mellowed samples, though it is suggested the pH values are somewhat lower due to lime consumption in flocculation, and possibly carbonation of lime, during mellowing and subsequent lime depletion during curing.

To corroborate the data discussed above on unmellowed and mellowed lime-stabilised (8%$Ca(OH)_2$ or 6%CaO) LOC presented in the DTG figures, similar samples were studied using X-ray diffraction (XRD) analysis (Figures 7.7.2-3). In general the X-ray data supported the interpretation of the DTG data.

During the mellowing period for (3 days at 20°C) prior to compaction, the XRD traces illustrated that ettringite was formed at the expense of lime and calcium sulphate (hemi-hydrate) in lime-stabilised LOC. Compaction and curing resulted in lime depletion, and, as shown by the DTG data mellowed samples exhibit greater gypsum contents compared to unmellowed samples. Again, this is thought to be a result of reduced pH levels due to lime consumption and possibly carbonation during mellowing, which tends to favour gypsum stability relative to ettringite.

9.2 GGBS or PC Stabilised LOC

The previous section clearly illustrates the problems associated with stabilising LOC with lime. Principally, although significant strength development was achieved after 4 weeks curing for lime contents in excess of 2% (Figures 7.3.2-7.3.3), considerable levels of expansion on soaking (Figures 7.4.5 and 7.4.6) was also apparent due to pyrites oxidation generating high sulphate levels, resulting in substantial ettringite formation. This, in turn, produced lime-stabilised LOC illustrating very poor durability characteristics (Figure 7.5.1 (A-B)). Therefore using lime to stabilise such a soil would be totally unacceptable. Small additions of lime are however required to modify soils in-situ, and alternative stabilisers were employed (i.e. GGBS and PC) in order to overcome the swelling and loss of durability problem.

The object of stabilisation was to provide cementation, reduce swelling and improve durability of lime-modified LOC. Clearly both stabilising agents effectively improved strength (Figures 8.1.1-8.1.4), reduced linear expansion (Figures 8.2.1-8.2.2) and increased durability (Figures 8.3.1-8.3.4) compared to samples stabilised with lime only. However, samples stabilised with PC produced superior strengths compared to samples at the same levels of GGBS addition. For example, LOC-1.5%CaO-8%GGBS samples exhibited inferior strengths compared to LOC-1.5%CaO-8%PC samples after 52 weeks curing at 20°C (Figure 8.1.2 and 8.1.3). A similar scenario was observed when $Ca(OH)_2$ was used as the soil modifier prior to compaction (Figures 8.1.4 (A-B) and (C-D)). The main reason for this is that GGBS relies on activation by lime. As previously stated lime is consumed during mellowing, and at high GGBS contents (>6%) an addition of 1.5%Ca /2%$Ca(OH)_2$ was not sufficient to sustain GGBS hydration, and that after 12 weeks curing GGBS hydration had ceased, resulting in little further significant strength gain. However PC not only hydrates at a faster rate than GGBS, but also produces lime during hydration. It is proposed that this extra lime combines in pozzolanic reactions with clay particles in the LOC to produce even more cementitious gels and phases over time (Herzog, 1963; Sherwood, 1992, 1993). Similar to the lime-stabilised samples, curing at lower temperatures resulted in reduced strengths in GGBS and PC stabilised samples, though PC-stabilised samples exhibited consistently greater strengths, especially after extended curing periods. Thus, increasing PC contents ultimately lead to improved strength when compared to samples containing similar GGBS contents.

In contrast, additions of PC at the same levels of additions as GGBS produced substantially greater expansion (Figure 8.2.1 A-B). Expansion in lime-stabilised soils is caused by ettringite formation during conditions of saturation and is dependant on the availability of lime, sulphate and alumina and critically on the pH range (>10.5) (Gaze and Crammond, 2000; Santhana et al. 2001). PC hydration produces lime and therefore a high pH is maintained. In LOC-lime-PC mixtures, there is also excess lime and sulphates available from pyrites oxidation and at high pH alumina is released from the clay. These factors lead to enhanced expansion (Figures 8.2.1 (A-B)), although not as high as for equivalent amounts of lime only (Figures 7.4.7(A) and 7.4.8 (A)) because although strengths at 4 weeks are similar the lime content in the lime-stabilised LOC samples is much greater than in PC-stabilised LOC. Although strength levels are lower in GGBS-stabilised LOC than in PC-stabilised LOC (Figures 8.1.2-8.1.3), the hydration process of GGBS removes available lime, thus reducing the pH of the system to levels where ettringite is not stable and encouraging gypsum formation and also reducing the amount of lime available to form both ettringite and gypsum (Wild and Tasong, 1999). Therefore expansion is much reduced. Also mellowing is particularly advantageous because it allows the early deleterious reactions to occur prior to compaction (Figure 8.2.2) further reducing any potential future expansions during soaking.

This is clearly reflected in the relative durabilities of the GGBS-stabilised, PC-stabilised and lime-stabilised LOC. The huge expansion (Figures 7.4.5-7.4.8) accompanying the soaking of lime-stabilised LOC lead to very poor durability indices (Figure 7.5.1), particularly at high lime contents. The expansion of the PC-stabilised LOC was much lower than this (Figure 8.2.1) and hence the durability indices were higher (Figure 8.3.1-8.3.4). In the case of GGBS-stabilised LOC however, expansion was reduced to a very small level (Figures 8.2.1-8.2.2) and therefore although the strength achieved was not as high as with PC, the durability of the GGBS-stabilised material was significantly improved. Also, mellowing as would be expected, further improved durability.

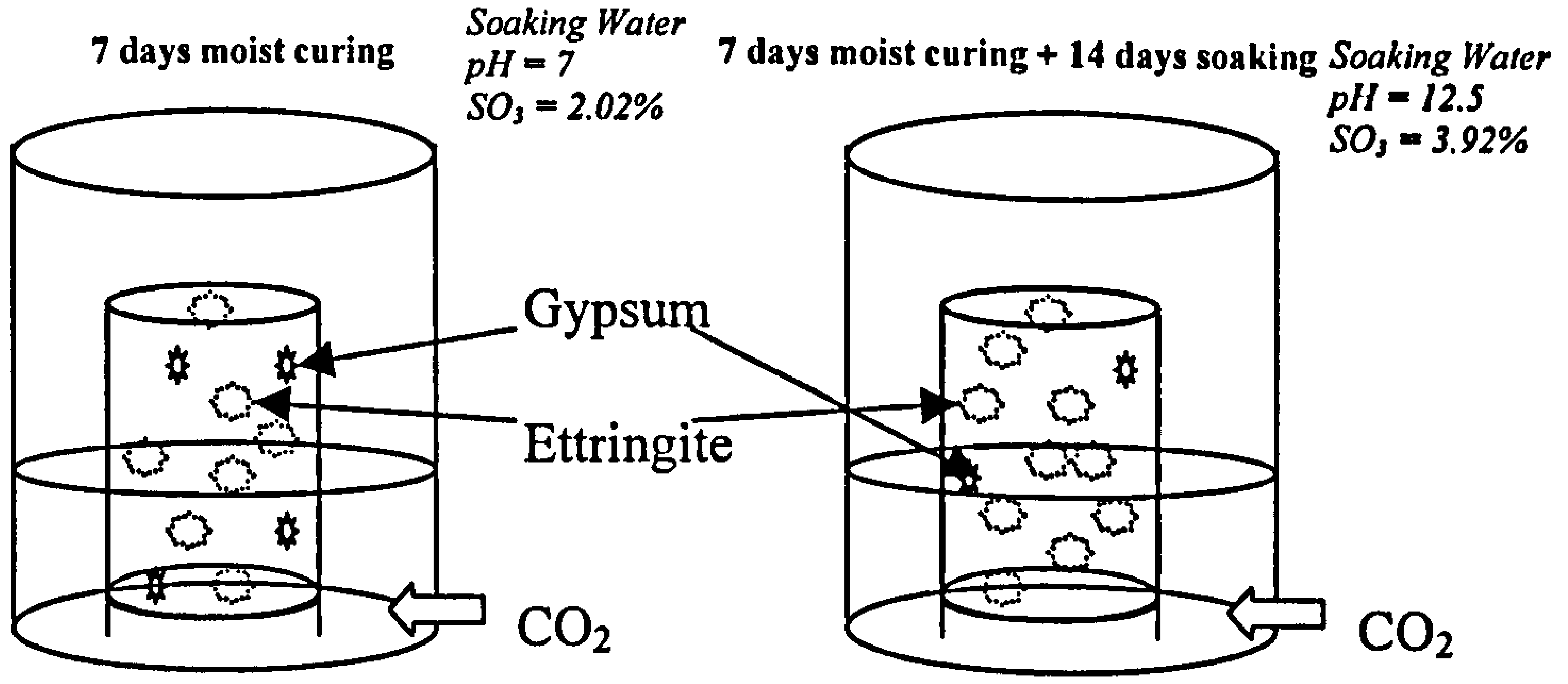
For problem soils such as the Lower Oxford Clay (LOC), which contain significant levels of pyrites that oxidise to produce sulphates, stabilisation methods using GGBS is a possible solution. However, the amount of lime initially added to the soil for modification is critical. If too much lime is added then the excess lime will maintain a sufficiently high pH and promote extensive oxidation of pyrites to sulphate and continued ettringite formation and loss of durability. However, if insufficient lime is added, the pH will not be maintained at a sufficient level to ensure continued GGBS hydration and hence poor bonding and strength will develop in the stabilised clay soil. Thus to apply this method in practice and achieve a durable material with the necessary engineering properties as extensive programme of testing would first be required to establish an appropriate composition to achieve effective modification and stabilisation.

9.3 Practical Implications

The current work has clearly demonstrated that lime (either $Ca(OH)_2$ or CaO) increases the Atterberg limits and flattens the compaction curve of (i.e. increases OMC and decreases MDD) of a sulphide bearing clay soil, the Lower Oxford Clay, and it is apparent that CaO is more effective than $Ca(OH)_2$ at modifying the engineering properties of LOC, especially at low lime additions. Also the addition of lime to the LOC resulted in an immediate increase in the gypsum content of the clay as a result of pyrites oxidation, with additions of CaO being more effective than $Ca(OH)_2$ in pyrites oxidation due to the greater reactivity of the oxide and the exothermic hydration reaction which further accelerates reactions. After 7 days curing and 14 days soaking the SO_3 content of the LOC increased from <1%SO_3 to >3%SO_3, with samples containing greater amounts of added lime generally showing higher SO_3 contents. The almost immediate increase in sulphate levels has important ramifications on potential modifying/stabilising of sulphide rich clay soils as sulphate attack and subsequent heave and disruption was apparent in the current work and is well documented in lime-stabilised pavements. The current work suggests that it is important during preliminary investigations not only to procure sulphate contents of soils, but also sulphide contents as the sulphate content may significantly increase during the stabilisation process as a result of sulphide oxidation. Also it is known that increased curing periods prior to soaking of clay-lime samples resulted in reduced expansion due to the formation ettringite and subsequent depletion of calcium and sulphate ions (Abdi, 1992). If the curing period were extended from 7 days (in the current work) to 28 days, then expected expansion would be lower.

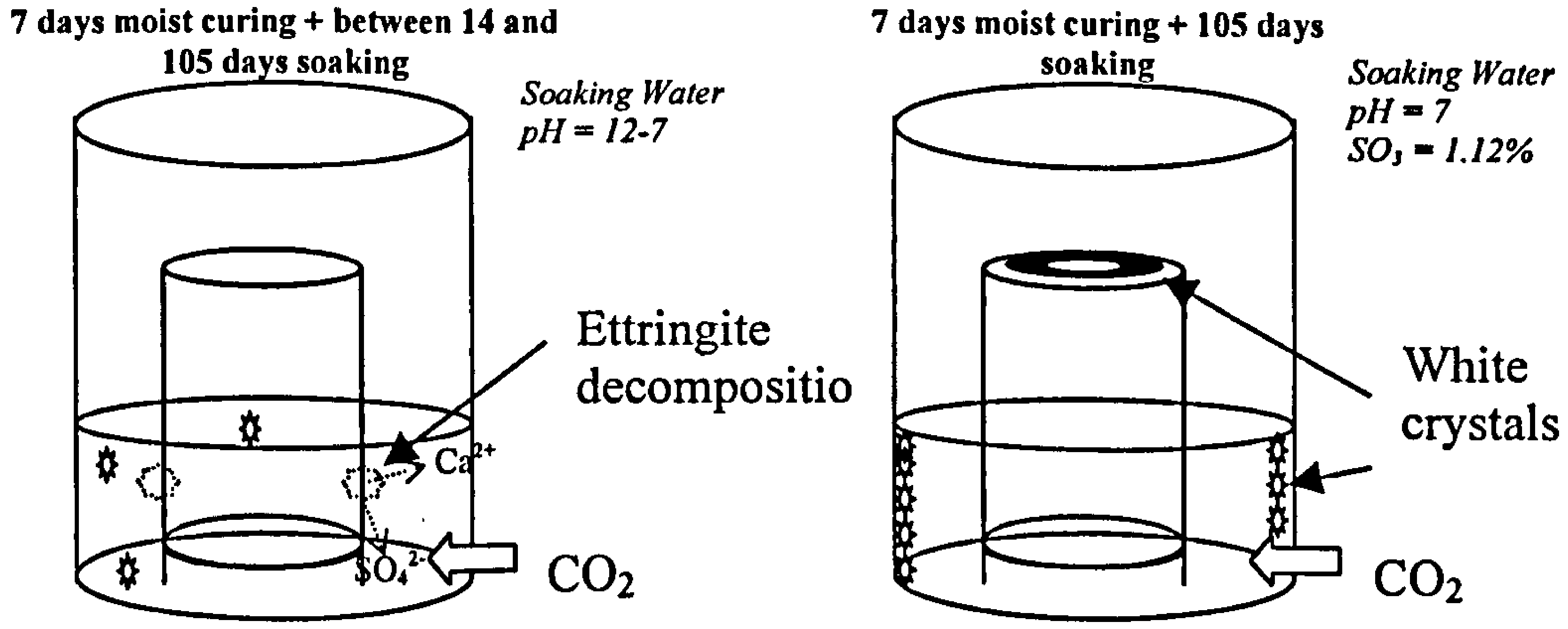
A period of mellowing prior to compaction (3 days at 20°C in the current work) significantly reduced expansion and heave and improved durability of LOC-lime mixes as freely available calcium and sulphate was consumed in ettringite formation, thus depleting the system of the calcium and sulphate and allowing the formation of expansive ettringite prior to compaction. Mellowing also further increased the consistency limits, and further increased OMC and decreased MDD with increasing mellowing time creating a less dense, more porous compacted sample as flocculation and phase formation continued unhindered. Again the changes were more pronounced with additions of CaO. However, it is thought strength development may be retarded in mellowed lime-stabilised soil pavements as lime, required for pozzolanic reactions, is consumed in flocculation and ettringite formation prior to compaction resulting in reduced strength over time. It is suggested that a period of mellowing undertaken prior to compaction is essential, as it not only improves the engineering properties of a clay soil – lime, but also encourages sulphide oxidation and consumes ions required for the formation of deleterious phases in the presence of excess water.

The introduction of a stabilising agent (GGBS or PC in the current work) significantly increased the strength development, linear expansion and durability of lime-modified LOC by the formation of cementing gels and phases at a much faster rate than the clay-lime pozzolanic reactions. It is clear that PC-stabilised lime-modified LOC showed greater strength development, especially after longer curing periods and higher temperatures. GGBS requires an alkaline environment in which to activate and hydrate. However PC does not and as it is known that lime is consumed during mellowing of lime-modified LOC, then the pH of the mellowed material will be depleted and as a consequence may not fully activate GGBS. Therefore it is in order to modify the engineering properties of a sulphide rich clay soil, to encourage sulphide oxidation and to fully hydrate any added GGBS an addition of lime in excess of 2%$Ca(OH)_2$ or 1.5%CaO may be needed. In the presence of excess water linear expansion is lower and durability is greater when GGBS is used to stabilise the LOC. Although the cementing phases formed during PC hydration are stronger and developed at a faster rate, GGBS hydration consumes more lime than it does produces resulting in depleted available calcium and therefore retarded deleterious ettringite formation. Also gypsum, which is increased in the LOC on lime addition, accelerates GGBS hydration whereas gypsum reacts with C-A-H phases and/or $Ca(OH)_2$ produced by alite and belite hydration to form colloidal ettringite in saturated PC-stabilised soils. Therefore it is suggested that stabilisation of sulphate or sulphide bearing clay soils using GGBS is more effective compared to PC in preventing the formation of deleterious phases and subsequent disruption and heave, though strength development is not as great.



A – Gypsum formed from FeS_2 oxidation – ettringite formed during curing from gypsum (more ettringite than gypsum).

B – Continued ettringite formation consuming gypsum in the presence of excess water and lime. pH high. Expansion high. Lime starts to carbonate in contact with CO_2. pH slowly declines.



C – pH falling due to lime carbonation. Ultimately, ettringite decomposition and subsequent leaching of calcium, sulphate and alumina ions into soaking water takes place. pH of soaking water drops to 7 and gypsum precipitated in soaking water.

D – pH at 7. White crystal salt formed around side and base of plastic cell. Reduction in SO_3 content in sample due to sulphate leaching as a consequence of ettringite carbonation.

Figure 9.1 Diagram explaining the changes in pH and SO_3 level of the unmellowed LOC-8%$Ca(OH)_2$ soaked in aerated water.

10. Conclusions and Recommendations for Further Work

10.1 Conclusions

The work presented in this thesis has critically assessed the effect of particular components of a sulphide-rich, naturally occurring, clay soil - Lower Oxford Clay (LOC) - on the engineering properties of that soil when it is modified or stabilised with lime. Laboratory studies were utilised to identify the influence of various parameters including temperature, lime content, lime type ($Ca(OH)_2$ or CaO), pyrites oxidation and pre-conditioning (mellowing) on the LOC, and their impact has been detailed and discussed. Furthermore, the ability to stabilise such a soil has been assessed utilising not only lime, but also GGBS and PC. Laboratory studies were undertaken to assess the effect of slag content, curing and soaking temperature and to compare slag-stabilised LOC with Portland cement (PC) stabilised LOC in tests, which included unconfined compressive strength, linear expansion measurements during saturation and durability measurements. The salient conclusions of the work are summarised below.

1. The addition of a small amount of lime (2%$Ca(OH)_2$ or 1.5%CaO) modified the engineering properties of the Lower Oxford Clay (LOC) by increasing the liquid limit (LL) and plastic limit (PL), and by increasing and decreasing the optimum moisture content (OMC) and maximum dry density (MDD) respectively, as a result of

flocculation caused by cation exchange between the clay particles and the added lime. Further increases of lime further modified the various engineering parameters up to an addition of 6%$Ca(OH)_2$ or 3-4.5%CaO. Lime additions in excess of this lime fixation point result only in supplying an excess of calcium to the mixture.

2. The introduction of a period of mellowing (3 days at 20°C) to the lime-modified LOC prior to testing further increased LL and PL, with greater increases achieved after an addition of 1.5%CaO rather than an addition of 2%$Ca(OH)_2$. Similarly, increased OMC and decreased MDD were apparent after mellowing. Significantly the LOC-1.5%CaO mixture proved to be less dense, and therefore more porous, than the LOC-2%$Ca(OH)_2$ mix as a result of the differences explained above and also the loss of moisture due to evaporation during the initial mixing period, supplying an apparently drier, more robust flocculated material after mellowing. Mellowing of LOC with increasing additions of lime showed further increased LL and PL, and further increased OMC and decreased MDD up to an addition of 6%$Ca(OH)_2$ or 3-4.5%CaO.
3. Increased curing time and increased curing temperatures generally resulted in increased strength development for lime-modified (2%$Ca(OH)_2$ or 1.5%CaO) LOC samples, though the changes were small and non-systematic. Further additions of lime to the LOC resulted in increased strength development due to the formation of cementitious phases as a result of pozzolanic reactions between the clay particles and the added lime. Strength development was noticeably better when curing for 4 weeks at 20°C rather than at 5°C.
4. After 1 weeks curing, mellowed (3 days at 20°C) lime-stabilised LOC samples exhibited superior strengths compared to similar unmellowed samples, though after 4 weeks curing the unmellowed samples were generally stronger as a result of ettringite formation during mellowing.

5. On soaking the linear expansion of lime-modified LOC was immediate, regardless of lime type, soaking environment and soaking temperature. Additions of 2%$Ca(OH)_2$ or 1.5%CaO to the LOC also resulted in increased SO_3 levels after mellowing and 7 days moist curing at 20°C, and SO_3 levels were further increased after 14 days soaking, especially in an aerated environment due to the oxidation of pyrites (FeS_2). Further increases in lime content to the LOC generally resulted in increased expansion on soaking, increased SO_3 contents and more alkaline soaking waters. Other than at high lime contents, samples soaked for extended soaking periods in aerated soaking waters resulted in significantly reduced SO_3 contents due to carbonation, ettringite decomposition and the release of sulphate.
6. Expansion was significantly reduced after mellowing as calcium and sulphate ions required for deleterious ettringite formation were consumed, and also because the less dense, more porous mellowed samples were more effective in accommodating heave. Although expansion was increased at 5°C, it is thought this was a result of inferior bonding rather than increased swelling due to ettringite formation or changes to the chemical system.
7. The durability of LOC-lime samples was reduced when cured and soaked at 5°C compared to 20°C. Although, increased lime contents resulted in increased durabilities at 5°C, at 20°C the LOC-2%$Ca(OH)_2$ exhibited better DI values due to the lack of available calcium. Other than at low lime levels, a maximum limit of 6%$Ca(OH)_2$ addition to the LOC proved most beneficial. This figure also corresponds to results attained in both the consistency (Atterberg) limits and Proctor compaction tests. As expected, durability was improved when a period of mellowing was employed prior to compaction.

8. The analytical data demonstrated that the fundamental difference between the LOC-$Ca(OH)_2$ and LOC-CaO systems was that the oxide was more reactive, generating heat on hydration, and therefore enhancing the rate of pyrites oxidation. In all samples, regardless of the system, ettringite formed during mellowing (3 days at 20°C) at the expense of calcium sulphate. Therefore mellowed LOC samples are depleted in lime, sulphate, pyrites and water and have a reduced pH level compared to unmellowed samples.
9. Increasing additions of ground granulated blastfurnace slag (GGBS) generally increased the strength development of mellowed LOC-1.5%CaO samples especially at 20°C as opposed to 10°C or 5°C. However additions of GGBS in excess of 6% and curing periods beyond 12 weeks did not significantly improve strength as the relatively small addition of lime was insufficient to provide activation of GGBS at extended curing periods for additions of >6%GGBS in addition to participating in cation exchange, flocculation and the formation of cementitious reaction products. Thus as a consequence after 12 weeks moist curing the GBBS hydration ceased. Similarly, increasing additions of Portland cement (PC) generally increased the strength of the mellowed LOC-1.5%CaO mixes especially at 20°C. However, samples containing additions of PC exhibited higher strengths than samples containing similar amounts of GGBS, even after 12 weeks curing, as PC produces lime on hydration, which is thought to react with pozzolanic material (i.e. clay minerals) to further improve strength.
10. Additions of either 4% or 8%GGBS or PC resulted in significantly reduced linear expansion in mellowed LOC-1.5%CaO when soaked in aerated water at 20°C. However, samples containing GGBS showed consistently less expansion than samples containing similar amounts of PC. A reduction in soaking temperature from 20°C to 5°C resulted in increased expansion in all samples though again GGBS-stabilised

samples proved to be more effective in preventing expansion compared to PC. Again, expansion was found to be less in the LOC-1.5%CaO-8%GGBS sample when a period of mellowing was employed prior to compaction.

11. Durabilities were increased when either GGBS or PC was added to lime-modified LOC, though samples containing high amounts of GGBS consistently showed greater DI values, again due to lime consumption during hydration and the presence of accelerating gypsum. A reduction in curing and soaking temperature from 20°C° to 5°C resulted in reduced DI values due to inefficient cementation. As expected mellowing further increased durability.
12. Most significantly, although lime-modified, PC-stabilised LOC showed greater strength development than similar GGBS-stabilised samples, when saturated GGBS-stabilised samples (containing 6% or 8% GGBS) exhibited less expansion and recorded higher durability indices than similar PC-stabilised samples.

10.2 Recommendations for Further Work

It is clear that several questions have been raised by the work presented in this thesis, the answers to which could not be incorporated in the current work due to time restraints. The following outlines areas worthy of further study.

The current work examines in detail the engineering performance of a naturally occurring sulphide rich clay soil when stabilised with lime, GGBS or PC. In order to appreciate the role of the soil, a comparative study specifically examining the role of sulphide oxidation and mellowing should be undertaken utilising a mono-mineralic sulphate/sulphide free soil such as china clay.

Although mellowing is outlined in the Department of Transport guidelines on soils stabilisation (DoT, 1995), there are no specific guidelines as to the moisture content of the mellowed material – a factor that may influence the ultimate strength and durability of the stabilised soil. A study of the effect of the moisture content of mellowed material on subsequent performance after compaction would prove beneficial during construction of stabilised soils, especially in sulphide-rich clay soils.

Saturation of stabilised LOC samples in CO_2-rich water resulted in reduced pH levels after extended soaking periods, and as relatively high pH levels are required to maintain the integrity of cementitious phases, the long-term strength of such soils is unclear. Thus further work is necessary to examine the effects of saturation of stabilised sulphide-rich samples at differing pH levels.

The durability index test (as outlined in Chapter 6) requires stabilised samples to be moist cured for a 3-week period prior to soaking (1 week) before obtaining compressive strength. However, in order to monitor the effectiveness of moist curing prior to soaking, it is suggested that a range of curing times be employed.

There is clearly a critical balance between the amount of lime required to be added to sulphide rich soils to effect modification, without producing excessive swelling and the level of lime required to effectively activate the GGBS and provide GGBS hydration over an extensive time period. Further research is required to establish guidelines with regard to the appropriate level of both lime and slag with respect to various sulphide levels in sulphide rich soils.

An analytical study of cured lime-modified/stabilised, sulphate/sulphide rich clay soil (such as the Lower Oxford Clay), either stabilised or unstabilised with a suitable stabilising agent (such as GGBS) subjected to moist curing and soaking at low temperatures (<15°C) would be beneficial with regards to examining the effects of the thaumasite form of sulphate attack (TSA) in these systems.

11 References

Abdi, M.R. (1992) "Effect of calcium sulphate on lime-stabilised kaolinite." PhD Thesis, Polytechnic of Wales (University of Glamorgan), Pontypridd, UK.

Abdi, M.R. and Wild, S. (1993) "Sulphate expansion of lime-stabilised kaolinite: I. Physical characteristics" Clay Minerals, 28, pp555-567.

Akpokodje, J.G. (1985) "The stabilisation of some arid zone soils with cement and lime" Q.J.Engineering Geology, London, 18, 173-180.

Allaway, W.H. (1945) "Availability of replaceable calcium from the different types of colloids as affected by degree of calcium saturation." Soil Sci., 59, pp207-217.

Al-Rawi, R.S. (1981) "Effect of curing temperature on lime stabilisation." Proc. 2nd Australian Conf. On Engineering and Materials, Sydney, pp611-622.

Arabi M. (1987) "Property changes in clay soils when using lime stabilisation." PhD Thesis, Polytechnic of Wales (University of Glamorgan), Pontypridd, UK.

Arabi, M and Wild, S. (1989) "Property changes in clay soils when using lime stabilisation." Municipal Engineer, 6, April, pp85-99.

Backes, C.A., Pulford, I.D. and Duncan, H.J. (1986) "Studies on the oxidation of pyrite in colliery spoil. I. The oxidation pathway and inhibition of the ferrous-ferric oxidation." Reclamation and Re-vegetation Research, 4, pp279-291.

Barker, A.P. and Hobbs, D.W. (1999) "Performance of Portland limestone cement in mortar prisms immersed in sulphate solution at 5°C." Cement and Concrete Composites 21, pp129-137.

Barth, T.F.W. (1962) "Theoretical petrology" 2nd Edition, John Wiley and Sons, USA.

Barshad, I. (1955) "Adsorptive and swelling properties of clay-water systems." 1st National Con. Clay and Clay Technology, Div. Of Mines, San Francisco, 169, 70-77.

Bell, F.G. (1987) "Lime stabilisation and clay mineralogy." Proc. Foundations and Tunnels, Vol. II.

Bell, F.G. (1988) "Stabilisation and treatment of clay soils with lime: Part1 – basic principles." Ground Engineering, SM 2, pp127-153.

Bell, F.G. and Coulthard, J.M (1990) "Stabilisation of clay soils with lime." Municipal Engineer, 7, June, pp125-140.

Bensted, J. (1999) "Thaumasite – background and nature in deterioration of cements, mortars and concretes." Cement and Concrete Composites, 21, pp117-121.

Bensted, J. and Varma, P. (1974) "Studies of thaumasite Part II." Silicate Industriels, Vol.39, pp11-19.

Bentur, B. (1976) "The effect of gypsum on the hydration and strength of C_3S pastes." Journal of American Ceramics Society, Vol. 59, pp210-213.

Bessey, G.E. and Lea, C.B.E. (1953) "The distribution of sulphates in clay soils and groundwater." Proc. of the Institute of Civil Engineers, Vol.2, Part1, pp159-181.

Bickley, J.A., Hemmings, R.T., Hooton, R.D. and Balinski, J. (1995) "Thaumasite related deterioration of concrete structures." American Concrete Inst. Proc. Concrete Technology: Past, Present and Future SP144, part 144, pp159-175.

Bolan, N.S., Syres, J.K. and Semner, M.E. (1993) "Calcium-induced sulphate adsorption by soils." Soil, Science Soc. Of America Journal, 57, pp691-696.

Braley, S.A. (1960) "The oxidation of pyrite conglomerates." Coal Industry Advisory Committee to Ohio River Valley Water Sanitation Commission, Research Project No. 370-6, Mellon Inst Pittsburgh, Pa., p2-3.

Brandl, H. (1981) "Alteration of soil parameters by stabilisation with lime." Proc. 10th Int. Conference on Soil Mechanics, Stockholm, Sweden, 3, pp587-594.

British Earth Sheltering Association (1994) ""Sod it!" : an introduction to earth sheltered development in England and Wales." Editor: Peter Carpenter, Coventry University SOBE.

British Standards BS 1047: (1983) ":Air cooled blastfurnace slag aggregate for use in construction." HMSO, London, UK

British Standards BS 1377 : (1990) British Standards methods for soils for civil engineering purposes." HMSO, London, UK.

British Standards BS 1924 : (1990) Part 2 : 1990 "Methods of test for cement-stabilised and lime-stabilised materials." British Standards Institute, HMSO, London, UK.

Brown, G. (1972) "The X-ray identification and crystal structure of clay minerals." Mineralogical Society, London, Jarrold and Sons, Norwich.

Building Research Establishment (BRE) (1981) "Concrete in sulphate-bearing soils and groundwater." BRE Digest 250, Building Research Establishment, Watford.

Building Research Establishment (BRE) (1991) "Sulphate and acid resistance of concrete in the ground." BRE Digest 363, Building Research Establishment, Watford.

Carson, R. (1962) "Silent Spring" Boston, Houghton Mifflin Company, USA.

Cassanova, I., Agullo, L. and Aguado, A. (1996) "Aggregate expansivity due to sulphide oxidation – I. Reaction system and rate model." Cement and Concrete Research Vol. 26, No.7, pp993-998.

Cassanova, L., Aguado, A. and Agullo. L. (1997) "Aggregate expansivity due to sulphide oxidation – II. Physico-chemical modelling of sulphate attack." Cement and Concrete Research, Vol.27, No.11, pp1627-1632.

Cernica, J.N. (1995) "Geotechnical Engineering – Soil Mechanics" John Wiley and Sons Inc., USA.

Chartschenko, I.J., Vole, K. and Stark, J. (1993) "Investigations on the influence of the pH value on the formation of ettringite." Wissenschaftliche Zeitung der Hoschschule fur Architektur und Basuwesen, Vol. 39, no.3 Weimar, Deutchland (*in German*).

Chatwin, C.P. (1961) "East Anglia and adjoining areas." 4th Edition, British Regional Geology, NERC, Inst. Of Geological Sciences, HMSO, London, UK.

Cobbe, M.I. (1988) "Lime-modification of kaolinite-illite clays." Civil Engineering Technology, February, pp9-15.

Collepardi, M. (1999) "Thaumasite formation and deterioration in historic buildings." Cement and Concrete Composites, 21, pp147-154.

Cowie, J. and Glasser, F.P. (1991) "The reaction between cement and natural waters containing dissolved carbon dioxide." Advances in Cement Research, 4, 15, July, pp119-134.

Cox, B.N., Hudson, J.D. and Martill, D.M. (1992) "Lithostratigraphic nomenclature of the Oxford Clay (Jurassic)" Proc. of Geologists Assoc., 103, pp343-345.

Crammond, N.J. and Halliwell, M.A. (1995) "The thaumasite form of sulphate attack in concretes containing a source of carbonate ions – a microstructural review." 2nd Symposium on Advances in Concrete Technology, ACI SP154, pp357-380.

Crammond, N.J. and Nixon, P.J. (1993) "Deterioration of concrete foundation piles as a result of thaumasite formation." 6th Conf. On Durability of Building Materials, Japan, Vol.1, pp295-305.

Cripps J.C. and Edwards, R.L. (1992) "Some geotechnical problems associated with pyrite bearing mudrocks." Ground Chemistry Implications for Construction, Proc. of the Int. Conf. On the Implications of Ground Chemistry and Microbiology for Construction, University of Bristol, UK.

Cripps, J.C., Hawkins, A.B. and Reid, J.M. (1994) "Engineering problems with pyritic mudrocks." Geoscientist, Vol.3, No.3, pp16-19.

Croft, J.B. (1964) "The pozzolanic reactivities of some New South Wales fly-ashes and their application to soil stabilisation." Proc. ARBB Australia, Vol.2, Part2, Paper 120, pp1144-1167.

Croft, J.B. (1967) "The influence of soil mineralogical composition on cement stabilisation." Geotechnique, 17, pp119-135.

Daimon, M. (1980) "Mechanism and Kinetics of slag cement hydration." 7th International Congress on the Chemistry of Cement, Paris, Sub-theme III-2, Vol.1, ppIII-2/1 – III-2/9.

Day, R.L. (1992) "The effect of secondary ettringite formation on the durability of concrete: A literature analysis." Research and Development Bulletin, RD108T, Portland Cement Association, ISBN 0 89312-169 X.

Deng, M. and Tang, M. (1994) "Formation and expansion of ettringite crystals." Cement and Concrete Research, 24, pp119-126.

Department of Environment, Transport and the Regions, Digest No.058 (1999) "Improving poor ground conditions. Lime and cement stabilisation of weak clay soils." Aggregates Advisory Service, Research Contract MP0623, Digest No.058, (3:2/99).

Department of Transport (DOT) (1995), "Design and construction of lime stabilised capping." Design Manual for Roads The Highways Agency, 74/95, Volume 4, Section 1, Part 6, May 1995.

Diamond, S., White, J.L. and Dolch, W.L. (1964) "Transformation of clay minerals by calcium hydroxide attack." Clay and Clay Minerals, Volume 12, pp359-379.

ELE (Internet Reference) http://www.eleint.com.

Freeman, L.L. (1956) "Variation in the lower zones of the Oxford Clay." Clay Minerals Bulletin, 3, pp50-61.

Gaze. M.E. (1997) "The effects of varying gypsum content on thaumasite formation in a cement:lime:sand mortar at 5°C." Cement and Concrete Research, Vol.27, No.2, pp259-265.

Gaze, M.E. and Crammond, N.J. (2000) "The formation of thaumasite in a cement:lime:sand mortar exposed to cold magnesium and potassium sulphate solutions." Cement and Concrete Composites, 22, pp209-222.

Glasser, F.P. (1996) "The role of sulphate mineralogy and cure temperature in delayed ettringite formation." Cement and Concrete Composites, 18, pp187-193.

Gouda, G.R., Roy, D.M. and Sarkar, A. (1975) "Thaumasite in deteriorated soil-cements." Cement and Concrete Research, Vol.5, pp519-522.

Greaves, H.M. (1996) "An introduction to lime stabilisation." Lime Stabilisation, Thomas Telford London.

Greaves, H.M. (2000) Private Communication, Buxton Lime Industries, Cheshire, UK.

Grim, R.E., Bray, R.M. and Bradley, W.F. (1937) "The mica in argillaceous sediments.2 Am. Mineralogist, 22, pp813-829.

Grim, R.E. (1968) "Clay Mineralogy." International Series in the Earth and Planetary Sciences, McGraw-Hill, Inc., USA.

Hawkins, A.B. (1992) "Some geotechnical problems associated with pyrites bearing mudrocks." Proc. Int. Conf. on the Implications of Ground Chemistry and Microbiology for Construction, University of Bristol.

Hawkins, A.B. and Pinches, G.M. (1987) "Cause and significance of heave at Llandough Hospital, Cardiff – a case history of ground floor heave due to gypsum growth." Quarterly Journal of Eng. Geology, London, Vol.20, pp41-57.

Herzog, A. (1963) "The strength of clay-cement." 4th Australia-New Zealand Conf. On the Soil Mechanics and Foundation Engineering, pp23-24.

Herzog, A and Mitchell, J.K. (1963) "Reactions accompanying the stabilisation of clay with cement." Highway Research Record, 36, pp146-171.

Higgins, D.D. (1998) "What's new with GGBS ?." Concrete Magazine, May 1998.

Higgins, D, D, and Kennedy, J. (1999) "Lime and ground granulated blast furnace slag stabilisation of boulder clay on the 'A421' Tingewick bypass." 3rd European Symposium on the Performance and Durability of Bituminous Material and Hydraulic Stabilised Composites: Leeds UK, 8-9th April.

Hilt, G.H and Davidson, D.T (1960) "Lime fixation in clayey soils." Highway Res. Board, Washington D.C., 262, pp20-32.

Hobbs, D.W. and Taylor, M.G. (2000) "Nature of the thaumasite sulphate attack mechanism in field concrete." Cement and Concrete Research, 30, pp529-533.

Hunter, D. (1988) "Lime-induced heave in sulphate bearing clay soils." ASCE J. of Geotechnical Eng., 112 (2), pp50-76, February.

Ingles, O.G. and Metcalf, J.B. (1972) "Soil stabilisation principles and practice." Butterworth, Sydney, pp103-142.

Kinuthia, J.M. (1997) "Property changes and mechanisms in lime-stabilised kaolinite in the presence of various metal sulphates." PhD thesis, University of Glamorgan, Pontypridd, UK.

Kinuthia, J.M., Wild, S. and Jones, G.I. (1999) "Effects of monovalent and divalent metal sulphates on consistency and compaction of lime-stabilised kaolinite." Applied Clay Science, 14, pp27-45.

Komnitsas, K., Xandis, A. and Adam, K. (1995) "Oxidation of pyrite and aresenopyrite in sulphidic soils in Lavrion." Minerals Engineering, Vol.8, No.12, pp1443-1454.

Kostov, I. (1968) "Mineralogy." Oliver and Boyd, Edinburgh and London.

Krahn, J. and Fredlund, D.G. (1972) "On total, matric and osomotic suction. " Soil Science, 114. pp339-348.

Kuzel, H.J. (1996) "Initial hydration reactions and mechanisms of delayed ettringite formation in Portland cements." Cement and Concrete Composites, 18, pp195-203.

Lees, G., Abdelkader, M.O. and Hamdani, S.K. (1982) "Effect of the clay fraction on some mechanical properties of lime-soil mixtures." Journal of the Institution of Highway Engineers, 29th November, pp3-9.

Li, G., Le Bescop, P and Moranville, M (1996) "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, pp195-201.

Liptay, G. (1971-75) "Atlas of thermoanalytical curves." Volumes 1-4, London, Heyden, ISBN 0855011548

Maclean, D.J. and Sherwood, P.T. (1961) "Study of the occurrence and effects of organic matter in relation to the stabilisation of soils with cement." Proc. 5th Int. Conf. Soil Mechanics, 2, 269-275.

Macneil, J. (1998) "Mushy mystery." Building Magazine, May 1st, pp66

Marshall, C.E. (1935) Layer lattices and base-exchange clays." Z, Krist, 91, pp433-449.

Mateous, M'(1964) "Soil-lime research at Iowa State University." Journal of Soil Mechanics, Foundations Division, American Society of Civil Engineers, SM2, pp127-153.

Matsushita, I., Suzuki, T., Moriga T., Ashida, T., Nakabayashi, I and Metson, J. (1993) "XPS study on the carbonation process of $Ca(OH)_2$" Journal Of The Ceramic Society Of Japan, Int. Edition, Vol.101, pp707-709.

Mehta, P.K. (1973) "Effect of lime on hydration of pastes containing gypsum and calcium aluminates or calcium sulpho-aluminate." J. American Ceramic Soc., 56, pp315-319.

Mehta, P.K. (1979) "The chemistry and technology of cements made from rice-husk ash." Proc. of Workshop on Production of Cement-Like Materials from Agro-Wastes, UIDO-ESCAP-RCTT-PCSIR, Peshawar, 1979.

Mehta, P.K. (1983) " Mechanism of sulphate attack on Portland cement." Cement and Concrete Research, 13, pp401-406.

Metcalf, J.B. (1963) "The effect of high curing temperature on the unconfined compressive strength of a heavy clay stabilised with lime and with cement." 4th Australian-New Zealand Conference on Soil Mechanics and Foundation Engineering, C.S.I.R.O, Victoria, pp126-129.

Midgely, H.G. (1978) "Chemical properties of aggregates." Mag. Concrete Research 10, (29), 75.

Millot, G. (1970) "Geology of Clays" Marson et C^{ie}, Paris.

Mitchell. J.K. and Hooper, D.R. (1961) "Influence of time between mixing and compaction on properties of lime stabilised expansive clay." Highway Research Board, Washington DC, Bulletin 304, pp14-31.

Mitchell, J.K. (1986) "Delayed failure of lime-stabilised pavement bases." J. Geotech. Eng. 112, pp274-279.

Mitchell, J.K. (1993) "Fundamentals of soil behaviour." 2nd Edition, John Wiley and Sons, New York, USA.

Neville, A.M. (1995) "Properties of concrete." 4th and Final Edition, Longman Press, England, ISBN 0-582-23070-599.

Nicolson, R., Gillam, W and Reardon, E. (1988) "Geochimica et Cosmochimica" Acta 52, pp1077-1085

Nishikawa, T., Suzuki, K., Ito, S., Sato, K. and Takebe, T. (1992) "Decomposition of synthesised ettringite by carbonation." Cement and Concrete Research, Vol.22, pp6-14.

(NLA) National Lime Association of America (1995) "Lime – handling, application and storage." Bulletin No.213, NLA, Arlington, Va., USA.

O'Farrell, M. **(1999)** "The durability of mortar with ground clay brick as partial cement replacement." PhD Thesis, University of Glamorgan, Pontypridd, UK.

Parsons, A.J., Inglethorpe, S.D.J., Morgan, D.J. and Dunham, A.C. (1997) "Evolved gas analysis (EGA) of brick clays." Journal of Thermal Analysis, Vol.48, pp49-62

Pauling L. (1930) "The structure of micas and related minerals." Proc. Nat. Acad. Sci., US, 16, pp123-129.

Perrin, R.M.S. (1971) "The clay mineralogy of British sediments." Mineralogical Society, W42-1252.

Perry, J., Snowdon, R. A. and Wilson, P. E. (1996) "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, London.

Powrie, W (1997) "Soil Mechanics – Concepts and Applications" Chapman and Hall, London, UK.

Ross, C.S. and Kerr, P.F. (1931) "The kaolin minerals." US Geol. Surv., Prof. Paper 165E, pp151-176.

Robbins, J (1990a) "…just add lime." New Civil Engineer, Roads Supplement, May, pp33-34.

Robbins, J. (1990b) "New M40 faces rebuild as lime base heaves." New Civil Engineer, July, pp5-6.

Roy, D.M. and Idorn, G.M. (1982) "Hydration, structure and properties of blast furnace slag cements, mortars and concretes." ACI Journal, Vol.79, November/December, pp444-457.

Russell, D.J. and Parker, A. (1979) "Geotechnical, mineralogical and chemical interrelationships in weathering profiles of an over-consolidated clay." Q. Jl. Engineering Geology, Vol.12, pp107-116

Santhanam, N., Cohen, M. and Olek, J. (2001) "Sulphate attack research - whither now?" Cement and Concrete Research, 31, pp845-851.

Seidell, A. (1940) "Solubilities of inorganic and metal organic compounds." 3rd Edition, Volume 1, D.Van Nostrand Company, Inc., New York, USA.

Sherwood, P.T. (1992) "Stabilised capping layers using either lime, or cement, or lime and cement." Contractor Report, No.151, Transport Research Laboratory.

Sherwood, P.T. (1993) "Soil stabilisation with cement and lime" Transport Research Laboratory, London:HSMO.

Shi, C. and Day, R.L. (1993) "Chemical activation of blended cements made with lime and natural pozzolans." Cement and Concrete Research, 23, pp1389-1396.

Singer and W.Stumm (1970) "Science" no.167, pp1121-1123

Sloane, R.L. (1965) "Early reactions in the kaolinite-hydrated lime-water system." Proc. 6th Int. Conf. Soil Mechanics and Foundation Engineering, Montreal, 1, pp121-125.

Smith, A. (1999) Private Communication from Hanson Brick Ltd.

Smolczyk, H.G. (1980) "Slag structure and identification of slags." Proc. 7th Int. Conf. On the Chemistry of Cement, Paris, France, pp III-1/3 – III 1/17.

Snedker, E.A. and Temporal, J. (1990) "M40 Motorway Banbury IV Contract – Lime stabilisation." Highway and Transportation, December.

Snedker, E.A. (1996) "M40 - Lime stabilisation experiences." Lime Stabilisation, Thomas Telford, London, pp142-158

Stark, J. and Frohburg, U. (1999) "Investigations with supersulphated cement." Modern Concrete Materials: Binders, Additions and Admixtures, Edited by Dhir, R.K. and Dyer, T.D, pp351-360

Stevens, G. and Littleton, I. (1989) "The influence of sulphate on lime stabilised Gault clay." ICI General Chemicals Report, No.8886, June.

Tasong, W.A., Wild, S. and Tilley, R.J.D. (1999) "Mechanisms by which ground granulated blast furnace slag prevents sulphate attack of lime-stabilised kaolinite." Cement and Concrete Research, 29, pp975-98.

Taylor, H.F.W. (1997) "Cement Chemistry." 2nd Edition, Thomas Telford, London, ISBN 07227725920.

Terzaghi, K. and Peck, R.B. (1967) "Soil mechanics in engineering practice." 2nd edition, John Wiley and Sons, New York, USA.

Thaumasite Expert Group (1999) "The thaumasite from of sulphate attack: Risks, diagnosis, remedial works and guidance on new construction." Department of the Environment, Transport and the regions, London, ISBN 1 85112 150 1.

Thomas, M.D.A., Kettle, R.J. and Morton, J.A. (1981) "Expansion of Cement - Stabilised Minestone due to the Oxidation of Pyrites" Transportation Research Record, Vol. 1219, pages 113-120, ISBN / ISSN 0361-1981.

Thompson, M.R. (1966) "Shear strength and elastic properties of soil-lime mixtures." Highway Research Record no.139, Washington, USA, pp1-14.

TRL408 Enabling the use of secondary aggregates and binders in pavement foundations. (date) Atkinson, V.M., Chaddock, B.C. and Dawson, A. R.

Uchikawa, H. (1986) "Effect of blending components on hydration and structure formation. " Proc. 8th Int. Congress on Chemistry of Cements, Rio de Janeiro, Vol.1, 99250-280.

Van Impe, (1989) "Soil improvement techniques and their evolution." A.A.Balkema, Rotterdam, Netherlands.

Varma, S.P. and Bensted, J. (1973) "Studies of Thaumasite." Silicates Industriels, Vol.38, part 2, pp29-32.

Veith, G., Wild, S. and Robinson, R. B, (1999) "Shear strength, permeability and porosity of Kimmeridge clay, stabilised with lime and ground granulated blastfurnace slag (GGBS)." Concrete Communication Conference '99, The 9th BCA Annual Conference on Higher Education and the Concrete Industry, 8-9th July 1999, Cardiff University, Theme 1:Sustainability and whole life cycle, 1999, 41-52, Publ. British Cement Association, ISBN 0 72101548 4.

Veith, G. (2000) "Engineering properties of sulphate-bearing clay soils with lime-activated ground granulated blast furnace slag (GGBS)." PhD Thesis, University of Glamorgan, Pontypridd, UK.

Wang, S-D., Pu, X-C., Scrivner, K.L. and Pratt, P.L. (1995) "Alkali-activated slag cement and concrete: a review of properties and problems." Advances in Cement Research, 7, No.27, July, 93-102.

Waswa, B., Wild, S., Jones, G.I. and Webb, D.J.T. (1993) "The potential of lime-stabilised murram soils as a building material in Kenya." Building Research and Information, Vol.21, No.5.

Whiston, C. (1987) "X-ray methods." Analytical Chemistry by Open Learning, Editor F.E.Pritchard, John Whiley and Sons, ISBN 0 471 91378 1 Pbk.

Wild, S., Arabi, M. and Leng-Ward, G. (1986) "Soil-lime reaction and micro-structural development at elevated temperatures. "Clay Minerals, 21, pp279-292.

Wild, S., Arabi, M. and Leng-Ward, G (1989) "Fabric development in lime treated clay soils." Ground Engineering, Volume 22, No. 3, April, pp35-38

Wild, S., Arabi, M.R. and Leng-Ward, G. (1993) "Sulphate expansion of lime-stabilised kaolinite: II Reaction products and expansion." Clay Minerals, 28, pp569-583.

Wild, S., Hadi, M. and Leng-Ward, G. (1990) "The influence of gypsum content on microstructural development, strength and expansion of cured PFA-lime mixes." Advances in Cement Research, 3, no.12, pp153-166

Wild, S, Khatib, J., Sabir, B.B. and Addis, S.D. (1996(a)) "The potential of fired brick clay as a partial replacement material." Concrete for environment Enhancement and Protection, Editor: Dhir, R.K. and Dyer, T.D. Published by E and FN Spon, London, UK. ISBN 0 419 21450 X.

Wild, S., Kinuthia, J.M., Robinson, R.B. and Humphreys, I. (1996(b)) "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, pp423-433.

Wild, S., Kinuthia, J.M., Jones, G.I. and Higgins, D.D. (1998) "Effects of partial substitution of lime with ground granulated blastfurnace slag (GGBS) on the strength properties of lime-stabilised sulphate-bearing clay soils." Engineering Geology, 51, pp37-53.

Wild, S., Kinuthia, J.N., Jones, G.I. and Higgins, D.D. (1999) "Suppression of swelling associated with ettringite formation in lime-stabilised sulphate bearing soils by partial substitution of lime with ground granulated blast furnace slag (GGBS)." Engineering Geology, 51, pp527-277.

Wild, S. and Tasong, W.A. (1999) "Influence of ground granulated blast furnace slag on the sulphate resistance of lime-stabilised kaolinite." Magazine of Concrete Research, 51, No.4, pp247-254.

Wilson, M.J. (1978) "Occurrence of thaumasite in weathered furnace slag, Merthyr Tydfil." Mineralogical Magazine, June, Vo.42, pp290-291.

Wu, X., Jiang, W. and Roy, D.M. (1990) "Early activation of slag cement." Cement and Concrete Research, 20, pp961-974.

Zhou, H., Wu, X., Xu, Z. and Tang, M. (1993) "Kinetic study of hydration of alkali-activated slag." Cement and Concrete Research, 23, pp1253-1258

Appendices

Appendix A.

Appendix B.

Experimental Results - LOC-lime system.

Experimental Results - LOC-lime-GGBS/PC system.

Appendix C.

Appendix A

A.1 Heat Generation by Quicklime in presence of Water:

$\Delta H1 \quad \Delta H2 \qquad\qquad \Delta H3$

$CaO + H_2O \rightarrow Ca(OH)_2$

$\Delta H1 \quad Ca + O \rightarrow CaO = -635.5$ kJ / mole

$\Delta H2 \quad H_2 + O \rightarrow H_2O = -285.8$ kJ / mole

$\Delta H3 \quad Ca + O_2 H_2 \rightarrow Ca(OH)_2 = -986.6$ kJ / mole

$\Delta H = \Delta H3 - (\Delta H1 + \Delta H2)$

$= -986.6 - (-635.5 + -285.8)$

-65.3 kJ / mole (-ve represents heat evolved)

1 mole of $Ca(OH)_2$ = 40 +34 = 74g $Ca(OH)_2$

-65.3 kJ of heat are released in forming 74g of $Ca(OH)_2$

Therefore, (-)65.3 / 74 = **0.882 kJ** of heat is generated during CaO hydration per g of $Ca(OH)_2$.

A.2 Volume increases due to ettringite formation.

The first scenario outlines the volume increase due to ettringite formation when gypsum is mixed with C_3A:

C_3A + $3C\underline{S}H_2 + 26H_2O \rightarrow C_6A\underline{S}_3H_{32}$

or

$3CaO.Al_2O_3 + 3CaO.3SO_3.6H_2O + 26H_2O \rightarrow 6CaO.Al_2O_3.3SO_3.32H_2O$

(168+54+48) + (168+240+108) + (468) → (336+54+48+240+576)

Atomic Mass

$C_3A = 270$ $3C\underline{S}H_2 = 516$ $26H_2O = 468$ $C_6A\underline{S}_3H_{32} = 1254$

Density

$C_3A = 3.03$ $3C\underline{S}H_2 = 2.32$ $26H_2O = 1$ $C_6A\underline{S}_3H_{32} = 1.76$

Volume (V=M/D)

$C_3A = 89.10 + 3C\underline{S}H_2 = 222.41 + 26H_2O = 468 \rightarrow C_6A\underline{S}_3H_{32} = 712.5$

779.51 → 712.5

Therefore the total volume would be reduced by **8.59%**

However, if H_2O consumed in this reaction is drawn from outside (i.e. if this reaction occurred in hardened material) then:

$C_3A = 89.10 + 3C\underline{S}H_2 = 222.41 \rightarrow C_6A\underline{S}_3H_{32} = 712.5$

311.51 → 712.5

Then a total volume increase of **128.2%** would be expected.

The second scenario of volume increase due to ettringite formation involves reactions between monosulphate and gypsum:

$C_4A\underline{S}H_{12} \quad + 2C\underline{S}H_2 \quad +16H_2O \quad \rightarrow C_6A\underline{S}_3H_{32}$

or

$4CaO.Al_2O_3.SO_3.12H_2O \quad + \quad 2CaO.2SO_3.2H_2O \quad +16H_2O\rightarrow$

$6CaO.Al_2O_3.3SO_3.32H_2O$

(224+54+48+80+216) + (112+160+72) + (288) → (336+54+48+240+576)

Atomic Mass(g)

$C_4A\underline{S}H_{12} = 622 + 2C\underline{S}H_2 = 344 + 16H_2O = 288 \quad \rightarrow C_6A\underline{S}_3H_{32} = 1254$

Density (g/cm^3)

$C_4A\underline{S}H_{12} = 1.95 \quad 2C\underline{S}H_2 = 2.32 \quad 16H_2O = 1 \quad \rightarrow C_6A\underline{S}_3H_{32} = 1.76$

Volume (cm^3) (V=M/D)

$C_4A\underline{S}H_{12} = 318.97 + 2C\underline{S}H_2 = 148.27 + 16H_2O = 288 \quad \rightarrow C_6A\underline{S}_3H_{32} = 712.5$

755.24 cm^3 → **712.5** cm^3

Therefore a total volume reduction of <u>5.66%</u> is expected.

However, if H_2O consumed in this reaction is drawn from outside:

$C_4A\underline{S}H_{12} = 318.97 + 2C\underline{S}H_2 = 148.27 \quad \rightarrow C_6A\underline{S}_3H_{32} = 712.5$

467.24 cm^3 → **712.5** cm^3

The resultant volume increase is <u>52.49%</u>

A.3 Sample material computation.

All samples were compacted at maximum dry density (MDD) and slightly wet of optimum moisture content (OMC) at 32% moisture addition (the reason for this is explained in chapter 6). Mellowing was carried out at OMC.

Example:

Mix LOC-8%$Ca(OH)_2$ = OMC 31% and MDD 1.34 Mg/m^3

Sample volume: $V = 2.254x10^{-4}$ m^3 (sample size h = 100mm and d =50 mm, plus 15% added for wastage*).

Determination of bulk density: $\varphi_b = \varphi_d \times (1+w) = 1.34 + (1 \times 0.31) = 1.7554 Mg/m^3$

Mass = density x volume = 1.7554 x $2.254x10^{-4}$ = 0.3956 kg

Amount of LOC :	1.00K
8% $Ca(OH)_2$	0.08L (as a percentage of the clay)
Total	1.08K (whole dry weight of soil plus additives)

M = whole dry weight of soil + additives + (water content x dry weight of soil + additives) = 1.08 + (0.31 x 1.08) = 1.4148K

Therefore 1.4148K = 395.667g thus K = **279.615g** (LOC)

thus L = 22.369g (8%$Ca(OH)_2$)

Total dry mass= **301.984g**

Moisture added prior to mellowing = 301.984g x 31% (OMC) = 93.615g

Moisture added after mellowing, prior to compaction = 395.599g x 1% (i.e.32%-OMC) = **3.955g**

(If a sample was compacted without a mellowing period, then all water (32%) was added during the initial mixing).

* a value of 15% was chosen because material loss between initial mixing and mellowing, and between mellowing and final compaction was expected to be high.

A.4 DTG Data Computations.

Gypsum content of the LOC

Let, Ra = initial weight of sample.

Rz = ignited or final weight of sample.

N = mass of H_2O lost (measured from TG trace).

R = ratio of Ra:Rz.

RaC = Corrected initial weight.

$CaSO_4.2H_2O$ = 172/36 amu.

Ra	Rz	R	N	% Gypsum
10.75	8.71	1.234072	0.0313	1.391111
15.72	12.48	1.256915	0.05008	1.522081
Average		**1.246844**		**1.456596**

In a LOC-2%$Ca(OH)_2$ sample there is 307.866g of LOC and 6.141g $Ca(OH)_2$.
Therefore total weight = 314.007
As 2%$Ca(OH)_2$ is equal to 1.5%CaO, then 6.141= 4.174 due to moisture loss. Corrected total weight now 312.040g.

312.040 / 314.007 x 100 **99.37**

Therefore 99.37% of the total moisture loss of a sample of LOC-2%$Ca(OH)_2$ sample after heating up to 1000°C is from the LOC, not the added lime.

To find the % gypsum content of LOC-2%$Ca(OH)_2$
(Rz/100 x 99.37) x r = **RaC**

(n x 172/36) / RaC x 100 = **% Gypsum in sample**

Appendix B – Experimental Results

B.1 Atterberg (Consistency) Limits Results

Atterberg Limits

		Ca(OH)$_2$ Content				
		0%	*2%*	*4%*	*6%*	*8%*
LL (Liquid Limit)	*UN*	59	68.5	68	72	68
(%)	*M*		68	80	87	79.5
PL (Plastic Limit)	*UN*	32	38	40	50.5	48
(%)	*M*		36	42	55.5	50
PI (Plasticity Index)	*UN*	27	30.5	28	21.5	20
(%)	*M*		32	38	31.5	29.5
		CaO Content				
		0%	*1.5%*	*3%*	*4.5%*	*6%*
LL (Liquid Limit)	*UN*	59	72.5	73.5	74	63.5
(%)	*M*		77.5	82	81	66
PL (Plastic Limit)	*UN*	32	44	48	51	45
(%)	*M*		54	54	54	47.5
PI (Plasticity Index)	*UN*	27	28.5	25.5	23	18.5
(%)	*M*		23.5	28	27	18.5

B.2.1 Proctor Compaction Results

Proctor Compaction

			Lime Addition		
			0%	*1.5% CaO*	*2%Ca(OH)$_2$*
Unmellowed	OMC	(%)	24.5	28	27
	MDD	(Mg/m^3)	1.427	1.365	1.39
6hrs at 10°C	OMC	(%)		29.5	29
	MDD	(Mg/m^3)		1.36	1.35
6hrs at 20°C	OMC	(%)		28	27.5
	MDD	(Mg/m^3)		1.355	1.38
3days at 10°C	OMC	(%)		30	30
	MDD	(Mg/m^3)		1.357	1.35
3days at 20°C	OMC	(%)		29	28
	MDD	(Mg/m^3)		1.36	1.37

B.2.2 Proctor Compaction Results - LOC with various additions of lime

Proctor Compaction

			Lime Addition							
			1.5% CaO	*3% CaO*	*4.5% CaO*	*6% CaO*	*2% $Ca(OH)_2$*	*4% $Ca(OH)_2$*	*6% $Ca(OH)_2$*	*8% $Ca(OH)_2$*
Unmellowed	OMC	(%)	28	28.5	28.5	28	27	27.5	28	27.5
	MDD	(Mg/m^3)	1.365	1.35	1.35	1.355	1.39	1.37	1.36	1.36
6hrs at 20°C	OMC	(%)	28	30.5	31	30.5	27.5	29	30.5	30
	MDD	(Mg/m^3)	1.36	1.345	1.345	1.35	1.38	1.36	1.355	1.35
3days at 20°C	OMC	(%)	29	30.5	31	31	28	30	30	29
	MDD	(Mg/m^3)	1.355	1.335	1.340	1.345	1.37	1.35	1.355	1.36

B.3.1 Unconfined Compressive Strength (UCS) results of lime-modified LOC.

Unconfined Compressive Strength (UCS)							
1 Weeks Curing		Unmellowed			3days at 20°C		
		Temperature (° C)			*Temperature (° C)*		
Lime Addition		5	10	20	5	10	20
1.5% CaO	(kN/m^2)	201.683	228.118	205.11	241.824	225.67	287.84
2%Ca(OH)$_2$	(kN/m^2)	221.265	182.103	325.533	153.71	178.186	185.04
4 Weeks Curing		Unmellowed			3days at 20°C		
		Temperature (° C)			*Temperature (° C)*		
Lime Addition		5	10	20	5	10	20
1.5% CaO	(kN/m^2)	98.394	314.784	368.611	181.245	192.654	276.093
2%Ca(OH)$_2$	(kN/m^2)	330.918	349.52	343.645	255.042	244.762	323.575

B.3.2 Unconfined Compressive Strength (UCS) results of LOC with various additions of Ca(OH)$_2$.

Unconfined Compressive Strength (UCS)							
1 Weeks Curing		Unmellowed			3days at 20°C		
		Temperature (° C)			*Temperature (° C)*		
Lime Addition		*5*	*10*	*20*	*5*	*10*	*20*
2%Ca(OH)$_2$	(kN/m^2)	221.265	182.103	325.533	153.71	178.186	185.04
4%Ca(OH)$_2$	(kN/m^2)	317.211	365.185	374.486	379.381	442.529	448.404
6%Ca(OH)$_2$	(kN/m^2)	317	393.087	460.642	429.802	449.872	528.686
8%Ca(OH)$_2$	(kN/m^2)	514.49	547.777	582.535	502.251	578.617	702.956
4 Weeks Curing		Unmellowed			3days at 20°C		
		Temperature (° C)			*Temperature (° C)*		
Lime Addition		*5*	*10*	*20*	*5*	*10*	*20*
2%Ca(OH)$_2$	(kN/m^2)	330.918	349.52	343.645	255.042	244.762	323.575
4%Ca(OH)$_2$	(kN/m^2)	573.722	701.488	882.122	397.004	482.181	709.81
6%Ca(OH)$_2$	(kN/m^2)	497.846	575.191	853.24	475.327	640.297	890.934
8%Ca(OH)$_2$	(kN/m^2)	675.053	811.141	955.551	536.518	652.046	912.473

B.4.1 Expansion measurements of unmellowed and mellowed lime-modified LOC in various soaking environments at 20°C and 5°C.

	Static Environment		Aerated Environment		Aerated Environment with Mellowing at 20°C		Aerated Environment with Mellowing at 5°C	
Days	2%Ca(OH)₂	1.5% CaO	2%Ca(OH)₂	1.5% CaO	2%Ca(OH)₂	1.5% CaO	2%Ca(OH)₂	1.5% CaO
1	0	0	0	0	0	0	0	0
2	0.2	-0.06	0	-0.001	0	0		
3	0.3	0	0.06	0.07	0.01	0		
4	0.5	0.04	0.1	0.12	0.03	0.01	0.39	0.82
5	0.68		0.17	0.18	0.04	0.02	1.27	0.86
6	0.7				0.05	0.03	1.33	0.9
7	0.83	0.06			0.06	0.03	1.34	0.91
8	1.8	0.07	0.23	0.24	0.08	0.05	1.91	1.62
9	2.98	1.09	1.37	1.62	0.75	0.9	2.5	2.3
10	3.5	1.65	2.12	2.48	1.14	1.13	2.9	3.2
11	4	2.24	2.6	3.07	1.43	1.43	3.75	4.3
12	4.3		3.13	3.78	1.63	1.63	4.12	4.63
13	4.59				1.87	1.88	4.46	4.96
14	4.89	3.23			2.05	2.06	5.11	5.16
15		3.48	3.96	3.99	2.21	2.2	5.43	5.28
16	5.34	3.65	4.19	4.31	2.32	2.29		
17		3.87	4.53	4.5	2.42	2.39		
18		4	4.54	4.75	2.5	2.44	5.68	5.72
19	5.89		4.96	4.89	2.6	2.46	5.89	5.9
20					2.67	2.49	6.01	5.89
21	6.03				2.73	2.54	6.19	5.89
22	6.11	4.44			2.78	2.63	6.33	5.89
23	6.21	4.51	5.07	5.32	2.84	2.67		
24		4.6	5.14	5.39	2.89	2.7		
25		4.65	5.22	5.41	2.95	2.78		
26	6.44		5.28	5.51	2.99	2.82	6.78	5.89
27	6.53				3.03	2.86	6.95	6.27
28		4.81			3.06	2.85	7.05	6.46
29		4.86	5.34	5.66	3.09	2.89	7.16	6.64
30		4.9	5.39	5.69	3.11	2.89		
31			5.41	5.73	3.14	2.92		
32		4.98			3.17	2.97	7.41	6.97
33	6.85		5.49	5.8	3.19	2.99	7.47	7.06
34	6.9				3.21	3.01	7.56	7.15
35	6.93	5.1			3.23	3.02		
36		5.12	5.58	5.9	3.25	3.03	7.69	7.26
37	6.99		5.6	5.93	3.27	3.06		
38					3.28	3.08		
39		5.21			3.3	3.1	7.9	7.42
40	7.16		5.7	6.04	3.32	3.11	7.91	7.45
41					3.34	3.12		
42		5.3			3.36	3.14		
43		5.32	5.8	6.13	3.38	3.16		
44		5.32	5.82	6.17	3.4	3.18		
46				6.19			8.27	7.68
47	7.34		5.84				8.32	7.72

48				6.23	3.4	3.23		
49	7.36	5.39						
51			5.91	6.29				
54					3.46	3.24		
55		5.53	6	6.41				
56	7.5							
57					3.5	3.28		
58					3.51	3.29	8.75	8.01
60		5.63	6.09	6.43				
61	7.61				3.55	3.31		
64							8.82	8.02
65	7.97				3.56	3.35		
66		5.71	6.15	6.52				
68					3.58	3.35		
69	7.74				3.6	3.37		
70								
71	7.75							
72		5.78	6.2	6.67	3.62	3.39		
75	7.8							
79	7.8							
85	7.88							
88		6.05	6.53	6.85				
89					3.65	3.43		
90					3.66	3.44		
92					3.68	3.44		
93	8.08				3.7	3.44		
96					3.74	3.44		
97					3.74	3.44	9.67	8.02
99					3.76	3.44		
100	8.15				3.77	3.44		
104					3.81	3.44		
105	8.27	6.21						
107			6.79	7.02	3.83	3.44		
110					3.84	3.44		
113					3.89	3.44		

B.4.2 Thermogravimetric data illustrating the changes in $CaCO_3$ and gypsum content (as a percentage of the LOC) of mellowed lime-modified LOC samples soaked in an aerated environment.

%$CaCO_3$		
Days Soaking in Aerated Environment	*LOC-2%$Ca(OH)_2$*	*LOC-1.5%CaO*
0	15.07047	15.07047
3	13.98574	9.754
10	12.38883	10.35415
24	12.43854	10.07125
112	17.39211	16.87236
%Gypsum		
Days Soaking in Aerated Environment	*LOC+2%$Ca(OH)_2$*	*LOC+1.5%CaO*
0	1.456596	1.456596
3	4.302148	4.085149
10	2.87	3.9
24	2.529837	3.405879
112	2.44865	2.09957

B.4.3 Expansion measurements of unmellowed LOC with various additions of $Ca(OH)_2$ in a static soaking environment at 20°C

Static Environment without mellowing at 20C				
Days	*2%Ca(OH)₂*	*4% Ca(OH)₂*	*6% Ca(OH)₂*	*8% Ca(OH)₂*
1	0	0	0	0
2	0.2	0.06	0.1	0.21
3	0.3	0.15	0.2	0.29
4	0.5	0.25	0.3	0.39
5	0.68	0.34	0.39	0.45
6	0.7	0.39	0.46	0.5
7	0.83	0.69	0.55	0.66
8	1.8	1.69	1.55	2.66
9	2.98	2.69	2.68	3.94
10	3.5	3	3	4.3
11	4	4	4	4.6
12	4.3	4.47	4.48	4.75
13	4.59	4.96	4.96	5.24
14	4.89	5.5	5.54	5.82
16	5.34	6.4	7.47	6.76
19	5.89	6.82	7.94	8.29
21	6.03	8.23	8.37	8.73
22	6.11	8.38	8.67	9.05
23	6.21	8.47	8.98	9.36
26	6.44	8.71	9.72	10.19
27	6.53	8.81	10.04	10.49
33	6.85	9.11	11.41	11.85
34	6.9	9.22	11.82	12.00
35	6.93	9.22	11.82	12.23
37	6.99	9.3	12.19	12.59
40	7.16	9.31	12.79	13.09
41	7.20	9.41	12.87	13.17
47	7.34	9.57	13.74	14.53
49	7.36	9.61	13.85	14.9
56	7.5	9.67	14.3	15.17
61	7.61	9.73	14.48	15.26
65	7.97	9.74	14.54	15.28
69	7.74	9.78	14.59	15.3
71	7.75	9.8	14.59	15.3
75	7.8	9.82	14.61	15.32
79	7.8	9.83	14.63	15.32
85	7.88	9.87	14.67	15.34
93	8.08	9.89	14.71	15.36
100	8.15	9.92	14.74	15.36
105	8.27	10.1	14.74	15.39

B.4.4 Expansion measurements of unmellowed LOC with various additions of $Ca(OH)_2$ in an aerated soaking environment at 20°C.

Aerated Environment without mellowing at 20C				
Days	*2%$Ca(OH)_2$*	*4% $Ca(OH)_2$*	*6% $Ca(OH)_2$*	*8% $Ca(OH)_2$*
1	0	0	0	0
2	0.08	0.1	0.16	0.16
3	0.11	0.19	0.2	0.26
4	*0.14*	*0.23*	*0.3*	*0.3*
5	*0.17*	*0.26*	*0.4*	*0.4*
6	0.19	0.33	0.48	0.44
7	0.25	0.44	0.6	0.53
8	1.2	1.58	1.72	1.75
9	*1.8*	*2*	*2.5*	*2.8*
10	2.25	3.14	3.31	3.46
13	3.02	3.8	4.92	5.1
14	3.19	5.17	5.31	5.51
15	3.36	5.68	5.88	6
17	4.61	6.51	7.7	7.76
20	4.97	7.88	8.08	7.99
22	5.06	8.26	8.48	8.33
23	5.11	8.53	8.78	8.6
24	5.18	8.78	9.05	8.79
27	5.32	9.41	9.8	9.42
28	5.37	9.64	10.09	9.68
29	5.39	9.8	10.29	9.93
33	5.52	10.57	12.4	10.95
35	5.55	10.8	12.79	11.29
38	5.5	11	12.16	11.63
41	5.66	11.31	12.79	12.08
42	5.67	11.34	12.82	12.2
47	5.78	11.68	13.99	1373
49	5.79	11.71	14.06	13.82
56	5.89	11.97	14.89	14.4
62	5.95	12.1	15.38	14.72
66	5.99	12.16	15.55	14.8
70	6.04	12.19	15.72	14.89
72	6.08	12.23	15.81	14.91
76	6.07	12.28	15.99	14.96
80	6.13	12.32	16.12	15
86	6.13	12.4	16.28	16.05
94	6.13	12.4	16.36	16.06
101	6.13	12.4	16.41	16.06
105	6.13	12.57	16.41	16.06

B.4.5 Expansion measurements of mellowed LOC with various additions of $Ca(OH)_2$ in a soaking environment at 20°C

<u>Aerated Environment with mellowing at 20°C</u>				
Days	*2%$Ca(OH)_2$*	*4% $Ca(OH)_2$*	*6% $Ca(OH)_2$*	*8% $Ca(OH)_2$*
1	0	0	0	0
2	0.34	0.47	0.58	0.48
3	0.47	0.59	0.73	0.62
4	0.52	0.63	0.78	0.68
5	0.56	0.7	0.84	0.72
6	*0.56*	*0.8*	*0.9*	*0.9*
7	*0.65*	*0.9*	*1*	*1.5*
8	0.71	1.01	1.1	1.93
9	1.38	2.07	2.03	3.02
10	1.69	2.58	2.55	3.54
11	*2.5*	*3*	*3*	*4*
12	3.18	3.53	3.58	4.7
15	3.49	4.6	4.65	5.8
16	3.57	4.8	4.96	6.09
17	3.63	5.14	5.29	6.44
19	3.73	5.7	5.88	8.07
22	3.91	6.63	6.83	9.09
23	4	6.91	7.12	9.14
24	4.01	7.11	7.32	9.21
26	4.03	7.48	7.52	9.27
29	4.14	7.77	8.04	9.48
30	4.14	7.93	8.24	9.53
31	4.16	8.04	8.37	9.57
35	4.25	8.69	8.93	9.57
38	4.27	8.89	9.04	9.63
40	4.3	9.08	9.13	9.72
43	4.33	9.36	9.24	9.79
44	4.34	9.38	9.25	9.8
49	4.41	9.61	9.41	9.99
51	4.41	9.62	9.42	10.5
56	4.42	9.7	9.48	11.9
61	4.44	9.72	9.52	11.95
66	4.45	9.75	9.54	
72	4.47	9.77	9.55	
74	4.47	9.77	9.55	
78	4.47	9.79	9.56	
82	4.48	9.79	9.57	
89	4.5	9.83	9.6	
96	4.54	9.88	9.7	
103	4.57	9.9	9.71	
110	4.6	9.9	9.71	

B.4.6 Expansion measurements of mellowed LOC with various additions of $Ca(OH)_2$ in an aerated soaking environment at 5°C

Aerated Environment with mellowing at 5°C				
Days	*2%Ca(OH)2*	*4% Ca(OH)2*	*6% Ca(OH)2*	*8% Ca(OH)2*
1	0	0	0	0
4	-0.06	0	0.07	-0.12
5	-0.08	0.03	0.09	-0.12
6	-0.12	0.02	0.08	-0.13
7	*-0.08*	*0.03*	*0.06*	*-0.12*
8	-0.08	0.03	0.05	-0.11
11	3.49	3.47	3.75	3.34
12	4.07	4.25	4.56	4.14
13	4.22	5.09	4.97	4.99
16	4.87	6.2	6.67	6.28
18	6.5	8	8	7.5
20	8.49	12.97	10.53	10.15
21	8.7	13.49	14.53	10.16
22	8.9	14.72	13.79	9.4
23	9.06			9.58

B.4.7 pH of soaking waters containing LOC with various percentage additions of $Ca(OH)_2$ in a static environment at 20°C.

Days	2%$Ca(OH)_2$	4% $Ca(OH)_2$	6% $Ca(OH)_2$	8% $Ca(OH)_2$
0				
7	7	7	7	7
14	7	7	7.5	7.5
21	10.5	11.5	12	12.5
28	9	10	11	11
35	10	11	12.5	13
42	10	11	12	12.5
49	10	11	12	12.5
56	10	11	12	12.5
63	10	11	12	12.5
70	10	11	12	12.5
77	10	11	12	12.5
84	10	10.5	11.5	12.5
91	9.5	-	11.5	12.5
98	9	-	11.5	12
105	9	-	11	12

B.4.8 pH of soaking water containing LOC with various percentage additions of $Ca(OH)_2$ in an aerated environment at 20°C

Days	2% $Ca(OH)_2$	4% $Ca(OH)_2$	6% $Ca(OH)_2$	8% $Ca(OH)_2$
0				
7	7	7	7	7
14	7	7	8	7.5
21	9	12	12.5	12
28	9	11	12	12
35	7	10	11	11.5
42	7	8	8	9
49	7	7.5	7.5	8
56	7	7	7	7
63	7	7	7	7
70	7	7	7	7
77	7	7	7	7
84	7	7	7	7
91	7	7	7	7
98	7	7	7	7
105	7	7	7	7

B.4.9 pH of soaking waters containing LOC with various percentage additions of $Ca(OH)_2$ after mellowing in an aerated environment at 20°C

Days	2% $Ca(OH)_2$	4% $Ca(OH)_2$	6% $Ca(OH)_2$	8% $Ca(OH)_2$
0				
7	7	7	7	7
14	7	7	7.5	8
21	7.5	7.5	10	10
28	7.5	8	10	11
35	7	9	11.5	12.5
42	7	9.5	11	12
49	7	8	8	8
56	7	7	7.5	7.5
63	7	7	7.5	7.5
70	7	7	7.5	7.5
77	7	7	7.5	-
84	7	7	7	-
91	7	7	7	-
98	7	7	7	-
105	7	7	7	-

B.4.10 pH of soaking waters containing LOC with various percentage additions of $Ca(OH)_2$ after mellowing in an aerated environment at 5°C.

Days	2% $Ca(OH)_2$	4% $Ca(OH)_2$	6% $Ca(OH)_2$	8% $Ca(OH)_2$
0				
7	7	7	7	7
14	8	7	7	11.5
21	7	8	11	12
28				

B.4.11 SO_3 Contents of lime-modified LOC after a range of soaking times and environments at 20°C and 5°C

Sulphate (SO_3) Contents			
Static Soaking Environment (20°C)			
Days	LOC	+ 2%Ca(OH)2	+1.5%CaO
0	0.9	0.9	0.9
7	0.88	1.53	2.32
21	0.88	2.86	1.46
112	0.88	2.22	1.06
Aerated Soaking Environment (20°C)			
Days	LOC	+ 2%Ca(OH)2	+1.5%CaO
0	0.9	0.9	0.9
7	0.88	1.53	2.32
21	0.88	2.52	4.25
112	0.88	1.24	1.75
Aerated Soaking Environment (20°C) after Mellowing (3 days)			
Days	LOC	+ 2%Ca(OH)2	+1.5%CaO
0	0.9	0.9	0.9
7	0.88	1.92	2.11
21	0.88	2.23	4.11
112	0.88	1.24	0.88
Aerated Soaking Environment (5°C) after Mellowing (3 days)			
Days	LOC	+ 2%Ca(OH)2	+1.5%CaO
0	0.9	0.9	0.9
7	0.88	1.92	2.11
21	0.88	3.26	4.13

B.4.12 SO_3 Contents of LOC with various additions of $Ca(OH)_2$ after a range of soaking times and environments at 20°C and 5°C

Sulphate (SO_3) Contents			
Static Soaking Environment (20°C)			
Days	4%$Ca(OH)_2$	6%Ca(OH)2	8%$Ca(OH)_2$
7	2.10	2.02	1.81
21	2.60	2.81	3.92
112	3.45	5.63	3.61
Aerated Soaking Environment (20°C)			
Days	4%$Ca(OH)_2$	6%Ca(OH)2	8%$Ca(OH)_2$
7	2.10	2.02	1.81
21	2.58	2.72	3.92
112	1.27	3.34	2.60
Aerated Soaking Environment (20°C) after Mellowing (3 days)			
Days	4%$Ca(OH)_2$	6%Ca(OH)2	8%$Ca(OH)_2$
7	1.32	1.28	1.29
21	1.62	2.88	3.09
112	1.44	1.46	1.32
Aerated Soaking Environment (5°C) after Mellowing (3 days)			
Days	4%$Ca(OH)_2$	6%Ca(OH)2	8%$Ca(OH)_2$
7	1.32	1.28	1.29
21	3.37	4.90	4.81
23	3.94	4.39	4.82

B.5 Durability Indices (DI) of mellowed and unmellowed LOC with various additions of $Ca(OH)_2$ at 20°C and 5°C

Durability Index (DI) %		*$Ca(OH)_2$ Content*			
		2%	***4%***	***6%***	***8%***
Unmellowed	**at 20°C**	24.35	12.59	15.83	14.24
Mellowed at	**20°C**	23.45	18.8	22.5	20.10
Unmellowed	**at 20°C**	0	3.75	8.40	9.35
Mellowed at	**20°C**	0	5.42	8.80	11.70

B.6.1 UCS results of lime-modified LOC after curing for 1, 4 12, 24 and 52 weeks at 5°C, 10°C and 20°C.

Unconfined Compressive Strength (UCS) (kN/m^2)						
	1.5%CaO			2%Ca(OH)$_2$		
Curing Time	5°C	10°C	20°C	5°C	10°C	20°C
1 Week	241	225	273	204	195	260
4 Weeks	181	192	276	189	191	222
12 Weeks	122	350	347	85	279	279
24 Weeks	334	363	311	105	226	188
52 Weeks	100	244	310	62	308	260

B.6.2 UCS results of 1.5%CaO-modified LOC with various additions of PC after curing for 1, 4 12, 24 and 52 weeks at 5°C, 10°C and 20°C.

Unconfined Compressive Strength (UCS) (kN/m^2)												
1.5%CaO	+2%PC			4%PC			6%PC			8%PC		
Curing Time	5°C	10°C	20°C	5°C	10°C	20°C	5°C	10°C	20°C	5°C	10°C	20°C
1 Week	165	419	374	523	560	602	613	520	695	613	520	695
4 Weeks	358	361	548	524	487	715	569	643	1016	677	809	1092
12 Weeks	561	818	788	458	593	1025	560	940	1382	675	891	1561
24 Weeks	274	763	953	536	735	899	517	1024	1765	769	129	1775
52 Weeks	556	383	915	630	896	1099	1205	1612	1552	1310	1338	1772

B.6.3 UCS results of 1.5%CaO-modified LOC with various additions of GGBS after curing for 1, 4 12, 24 and 52 weeks at 5°C, 10°C and 20°C.

Unconfined Compressive Strength (UCS) (kN/m^2)

1.5%CaO	+2%GGBS			4%GGBS			6%GGBS			8%GGBS		
Curing Time	*5°C*	*10°C*	*20°C*	*5°C*	*10°C*	*20°C*	*5°C*	*10°C*	*20°C*	*5°C*	*10°C*	*20°C*
1 Week	121	292	403	476	427	572	385	418	491	385	418	491
4 Weeks	367	449	491	487	527	524	527	625	703	335	589	747
12 Weeks	167	452	541	416	611	700	393	716	1034	698	937	1026
24 Weeks	267	580	514	353	392	595	384	450	997	515	595	1019
52 Weeks	291	351	627	528	539	615	7961	732	1137	428	792	987

B.6.4 UCS results of 2%$Ca(OH)_2$-modified LOC with additions of 4% and 8% PC or GGBS after curing for 1, 4 12, 24 and 52 weeks at 5°C, 10°C and 20°C.

Unconfined Compressive Strength (UCS) (kN/m^2)

2%$Ca(OH)_2$	4%GGBS			8%GGBS			4%PC			8%PC		
Curing Time	*5°C*	*10°C*	*20°C*	*5°C*	*10°C*	*20°C*	*5°C*	*10°C*	*20°C*	*5°C*	*10°C*	*20°C*
1 Week	117	375	437	141	419	593	185	427	550	488	457	479
4 Weeks	425	487	537	615	676	719	297	440	478	534	611	752
12 Weeks	588	627	759	746	824	888	691	811	856	780	816	1204
24 Weeks	310	745	813	633	754	892	429	594	888	566	1191	1498
52 Weeks	467	865	905	596	1367	1315	666	1035	1505	931	1716	2315

B.7.1 Linear Expansion measurements of LOC additions of 2%$Ca(OH)_2$ and 1.5%CaO with various additions of GGBS or PC after mellowing and soaking in an aerated environment at 20°C.

Days	*2% Ca(OH)₂*	*1.5% CaO*	*1.5% CaO-4%PC*	*1.5% CaO-4% GGBS*	*1.5% CaO-8%PC*	*1.5% CaO-8% GGBS*
0	0	0	0	0	0	0
1	0	0	-0.06	0	-0.06	0.05
2	0.01	0	-0.06	0.01	-0.06	0.05
3	0.03	0.01	-0.05	0.02	-0.06	0.05
4	0.04	0.02	-0.05	0.03	-0.06	0.05
5	0.05	0.03	-0.03	0.02	-0.05	0.04
6	0.06	0.03	-0.03	0.02	-0.05	0.03
7	0.08	0.05	-0.05	0.03	-0.03	0.03
8	0.75	0.9	0.35	0.13	0.32	0.06
9	1.14	1.13	0.65	0.32	0.59	0.07
10	1.43	1.43	0.85	0.35	0.75	0.07
11	1.63	1.63	1.1	0.4	0.9	0.08
12	1.87	1.88	1.31	0.43	1.12	0.09
13	2.05	2.06	1.45	0.45	1.21	0.11
14	2.21	2.2	1.57	0.47	1.29	0.13
15	2.32	2.29	1.66	0.48	1.32	0.14
16	2.42	2.39	1.71	0.55	1.37	0.15
17	2.5	2.44	1.75	0.54	1.39	0.15
18	2.6	2.46	1.83	0.53	1.41	0.16
19	2.67	2.49	1.87	0.54	1.43	0.17
20	2.73	2.54	1.9	0.55	1.44	0.17
21	2.78	2.63	1.94	0.57	1.46	0.18
22	2.84	2.67	1.96	0.58	1.47	0.19
23	2.89	2.7	1.99	0.59	1.49	0.2
24	2.95	2.78	2.02	0.61	1.5	0.2
25	2.99	2.82	2.05	0.62	1.51	0.21
26	3.03	2.86	2.07	0.63	1.53	0.21
27	3.06	2.85	2.08	0.64	1.53	0.22
28	3.09	2.89	2.08	0.66	1.53	0.21
29	3.11	2.89	2.09	0.66	1.53	0.21
30	3.14	2.92	2.1	0.67	1.54	0.21
31	3.17	2.97	2.11	0.68	1.55	0.21
32	3.19	2.99	2.13	0.69	1.55	0.21
33	3.21	3.01	2.14	0.7	1.55	0.21
34	3.23	3.02	2.14	0.7	1.55	0.21
35	3.25	3.03	2.15	0.71	1.55	0.21
36	3.27	3.06	2.16	0.71	1.55	0.21
37	3.28	3.08	2.16	0.71	1.55	0.21
38	3.3	3.1	2.18	0.72	1.55	0.21
39	3.32	3.11	2.2	0.74	1.56	0.21
40	3.34	3.12	2.2	0.75	1.57	0.22
41	3.36	3.14	2.2	0.76	1.57	0.22
42	3.38	3.16	2.21	0.77	1.58	0.22
43	3.4	3.18	2.22	0.78	1.59	0.22
47	3.4	3.23	2.24	0.82	1.59	0.22

53	3.46	3.24	2.26	0.97	1.6	0.22
56	3.5	3.28	2.27	1	1.59	0.22
57	3.51	3.29	2.27	1.01	1.59	0.23
60	3.55	3.31	2.29	1.05	1.6	0.23
64	3.56	3.35	2.21	1.11	1.61	0.23
67	3.58	3.35	2.2	1.2	1.61	0.23
68	3.6	3.37	2.2	1.22	1.61	0.23
71	3.62	3.39	2.21	1.25	1.61	0.23
88	3.65	3.43	2.21	1.42	1.61	0.23
89	3.66	3.44	2.21	1.46	1.61	0.23
91	3.68	3.44	2.22	1.54	1.61	0.23
92	3.7	3.44	2.22	1.57	1.61	0.23
95	3.74	3.44	2.22	1.65	1.61	0.23
96	3.74	3.44	2.22	1.67	1.61	0.23
98	3.76	3.44	2.22	1.73	1.61	0.23
99	3.77	3.44	2.22	1.75	1.61	0.23
103	3.81	3.44	2.22	1.86	1.61	0.23
106	3.83	3.44	2.22	1.95	1.61	0.23
109	3.84	3.44	2.22	2.03	1.61	0.23
112	3.89	3.44	2.22	2.14	1.63	0.23
113	3.91	3.44	2.23	2.16	1.63	0.23
116	3.95	3.44	2.25	2.26	1.64	0.23
119	3.98	3.44	2.25	2.35	1.64	0.23
123	3.98	3.44	2.25	2.44	1.64	0.23
127	4	3.44	2.25	2.53	1.64	0.23
139	4.04	3.44	2.25	2.64	1.64	0.23
140	4.05	3.44	2.25	2.64	1.64	0.23
144	4.09	3.44	2.25	2.64	1.64	0.23
153	4.14	3.44	2.25	2.64	1.64	0.23
164	4.2	3.44	2.25	2.64	1.64	0.23

B.7.2 Linear Expansion measurements of LOC additions of 2%$Ca(OH)_2$ and 1.5%CaO with various additions of GGBS or PC after mellowing and soaking in an aerated environment at 5°C.

Days	*2% $Ca(OH)_2$*	*1.5% CaO*	*1.5% CaO-4%PC*	*1.5% CaO-4% GGBS*	*1.5% CaO-8%PC*	*1.5% CaO-8% GGBS*
1	0	0	0	0	0	0
4	0.39	0.82	0.52	1.17	0.22	0.87
5	1.27	0.86	1.02	1.69	0.44	0.69
6	1.33	0.9	1.08	1.75	0.49	0.81
7	1.34	0.91	1.1	1.77	0.52	0.83
8	1.91	1.62	1.41	2.71	0.66	1.96
11	3.75	4.3	3.06	3.55	1.58	2.18
12	4.12	4.63	3.38	3.6	1.78	2.2
13	4.46	4.96	3.68	3.61	1.95	2.22
14	5.11	5.16	3.99	3.61	2.14	2.24
15	5.43	5.28	4.29	3.61	2.28	2.23
18	5.68	5.72	4.92	3.62	2.57	2.37
19	5.89	5.9	5.09	3.62	2.65	2.29
20	6.01	5.89	5.19	3.62	2.69	2.27
21	6.19	5.89	5.43	3.62	2.74	2.29
22	6.33	5.89	5.39	3.62	2.77	2.29
26	6.78	5.89	5.61	3.62	2.83	2.27
27	6.95	6.27	5.67	3.65	2.97	2.29
28	7.05	6.46	5.68	3.66	2.87	2.27
29	7.16	6.64	5.72	3.67	2.9	2.29
32	7.41	6.97	5.76	3.67	2.93	2.3
33	7.47	7.06	5.77	3.67	2.92	2.29
34	7.56	7.15	5.77	3.67	2.92	2.3
36	7.69	7.26	5.78	3.67	2.94	2.31
39	7.9	7.42	5.8	3.67	2.95	2.31
40	7.91	7.45	5.82	3.67	2.95	2.31
46	8.27	7.68	5.84	3.67	2.97	2.33
47	8.32	7.72	5.85	3.67	2.97	2.32
58	8.75	8.01	6.94	3.73	3.03	2.28
64	8.82	8.02	6.95	3.73	3.03	2.29
97	9.67	8.02	8.03	3.73	3.09	2.31
110	9.83	8.67	7.89	3.73	3.12	2.35
137	9.83	9.25	7.94	4.73	3.17	2.39

B.7.3 Linear Expansion measurements of 1.5% CaO-8% GGBS soaked in static environment without mellowing, at 20°C

Day	1.5%CaO-8%GGBS
1	0
2	-0.04
3	0
4	0.04
7	0
8	-0.01
9	0.11
10	0.14

11	0.16
14	0.19
15	0.19
16	0.19
17	0.2
18	0.21
22	0.22
23	0.22
24	0.22
25	0.23
28	0.25
29	0.25
30	0.25
32	0.25
35	0.26
36	0.26
39	0.27
42	0.28
43	0.27
44	0.27
49	0.28
55	0.29
60	0.29
66	0.29
72	0.29
88	0.31
107	0.32
134	0.34

B.7.4 Linear Expansion measurements of 1.5% CaO-8% GGBS soaked in an aerated environment without mellowing, at 20°C

Days	1.5%CaO-8%GGBS
1	0
2	-0.002
3	0.19
4	0.21
5	0.2
8	0.17
9	0.23
10	0.16
11	0.27
12	0.29
15	0.3
16	0.31
17	0.32
18	0.32
19	0.32
23	0.33
24	0.34
25	0.34

26	0.34
29	0.36
30	0.36
31	0.36
33	0.37
36	0.37
37	0.37
40	0.38
43	0.39
44	0.4
47	0.4
49	0.4
51	0.39
55	0.39
60	0.39
66	0.4
72	0.42
88	0.46
107	0.44
134	0.36

B.8.1 Durability Indices (%) of 1.5%CaO-modified LOC with various additions of PC or GGBS, with and without mellowing, at 5°C and 20°C.

Durability Indices (%)					
	1.5%CaO	*1.5%-2%PC*	*1.5%-2%GGBS*	*1.5%-4%PC*	*1.5%-4%GGBS*
Unmellowed at 20°C	18.85	39.95	37.89	34.08	52.27
Mellowed at 20°C	24.46	46.03	56.7	62.56	57.1
Unmellowed at 5°C	12	18.07	10.1	29.44	58.85
Mellowed at 5°C	16.47	14.16	18.92	8.97	30.92
	1.5%-6%PC	*1.5%-6%GGBS*	*1.5%-8%PC*	*1.5%-8%GGBS*	
Unmellowed at 20°C	44.5	59.1	42.09	73.35	
Mellowed at 20°C	61	91.5	66.81	87.68	
Unmellowed at 5°C	45.477	61	49.87	68.43	
Mellowed at 5°C	11.34	93.23	12.27	100	

B.8.2 Durability Indices (%) of 2%Ca(OH)$_2$-modified LOC with various additions of PC or GGBS, with and without mellowing, at 5°C and 20°C.

Durability Indices (%)					
	2%Ca(OH)$_2$	*2%-4%PC*	*2%-4%GGBS*	*2%-8%PC*	*2%-8%GGBS*
Unmellowed at 20°C	24.35	50.86	75	45.2	91.69
Mellowed at 20°C	18.68	76.21	74.22	78.46	80.27
Unmellowed at 5°C	0	21	27	29	42
Mellowed at 5°C	0	35.75	14.94	43.38	61.78

Appendix C

XRD Traces

Trace	Sample
3	Lower Oxford Clay (LOC).
4	LOC-8%Ca(OH)$_2$ - dry mix.
5	LOC-8%Ca(OH)$_2$ - unmellowed mix.
6	LOC-8%Ca(OH)$_2$ - mellowed (3 days at 20°C) mix.
7	LOC-8%Ca(OH)$_2$ - unmellowed mix, cured for 1 week.
8	LOC-8%Ca(OH)$_2$ - unmellowed mix, cured for 4 weeks.
9	LOC-8%Ca(OH)$_2$ - mellowed mix, cured for 1 week.
10	LOC-8%Ca(OH)$_2$ - mellowed mix, cured for 4 weeks.
11	LOC-6%CaO - dry mix.
12	LOC-6%CaO - unmellowed mix.
13	LOC-6%CaO - mellowed (3 days at 20°C) mix.
14	LOC-6%CaO - unmellowed mix, cured for 1 week.
15	LOC-6%CaO - unmellowed mix, cured for 4 weeks.
16	LOC-6%CaO - mellowed mix, cured for 1 week.
17	LOC-6%CaO - mellowed mix, cured for 4 weeks.

XRD TRACE: 3 - Lower Oxford Clay

2θ	D space	Peak	I	G	K	H-H	C	Q	PG.	SID.	PY.	CH.	E
8.45	10.4459	1	S										
11.3	7.81129	2		100									
12	7.35563	3			10+								
14.4	6.12969	4				10							
17.4	5.07285	5	M										
19.45	4.53818	6											
20.5	4.30574	7		51				35					
21.55	4.09594	8							7				
22.75	3.87989	9			4		12		50				
24.6	3.58811	10			10+					25			
25	3.5307	11				9							
26.2	3.36899	12	VS		4			100					
27.6	3.1981	13							10				
28.2	3.13006	14			3				60		36		
29.1	3.03325	15	MS	57	3	10	100						
30.4	2.90354	16											
30.9	2.85656	17				10	3						
31.6	2.79328	18	M							100			
32.75	2.69519	19									84		
34.6	2.55109	20	S/VS		6								

Key:

I = Illite
G = Gypsum
K = Kaolinite
H-H = Hemi-hydrate
C = Calcite

Q = Quartz
PG = Plagioclase
SID = Siderite
PY = Pyrites
CH = Calcium Hydroxide
E = Ettringite

Intensity

VS = Very Strong
S = Strong
MS = Moderately Strong
M = Moderate

XRD TRACE: 4 - LOC-8%$Ca(OH)_2$ - dry mix.

2θ	D space	Peak	I	G	K	H-H	C	Q	PG.	SID.	PY.	CH.	E
8.5	10.3844	1	S										
11.3	7.81129	2		100									
12.1	7.29484	3			10+								
14.4	6.12969	4				10							
17.8	4.95885	5	M									VS	
19.5	4.52654	6											
20.6	4.28483	7		51				35					
22.75	3.87989	8							7				
24.6	3.58811	9			4		12		50				
24.9	3.54488	10			10+					25			
26.3	3.35618	11				9							
27.6	3.1981	12	VS		4			100					
28.5	3.09711	13							10			23	
29.2	3.02286	14			3				60		36		
29.6	2.98201	15	MS	57	3	10	100						
30.9	2.85656	16											
31.8	2.77571	17				10	3						
32.8	2.69108	18	M							100			
33.9	2.60376	19									84	VVS	
34.8	2.53642	20	S/VS		6		•						

Key:

I = Illite
G = Gypsum
K = Kaolinite
H-H = Hemi-hydrate
C = Calcite

Q = Quartz
PG = Plagioclase
SID = Siderite
PY = Pyrites
CH = Calcium Hydroxide
E = Ettringite

Intensity

VS = Very Strong
S = Strong
MS = Moderately Strong
M = Moderate

XRD TRACE 5 - LOC-8%Ca(OH)$_2$ - unmellowed mix.													
2θ	D space	Peak	I	G	K	H-H	C	Q	PG.	SID.	PY.	CH.	E
8.5	10.3844	1	S										
11.9	7.41744	2			10+								
17.8	4.95885	3	M									VS	
19.5	4.52654	4											
20.6	4.28483	5		51				35					
22.8	3.87138	6			4		12		50				31
24.6	3.58811	7			10+					25			
26.3	3.35618	8											
26.9	3.28132	9	VS		4			100					
27.6	3.1981	10							10				
28.4	3.10801	11										23	
29.1	3.03325	12	MS	57	3	10	100						
30.7	2.87516	13				10	3						
31.6	2.79327	14	M							100			22
32.8	2.69108	15									84		
33.9	2.60376	16										VVS	
34.8	2.53642	17	S/VS		6								29

Key:

I = Illite
G = Gypsum
K = Kaolinite
H-H = Hemi-hydrate
C = Calcite

Q = Quartz
PG = Plagioclase
SID = Siderite
PY = Pyrites
CH = Calcium Hydroxide
E = Ettringite

Intensity

VS = Very Strong
S = Strong
MS = Moderately Strong
M = Moderate

XRD TRACE: 6 - LOC-8%Ca$(OH)_2$ - mellowed (3 days at 20°C) mix.

2θ	D space	Peak	I	G	K	H-H	C	Q	PG.	SID.	PY.	CH.	E
8.6	10.26	1	S										100
11.4	7.743	2		100									
12.1	7.295	3			10+								
15.7	5.622	4				10							76
17.9	4.931	5	M									VS	
19.6	4.503	6											
20.75	4.254	7		51				35					
22.8	3.871	8							7				31
24.7	3.574	9			4		12		50				
25.1	3.517	10			10+					25			
26.6	3.318	11				9							
27.1	3.257	12	VS		4			100					
27.7	3.187	13							10				
28.5	3.097	14			3				60		36	23	
29.2	3.023	15	MS	57	3	10	100						
30.9	2.857	16											31
31.9	2.767	17				10	3						
32.8	2.691	18	M							100			
33.8	2.611	19									84	VVS	
34.8	2.536	20	S/VS		6								29

Key:
I = Illite
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K = Kaolinite
H-H = Hemi-hydrate
C = Calcite
Q = Quartz
PG = Plagioclase
SID = Siderite
PY = Pyrites
CH = Calcium Hydroxide
E = Ettringite

Intensity
VS = Very Strong
S = Strong
MS = Moderately Strong
M = Moderate

XRD TRACE: 7 - LOC-8%$Ca(OH)_2$ - unmellowed mix, cured for 1 week

2θ	D space	Peak	I	G	K	H-H	C	Q	PG.	SID.	PY.	CH.	E
8.6	10.26	1	S										100
11.3	7.811	2		100									
12.1	7.295	3			10+								
15.6	5.658	4											76
17.8	4.959	5	M									VS	
19.5	4.527	6						35					
20.6	4.285	7		51									
22.7	3.888	8							7				31
24.6	3.588	9			4		12		50				
25.1	3.517	10			10+					25			
26.3	3.356	11				9							
27.1	3.257	12	VS		4			100					
27.7	3.187	13							10				
28.3	3.119	14			3				60		36	23	
29.2	3.023	15	MS	57	3	10	100						
30.9	2.857	16											22
31.8	2.776	17				10	3						
32.8	2.691	18	M							100	84		
33.8	2.611	19										VVS	
34.8	2.536	20	S/VS		6								29

Key:

I = Illite
G = Gypsum
K = Kaolinite
H-H = Hemi-hydrate
C = Calcite

Q = Quartz
PG = Plagioclase
SID = Siderite
PY = Pyrites
CH = Calcium Hydroxide
E = Ettringite

Intensity

VS = Very Strong
S = Strong
MS = Moderately Strong
M = Moderate

XRD TRACE: 8 - LOC-8%$Ca(OH)_2$ - unmellowed mix, cured for 4 weeks

2θ	D space	Peak	I	G	K	H-H	C	Q	PG.	SID.	PY.	CH.	E
8.6	10.2637	1	S										
8.8	10.0304												100
11.3	7.81129	2		100									
12.1	7.29484	3			10+								
15.6	5.65818	4											76
17.8	4.95885	5	M									VS	
19.5	4.52654	6											
20.6	4.28483	7		51				35					
22.7	3.88844	8			4		12		50				31
24.6	3.58811	9			10+					25			
25.1	3.51664	1											
26.3	3.35618	11	VS		4			100					
27.3	3.23324	12											
27.7	3.18656	13							10				
28.4	3.10801	14			3				60		36	23	
29.2	3.02286	15	MS	57	3	10	100						
30.9	2.85656	16				10	3						22
31.8	2.77571	17	M							100			
32.9	2.68291	18									84		
33.9	2.60376	19										VVS	
34.7	2.54373	20	S/VS		6								29

Key:

I = Illite
G = Gypsum
K = Kaolinite
H-H = Hemi-hydrate
C = Calcite

Q = Quartz
PG = Plagioclase
SID = Siderite
PY = Pyrites
CH = Calcium Hydroxide
E = Ettringite

Intensity

VS = Very Strong
S = Strong
MS = Moderately Strong
M = Moderate

XRD TRACE: 9 - LOC-8%$Ca(OH)_2$ - mellowed mix, cured for 1 week.

2θ	D space	Peak	I	G	K	H-H	C	Q	PG.	SID.	PY.	CH.	E
8.5	10.3844	1	S										100
11.3	7.81129	2		100									
12	7.35563	3			10+								
16.6	5.31732	4											
17.5	5.04386	5	M										
17.75	4.97282	6										VS	
19.5	4.52654	7											
20.6	4.28483	8	51					35					
22.7	3.88844	9			4		12		50				31
24.5	3.60276	1			10+								
25.1	3.51664	11				9							
26.4	3.34347	12	VS		4			100					
26.8	3.29357	13											
27.1	3.25711	14											
27.4	3.22144	15							10				
28.4	3.10801	16			3				60		36	23	
29.2	3.02286	17	MS	57	3	10	100						
29.6	2.98201	18											
30.9	2.85656	19				10	3						22
31.8	2.77571	20	M							100			
32.8	2.69108	21									84		
33.8	2.61147	22										VVS	
34.6	2.55109	23	S/VS		6								29

Key:

I = Illite
G = Gypsum
K = Kaolinite
H-H = Hemi-hydrate
C = Calcite

Q = Quartz
PG = Plagioclase
SID = Siderite
PY = Pyrites
CH = Calcium Hydroxide
E = Ettringite

Intensity

VS = Very Strong
S = Strong
MS = Moderately Strong
M = Moderate

XRD TRACE: 10 - LOC-8%Ca(OH)$_2$ - mellowed mix, cured for 4 weeks													
2θ	D space	Peak	I	G	K	H-H	C	Q	PG.	SID.	PY.	CH.	E
8.6	10.2637	1	S										100
11.3	7.81129	2		100									
12.1	7.29484	3			10+								
15.7	5.62214	4											76
17.5	5.04386	5A	M										
17.8	4.95885	5										VS	
19.5	4.52654	6											
20.6	4.28483	7		51				35					
22.7	3.88844	8			4		12		50				31
24.7	3.57359	9			10+					25			
25.1	3.51664	10				9							
26	3.39491	11											
26.4	3.34347	12	VS		4			100					
26.9	3.28132	13											
27.3	3.23324	14											
27.7	3.18656	15							10				
28.4	3.10801	16			3				60		36	23	
29.2	3.02286	17	MS	57	3	10	100						
29.7	2.97197	18											
30.9	2.85656	19				10	3						22
31.8	2.77571	20	M							100			
32.8	2.69108	21									84		
34	2.59611	22										VVS	
34.7	2.54373	23	S/VS		6								29

Key:

I = Illite
G = Gypsum
K = Kaolinite
H-H = Hemi-hydrate
C = Calcite

Q = Quartz
PG = Plagioclase
SID = Siderite
PY = Pyrites
CH = Calcium Hydroxide
E = Ettringite

Intensity

VS = Very Strong
S = Strong
MS = Moderately Strong
M = Moderate

XRD TRACE: 11 - LOC-6%CaO - dry mix

2θ	D space	Peak	I	G	K	H-H	C	Q	PG.	SID.	PY.	CH.	E
8.5	10.3844	1	S										
11.3	7.81129	2		100									
12.1	7.29484	3			10+								
14.4	6.12969	4				10							
17.6	5.0152	5	M									VS	
19.6	4.50345	6											
20.6	4.28483	7		51				35					
22.8	3.87139	8			4		12		50				
24.6	3.58811	9			10+					25			
24.9	3.54488	10				9							
26.4	3.34347	11	VS		4			100					
27.1	3.25711	12							10				
27.7	3.18656	13											
28.3	3.119	14			3				60		36	23	
29.1	3.03325	15	MS	57	3	10	100						
30.7	2.87517	16				10	3						
31.7	2.78447	17	M							100			
32.8	2.69108	18									84		
33.7	2.61922	19										VVS	
34.7	2.54373	20	S/VS		6								

Key:

I = Illite
G = Gypsum
K = Kaolinite
H-H = Hemi-hydrate
C = Calcite

Q = Quartz
PG = Plagioclase
SID = Siderite
PY = Pyrites
CH = Calcium Hydroxide
E = Ettringite

Intensity

VS = Very Strong
S = Strong
MS = Moderately Strong
M = Moderate

XRD TRACE: 12 - LOC-6%CaO - unmellowed mix

2θ	D space	Peak	I	G	K	H-H	C	Q	PG.	SID.	PY.	CH.	E
5.8	15.2185	1											
8	11.0334	2											
8.5	10.3844	3	S										100
12	7.35563	4			10+								
14.4	6.12969	5				10							
17.5	5.04386	6	M									VS	
19.6	4.50345	7											
20.6	4.28483	8		51				35					
22.8	3.87139	9			4		12		50				31
24.7	3.57359	10			10+					25			
24.9	3.54488	11				9							
26.4	3.34347	12	VS		4			100					
26.9	3.28132	13											
27.2	3.24513	14											
27.7	3.18656	15							10				
28.3	3.119	16			3				60		36	23	
29.2	3.02286	17	MS	57	3	10	100						
30.6	2.88456	18				10	3						22
31.7	2.78447	19	M							100			
32.8	2.69108	20									84		
33.8	2.61147	21										VVS	
34.7	2.54373	22	S/VS		6								29

Key:

I = Illite
G = Gypsum
K = Kaolinite
H-H = Hemi-hydrate

C = Calcite
CH = Calcium Hydroxide
E = Ettringite

Q = Quartz
PG = Plagioclase
SID = Siderite
PY = Pyrites

Intensity

VS = Very Strong
S = Strong
MS = Moderately Strong
M = Moderate

XRD TRACE: 13 - LOC-6%CaO - mellowed (3 days at 20°C) mix

2θ	D space	Peak	I	G	K	H-H	C	Q	PG.	SID.	PY.	CH.	E
8.6	10.2637	1	S										100
11.4	7.74277	2		100									
12	7.35563	3			10+								
15.4	5.73166	4											76
17.7	4.98687	5	M									VS	
19.6	4.50345	6											
20.7	4.26413	7		51				35					
22.8	3.87139	8			4		12		50				31
24.6	3.58811	9			10+					25			
24.9	3.54488	10				9							
26.4	3.34347	11	VS		4			100					
28.3	3.119	12			3				60		36	23	
29.2	3.02286	13	MS	57	3	10	100						
30.9	2.85656	14				10	3						22
31.8	2.77571	15	M							100			
32.8	2.69108	16									84		
33.8	2.61147	17										VVS	
34.7	2.54373	18	S/VS		6								29

Key:

I = Illite
G = Gypsum
K = Kaolinite
H-H = Hemi-hydrate
C = Calcite

Q = Quartz
PG = Plagioclase
SID = Siderite
PY = Pyrites
CH = Calcium Hydroxide
E = Ettringite

Intensity

VS = Very Strong
S = Strong
MS = Moderately Strong
M = Moderate

XRD TRACE: 14 - LOC-6%CaO - unmellowed mix, cured for 1 week													
2θ	D space	Peak	I	G	K	H-H	C	Q	PG.	SID.	PY.	CH.	E
5.8	15.2185	1											
7.7	11.4633	2											
8.6	10.2637	3	S										100
11.3	7.81129	4		100									
12.1	7.29484	5			10+								
15.5	5.69468	6											76
17.7	4.98687	7	M									VS	
19.5	4.52654	8											
20.6	4.28483	9		51				35					
22.8	3.87139	10			4		12		50				31
24.6	3.58811	11			10+								
25.1	3.51664	12											
26.3	3.35618	13	VS		4			100					
28.3	3.119	14			3				60		36	23	
29.2	3.02286	15	MS	57	3	10	100						
29.6	2.98201	16											
30.9	2.85656	17				10	3						22
31.8	2.77571	18	M							100			
32.8	2.69108	19									84		
33.8	2.61147	20										VVS	
34.7	2.54373	21	S/VS		6								29

Key:

I = Illite
G = Gypsum
K = Kaolinite
H-H = Hemi-hydrate
C = Calcite

Q = Quartz
PG = Plagioclase
SID = Siderite
PY = Pyrites
CH = Calcium Hydroxide
E = Ettringite

Intensity

VS = Very Strong
S = Strong
MS = Moderately Strong
M = Moderate

XRD TRACE: 15 - LOC-6%CaO - unmellowed mix, cured for 4 weeks

2θ	D space	Peak	I	G	K	H-H	C	Q	PG.	SID.	PY.	CH.	E
8.6	10.2637	1	S										100
10.2	8.65368	2		100									
12	7.35563	3			10+								
15.5	5.69468	4	M										76
17.75	4.97282	5										VS	
19.6	4.50345	6											
20.6	4.28483	7		51				35					
22.8	3.87139	8			4		12		50				31
24.6	3.58811	9			10+					25			
24.9	3.54488	10				9							
26.3	3.35618	11	VS		4			100					
27.7	3.18656	12							10				
28.4	3.10801	13							60		36	23	
29.2	3.02286	14	MS	57	3	10	100						
29.5	2.99212	15											
30.75	2.87049	16				10	3						22
31.9	2.76701	17	M							100			
32.8	2.69108	18									84		
33.8	2.61147	19										VVS	
34.75	2.54007	20	S/VS		6								29

Key:

I = Illite
G = Gypsum
K = Kaolinite
H-H = Hemi-hydrate
C = Calcite

Q = Quartz
PG = Plagioclase
SID = Siderite
PY = Pyrites
CH = Calcium Hydroxide
E = Ettringite

Intensity

VS = Very Strong
S = Strong
MS = Moderately Strong
M = Moderate

XRD TRACE: 16 - LOC-6%CaO - mellowed mix, cured for 1 week.

2θ	D space	Peak	I	G	K	H-H	C	Q	PG.	SID.	PY.	CH.	E
8.5	10.38	1	S										100
11.3	7.811	2		100									
12	7.356	3			10+								
15.4	5.732	4											76
17.75	4.973	5	M									VS	
19.6	4.503	6		51				35					
21.6	4.086	7							7				
22.8	3.871	8			4		12		50				31
24.6	3.588	9			10+					25			
24.9	3.545	10				9							
26.4	3.343	11	VS		4			100					
26.9	3.281	12											
27.5	3.21	13							10				
28.3	3.119	14			3				60		36	31	
29.2	3.023	15	MS	57	3	10	100						
29.6	2.982	16											
30.8	2.866	17				10	3						22
31.8	2.776	18	M							100			
32.8	2.691	19									84		
33.8	2.611	20										VVS	
34.8	2.536	21	S/VS		6								29

Key:

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SID = Siderite
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CH = Calcium Hydroxide
E = Ettringite

Intensity

VS = Very Strong
S = Strong
MS = Moderately Strong
M = Moderate

XRD TRACE: 17 - LOC-6%CaO - mellowed mix, cured for 4 weeks

2θ	D space	Peak	I	G	K	H-H	C	Q	PG.	SID.	PY.	CH.	E
6	14.7113	1											
8.6	10.2637	2	S										100
11.4	7.74277	3		100									
12.1	7.29484	4			10+								
15.8	5.58656	5											76
17.4	5.07285	6	M									VS	
19.6	4.50345	7											
21.6	4.08646	8											
22.8	3.87139	9			4		12		50				
23.2	3.80464	10											31
24.6	3.58811	11			10+					25			
25.1	3.51664	12											
26.3	3.35618	13	VS		4			100					
26.9	3.28132	14											
27.6	3.1981	15							10				
28.3	3.119	16			3				60		36	31	
29.3	3.01255	17	MS	57	3	10	100						
30.9	2.85656	18				10	3						22
31.9	2.76701	19	M							100			
32.8	2.69108	20									84		
34.8	2.53642	21	S/VS		6								29

Key:

I = Illite
G = Gypsum
K = Kaolinite
H-H = Hemi-hydrate
C = Calcite

Q = Quartz
PG = Plagioclase
SID = Siderite
PY = Pyrites
CH = Calcium Hydroxide
E = Ettringite

Intensity

VS = Very Strong
S = Strong
MS = Moderately Strong
M = Moderate