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THE PERFORMANCE OF CEMENT STABILISED MINESTONE

MICHAEL DAVID ARTHUR THOMAS

Doctor of Philosophy

THE UNIVERSITY OF ASTON IN BIRMINGHAM

November 1986

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SUMMARY

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This study is concerned with the durability of cement stabilised minestone (CSM). Minestone is dominated by the clay-bearing mudrocks and shales of the Coal Measures. Consequently, engineering problems are often encountered due to the likelihood of these rocks undergoing volume change and degradation when exposed to fluctuations in moisture content. In addition, iron sulphides (chiefly pyrite) are frequently present in minestone as diagenetic minerals which on excavation have the potential to oxidise forming sulphate minerals. The oxidation of sulphides may in itself contribute to volume increase in pyritic rocks and sulphate minerals may combine with the products of cement hydration to produce further expansion.

The physical and chemical properties of a wide range of minestones are determined and attempts are made to correlate these with the engineering performance of cement stabilised specimens subjected to short-term immersion in water. Criteria, based on these raw material indices are proposed with a view to eliminating minestones which are unsuitable. A long-term durability study is also described. In this, the geochemical stability of pyrite in CSM was examined together with the role played by the sulphur bearing mineralogy in determining the engineering performance of CSM exposed to conditions of increased moisture availability.

The nature of a number of disrupted CSM pavements which have been examined are also discussed.

Key Words Cement Stabilisation, Minestone, Sulphate Attack, Pyrite

To Terry . . .

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1. INTRODUCTION

Colliery spoil is the inevitable by-product of the coal mining industry and has accumulated in vast spoil heaps throughout the coal mining regions of Great Britain. As coal mining technology has advanced so has the non-coal content of the excavated material from subsurface mining, the current proportion being some 35% (Glover, 1984). An estimated 50 Mtonnes of spoil is deposited at the surface each year to augment the existing stockpiles of about 3000 Mtonnes (Building Research Establishment, 1973).

In the past many spoil tips have been subjected to burning either started deliberately or as a result of spontaneous combustion due to the exothermic oxidation of pyrite (Guney, 1968). The residue is a brick-like material known as "burnt" or "red" shale, which has been used extensively in highway engineering as a fill material, granular sub-base and cement stabilised road-base. However, changes in spoil deposition have resulted in well-compacted tips which do not allow sufficient air circulation to promote burning and the increased efficiency of coal separation plants has reduced the proportion of combustible matter in the discard (Fraser, 1974). These changes have culminated in the depletion of "burnt" shale supplies and so the most widely available material the National Coal Board (NCB) has to offer is "unburnt" shale.

The utilisation of colliery spoil is in the economic interests of the NCB and in 1971 the "Minestone Executive" was created to research and develop new outlets for "Minestone" (Turnbull, 1984), "Minestone" being the commercial name for unburnt colliery spoil. The engineering properties of minestone are considerably different to those of the burnt shale and its potential for spontaneous combustion has

limited its use. Indeed, it was not until 1968 that the Ministry of Transport (1968) permitted the use of unburnt colliery shale as fill, following the recommendation that the material would be suitable if sufficient compaction was achieved (Lake,1968). Experience has since shown that well-compacted minestone embankments are not susceptible to spontaneous combustion (Ministry of Transport, 1968; Tanfield, 1971; Gibson, 1975; Hanquez, 1978; Fraser, 1974). Although the major outlet for minestone continues to be bulk fill applications, the Minestone Executive have promoted its use in a wide range of applications. These include cement stabilisation, reinforced earth structures, recultivation and reclamation, recovery of energy, production and manufacture of aggregates and as a cover for general landfill (National Coal Board, 1984).

The utilisation of minestone in cement stabilised pavement layers has been well researched and existing structures incorporating stabilised minestone prove its potential in this demanding role. The durability of cement stabilised minestone (CSM) has been the subject of recent studies (Kettle, 1983; McNulty, 1985) and suitable durability criteria for this material have been suggested. However, the inherent variability of minestone necessitates the rigorous testing of raw and stabilised materials to ensure sufficient strength and durability of the final product. The need for simple parameters to control the quality of CSM has existed since early studies (Kettle and Williams, 1969).

This study is partly concerned with establishing the raw material properties of minestone that affect both the strength and durability of the final stabilised product. Sixteen samples of minestone were sampled from colliery tips, and their physical, chemical and mineralogical characteristics were critically examined. CSM specimens were then produced for short-term strength and durability determinations. The latter was assessed by a simple immersion test. The results

were treated to statistical analysis and various correlations are presented.

The long-term durability of CSM pavements has been the cause of concern for some time (Morton *et al*, 1984). Many pavements have suffered considerable disruption following periods of 12 to 18 months satisfactory performance. Three such pavements were examined and sampled for laboratory investigation. The results of these studies are presented together with the hypotheses drawn from them. It is suggested that the geochemical alterations of pyritic minerals and the ongoing attack of existing sulphate minerals are responsible for the behaviour of these structures. A laboratory controlled investigation using the CSMs produced from the sixteen minestones employed in the short-term durability study was set up to substantiate the above hypotheses. The sulphur bearing mineralogy and engineering performance of these CSMs were monitored throughout long-term accelerated exposure (up to 410 days) to various environmental conditions. Attempts have been made to correlate the performance of these CSMs with the sulphur phases and sulphur limits are suggested.

2. CEMENT STABILISATION

2.1 Introduction

Soil stabilisation may be defined as, the treatment of soil in such a manner as to render its properties less affected by water or to increase its strength and durability. This is achieved by the alteration of soil properties to satisfy the engineering requirements. The techniques of stabilisation can be divided into three broad categories:-

1. Mechanical stabilisation involves adjustment to the particle size distribution of the soil prior to its use. Thus two or more soils are usually blended together to achieve a desired grading.
2. Physical stabilisation includes the addition of inert materials (such as membranes), densification (vibroflotation, dynamic compaction etc.), modifications to the fabric of clays (thermal or electrical treatments) and reduction in soil moisture content.
3. Chemical stabilisation involves the addition of a reactive agent such as lime, cement, sodium silicate or resins. The subsequent chemical reaction (between additive and soil) results in modification of the soil properties.

Of all the available techniques, cement stabilisation (a form of chemical stabilisation) has been utilised most frequently in the construction of pavements in

the U. K.

2.2 Cement Stabilised Soils in Highway Construction

The first documented use of cement stabilised soil in road construction dates back to trials on Salisbury Plain in 1917 (Brook-Bradley, 1952) but it was engineers in the United States who exploited the use of the material (Catton, 1959; Norling, 1960). The then Road Research Laboratory began laboratory and field trials using soil cement in 1939 (Maclean and Lewis, 1963). Since 1945 cement stabilised materials have been used for road construction in Great Britain (Sherwood, 1968) and their use in the construction of lightly trafficked roads and in the sub-base of major roads has steadily increased (Road Research Laboratory, 1966). One major setback for these materials was the poor performance of soil cement in the pavement experiments conducted at Alconbury Hill in 1957 (Croney and Loe, 1965). However, economic and environmental awareness (Kennedy, 1979; Sherwood and Roe, 1974) have increased the viability of soil cement as a realistic alternative to traditional road-making materials.

Current Department of Transport specifications (Department of Transport, 1977) divide cement stabilised materials into three subgroups, these are Lean Concrete, Cement-bound Granular Material and Soil Cement.

The materials that may be considered for use in these categories have to meet certain grading requirements. In the case of soil cement, the soil to be used is also restricted by plasticity limits. The stabilised materials must also satisfy strength limits and frost resistance criteria (Croney and Jacobs, 1970). The Department of Transport specification is currently under review, and it seems likely that additional durability criteria will be included in the near future (Rainbow and

Sleeman, 1984).

Soils are unlikely to present an "inert" aggregate for cement stabilisation. It is therefore necessary to consider the properties of a material that determine its suitability for use in soil cement.

2.3 The Nature of Soils

Soils are particulate materials composed of a variety of rock fragments and individual mineral fragments. As far as cement stabilisation is concerned the mineralogy may be split into three categories (Sherwood, 1961):

1. The "inert" constituents which tend to dominate the gravel, sand and silt size fractions. These inert minerals are dominated by quartz,
2. The "beneficial" constituents tend to be present in the fine fraction and include the carbonate minerals, the clays and some oxides,
3. The "deleterious" constituents notably the sulphates (and some sulphides) and organic matter.

The inert materials and some carbonate rock fragments contribute to the character of the soil cement mixture as a granular skeleton. Thus only their grading is of importance and they are not considered further. The oxides (e.g. iron and aluminium), which are of importance in the cement stabilisation of tropical soils, are of negligible interest here.

2.3.1 Clay Minerals

Clay minerals play an important part in both cement and lime stabilisation of soils. They basically consist of hydrated aluminium silicates in a crystalline form but of rather complicated structure. Despite the complexity of their molecular structure the minerals are formed essentially from two basic building blocks. These are silica tetrahedra and aluminium hydroxide octahedra (gibbsite). In the second building block the aluminium may often be partially replaced by iron or magnesium. The arrangement of these blocks into structural elements and the method of bond between adjacent structural elements determines the mineralogy of the structure.

In a two-layered mineral a gibbsite layer and a silica layer are held together by hydrogen bonds to form the single sheet of clay mineral, kaolin. Successive sheets may be stacked to form particles of kaolinite held by hydrogen bonds. Different arrangements of the structural elements give different clay minerals with the same general formula and engineering properties of pure kaolin.

In a three-layered mineral the gibbsite layer is 'sandwiched' between two silica layers to form the primary element. In the mineral montmorillonite the bonds between the elementary sheets are covalent bonds between oxygen atoms which are weak compared to the hydrogen bonds in kaolinite. Consequently water molecules can be absorbed and occupy the space between the sheets resulting in expansion of the mineral lattice.

The mineral illite has the same structural element as montmorillonite. However, some of the spaces between the sheets are occupied by potassium ions. These ions bond the sheets together more firmly than in montmorillonite and hence the lattice

is much less expansive. Illite exhibits more swelling than kaolinite but less than montmorillonite.

As with the two-layered mineral, variations in the stacking arrangement of the three-layered primary element results in polymorphic variations. Isomorphs of the clay minerals may be formed by the partial replacement of aluminium by another cation in the gibbsite layer. This frequently occurs in montmorillonite clays, but is rare in kaolins. In montmorillonite one sixth of the aluminium positions are occupied by magnesium cations. Since aluminium is trivalent and magnesium divalent there is a resulting positive charge deficiency. The balance is maintained by the adsorption of external cations onto the clay surfaces from the pore solution. The adsorbed ion may typically be sodium (Na), calcium (Ca), potassium (K), lithium (Li), or iron (Fe) but other cations may be involved. The ions, once adsorbed, may be replaced at a later stage by other cations from the pore fluid. For example sodium ions may be replaced by calcium ions.

The presence of these adsorbed cations does not change the basic structure of the clay mineral. However, they may change the engineering properties since they may interfere with the development of the water layers at the surface and affect the manner in which various basic sheets are connected.

The ability of a clay to adsorb ions is termed the cation exchange capacity and is a function of the mineral structure and particle size. It is defined in terms of the number of milliequivalents (meq) adsorbed per 100 g of clay, where 1 meq is 1 mg of hydrogen or the portion of any ion which will combine or displace 1 mg of hydrogen. The cation exchange capacity (cec) increases in the order kaolinite - illite - montmorillonite and lower capacities are exhibited by well crystalline minerals.

The simplest method of classifying the clay size fraction of a soil is by its Atterberg limits. These limits determine the range of moisture contents through which the soil behaves plastically. This gives a physical measure of the activity of the clay mineral. Generally the activity of the clay mineral increases in the same order as the cation exchange capacities.

2.3.2 Sulphate Minerals

Chemical attack on concrete by sulphate ions in groundwater or soil is a common problem (Building Research Establishment, 1975). With the cement stabilisation of sulphate bearing soils the problem of chemical attack on the cement minerals is intensified due to the intimate mixture of the cement and the soil.

Gypsum (selenite), $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, is the most commonly occurring sulphate in British soils. Magnesium sulphate, MgSO_4 , and sodium sulphate, NaSO_4 , variously hydrated, are frequently present. Much of the gypsum results from the breakdown of iron sulphides in the soil yielding sulphates which combine with any readily available calcium ions. Thus iron sulphides should perhaps be considered as potentially deleterious to soil cement mixes. Iron sulphides exist in many mudrocks as a variety of metastable sulphides as well as pyrite. They are all susceptible to oxidation which may be promoted by bacterial activity (Temple and Delchamps, 1953).

2.3.3 Organic Matter

Not all organic matter is deleterious and only empirical testing can evaluate the effect of any organic matter content in a soil. In general, partially decayed recent

organic matter (plant rootlets, peat, etc) is to be avoided. The effect of organic matter on cement hydration is discussed later.

2.4 Reactions Involved in Cement Stabilisation

Cement stabilisation is the combination of two types of reaction. The primary reactions are the normal hydration of the cement. The secondary reactions are those between the cement and the clay minerals.

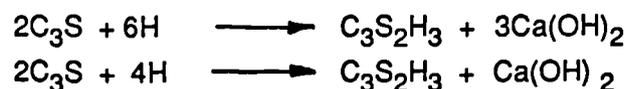
2.4.1 Portland Cement and Cement Hydration

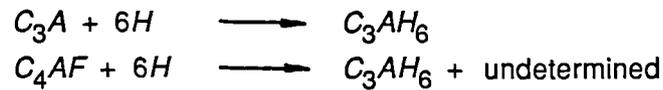
The chief raw materials of Portland cement are lime, limestone or chalk together with clay. The manufacturing process results in the formation of the anhydrides of calcium silicate and aluminate and the major components of Portland cement are:-

		Cement Chemistry Nomenclature
Tricalcium Silicate	$3\text{CaO} \cdot \text{SiO}_2$	C_3S
Dicalcium Silicate	$2\text{CaO} \cdot \text{SiO}_2$	C_2S
Tricalcium Aluminate	$3\text{CaO} \cdot \text{Al}_2\text{O}_3$	C_3A
Tetracalcium Aluminoferrite	$4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$	C_4AF

Other compounds in cements include oxides of magnesium, titanium, manganese, potassium and sodium together with between 1 to 3 % calcium sulphate (added specifically).

In the presence of water, the silicates and aluminates hydrate leading to the formation of a hardened cement paste. These reactions are:-





(*H* is the oxide of hydrogen (water) in cement chemistry nomenclature).

The hydrates of the calcium silicates and aluminates are normally described as amorphous, although electron microscopy is capable of exhibiting their crystalline character (Neville, 1981). The products of hydration (particularly the calcium silicate hydrates, $C_3S_2H_3$) are largely responsible for the characteristic early and long-term strength gains of soil cement (Highway Research Board, 1961).

In a mixture of cement paste and an inert aggregate (i.e. concrete) the principal bond is due to interlock although the bond is affected by the mineralogy, chemistry, electrostatic condition and capillary forces (Neville, 1981). A detailed account of the hydration of cement, describing the contribution of the hydration products to material performance and the associated chemistry can be found in Neville (1981) and Lea (1956).

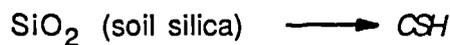
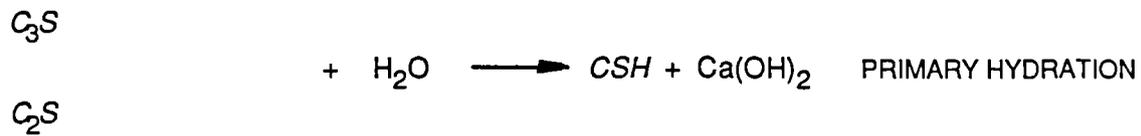
2.4.2 Cement-Mineral Reactions

The mechanical bond of cement/particle interlock becomes less important as the particle size decreases and more surface area becomes available for chemical interaction. Of all the products of hydration only the lime liberated as calcium hydroxide is known to have beneficial secondary reactions with the clay minerals and are thus considered as lime-clay reactions.

Lime-clay reactions can be simplified by splitting them into two basic reactions, short-term and long-term reactions. The phenomenon first realised is a reduction in the plasticity of the soil caused by cation exchange of the sodium or potassium

ions on the clay surfaces for calcium ions from the lime. This results in a flocculation of the clay particles (Hilt and Davidson, 1960; Noble, 1967) which then behave like silts and give the impression of a reduced clay-size fraction. These short-term reactions occur in the first few hours (Diamond and Kinter, 1966) and are often termed "lime modification" and can be caused by addition of relatively small amounts of cement (Highway Research Board, 1961).

The long-term, or pozzolanic reactions are a result of chemical reactions between lime and clay. Studies have shown these reactions as:



these secondary silicates and aluminates have been identified by X-Ray diffraction.

The increase in pH resulting from the $Ca(OH)_2$ also increases the solubility of silica and alumina (Andrews, 1966) and hence the formation of calcium silicate hydrates and calcium aluminate hydrates. The calcium silicate hydrate is thought to give long-term strength and to be similar to that formed from cement hydration (Eades and Grim, 1960) whilst the calcium aluminate hydrate gives early strength (Diamond and Kinter, 1966). This second phase of reactions is known as "lime

stabilisation".

The lime may also react with the other soil components and many other reactions also occur. Alternatively, the lime may carbonate due to the action of atmospheric carbon dioxide;



the calcium carbonate having weak cementitious properties (Stocker, 1963).

It must be realised that both modification and stabilisation are not merely determined by the clay-size fraction. The degree and rate of these reactions are largely dependent on the clay mineralogy and surface reactivity (Eades and Grim, 1960; Moh, 1965; Hilt and Davidson, 1961; Handy, 1958).

Briefly, montmorillonitic and mixed-layered clay derive more benefit from lime modification than do kaolinitic and illitic soils (Hilt and Davidson, 1960) but the secondary cementitious products formed by lime-montmorillonite are inferior to those present in lime modified kaolinitic and illitic soils (Noble, 1967).

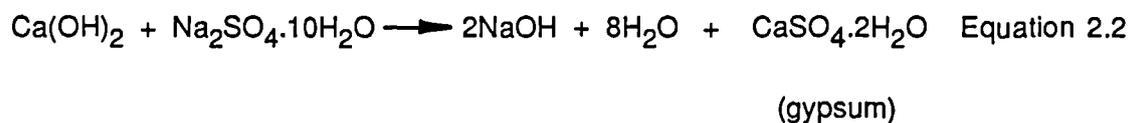
Due to the capacity of expansive clays to react with lime there is a corresponding depletion of the Ca(OH)_2 resulting in a reduction in the pH of the environment. Consequently the formation of the primary cement hydration products is retarded resulting in further inferior cementing compounds (Croft, 1967).

2.4.3 Cement-Sulphate Reactions

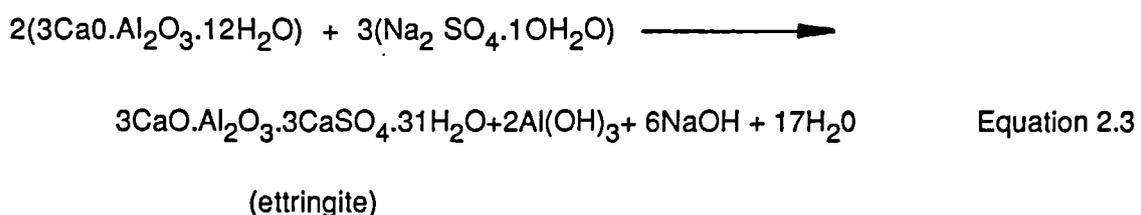
The degradation of concrete in sulphate bearing soils and groundwaters is a well established engineering phenomenon and simple precautions can be taken in construction to combat the problem (Building Research Establishment, 1975; Shirley, 1978). With soil stabilisation the problem is further complicated by the presence of sulphates in the material to be stabilised.

The most common sulphates in the U.K are those of calcium, sodium and magnesium. In solution these sulphates react with the hydration products, calcium aluminate hydrate and calcium hydroxide, to form calcium sulphotoaluminate (ettringite) and calcium sulphate (gypsum) respectively. The solubility of calcium sulphate is relatively low, 1.2 g/l, compared with magnesium and sodium sulphates which are respectively some 150 and 200 times more soluble. The action of the more soluble sulphates will be more rapid and possibly more serious (Sherwood and Ryley, 1970).

The action of sodium sulphate on calcium hydroxide can be written as:-



and on tri-calcium aluminate:-

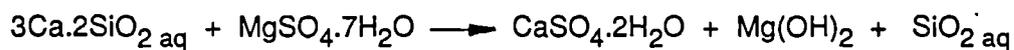


The reaction between various other sulphates and the cement hydration products are

similar to reactions, Equation 2.2 and 2.3. Calcium sulphate only attacks the calcium aluminate hydrate.

With these reactions there is an associated volume increase due to the lower mineral densities of the reaction products. In fact, gypsum occupies more than twice the volume of calcium hydroxide. In confined pore space crystallisation pressures are produced and these are capable of disrupting the cement paste leading to a significant loss of strength and often complete failure (Neville, 1981; Highway Research Board, 1961)

Magnesium sulphate may have a far more dramatic affect on cement pastes, as it also attacks the calcium silicate hydrates as well. The reaction is:-



The lower solubility of magnesium hydroxide results in a low pH (as OH⁻ ions do not readily enter solution) which allows the reaction to proceed, under certain conditions, to completion (Lea, 1956). There is evidence to suggest that a reaction between the magnesium hydroxide and the silica gel to form a hydrated magnesium silicate may cause further deterioration since it is non-cementitious as opposed to the silica gel (Neville, 1981).

Although the magnesium sulphate reacts directly with calcium aluminate in much the same manner as sodium sulphate, the pH value of the magnesium hydroxide solution is too low to stabilise the calcium sulphoaluminate (ettringite) produced. Further action of the magnesium sulphate on the ettringite may result in the production of calcium sulphate (gypsum).

Some of the methods used to reduce the vulnerability of concrete to sulphate attack may also alleviate the problem in soil cement. Sulphate-resisting cements have low tri-calcium aluminate values decreasing the likelihood of ettringite formation as in Equation 2.3. The inclusion of pozzolanic material removes much of the free calcium hydroxide restricting the formation of gypsum (Equation 2.2) and thus reducing the potential for disruption of the cement paste.

A previous study (Sherwood, 1958) on cement stabilised clays indicated that the resistance to attack by CaSO_4 was found to be related to the clay content of the material and the use of sulphate-resistant cement did not reduce the sulphate attack. Further examination, (Sherwood, 1962a), showed that lime stabilised soils were affected in a similar manner to cement stabilised soils, with both X-Ray diffraction and thermal analyses suggesting a transformation of gypsum to ettringite, explained by a reaction between the gypsum and clay resulting in the formation of ettringite. Following the results of these studies it was suggested that the formation of ettringite is responsible for the disintegration of both lime and cement stabilised soils. However, in the lime stabilised soils the formation of ettringite was primarily due to a reaction between the clay minerals and sulphate ions in the presence of lime and excess water. Attack on calcium aluminates in cement stabilised soils would make a secondary contribution to ettringite production. This above hypothesis would render the use of cements, low in calcium aluminates, ineffective. However, pozzolanic material may decrease these effects by reducing the free lime necessary for the sulphate-clay reaction.

In order to reduce the possibility of sulphate attack, current specifications (Department of Transport, 1977) include permissible acid soluble sulphate contents of 1% (SO_3) for granular and 0.25% (SO_3) for cohesive materials to be

used for cement stabilisation.

2.4.4 Cement-Organic Matter Reactions

Some organic matter has the ability to combine with the calcium cations liberated during cement hydration. This removal of the free cations results in a reduced alkalinity of the soil cement, which in turn may inhibit the normal hardening of the cement gel products (Sherwood, 1962b). The actual organic components do not interfere with cement hydration. A British Standard test for assessing the adverse effects of the organic matter does exist (British Standards Institution, 1975a) and consists of measuring the pH of a soil cement mixture 1 hour after mixing. A pH value below 12.1 indicates the presence of deleterious organic matter. The current specification (Department of Transport, 1977) does not make any direct reference to organic content but it is generally considered that provided the 7 day crushing strength of a cement stabilised material is in excess of 1.7 MPa the effects of organic matter may be ignored (Sherwood, 1962b). The current specification requires a strength of 3.5 MPa at 7 days.

2.5 Mechanisms of Cement Stabilisation

2.5.1 Granular Materials

A granular soil is defined as having a very small clay/silt fraction, being predominantly sand and gravel particles. These particles become partially coated with cement during stabilisation. The cementing action is similar to that in concrete. Bonding is principally at the points of contact and consequently an increase in contact area leads to increased strength. Well-graded, highly compacted materials will therefore benefit most from the cementing action. Typically these

materials would come under "Clause 807 Lean Concrete" or possibly "Clause 806 Cement Bound Granular Material" in the current specification (Department of Transport, 1977). These materials have upper and lower grading limits, placed on the material to be stabilised.

2.5.2 Cohesive Soils

In clayey soils the clay particles, which individually are smaller than the cement particles, form aggregations and an intimate mix of cement and clay can not be achieved. Consequently the aggregations become coated with cement, in the same manner as the individual particles in granular materials, and a skeleton of cement is formed. The strength of the materials is often thought to be due solely to the strength and extent of this framework (Highway Research Board, 1961; Lilley, 1979; Davidson, 1961). The clay is assumed to have no strength and the skeleton serves to hold the aggregations in place and also to prevent them swelling. The latter is achieved not only by the strength of the skeletal framework but also by the water proofing effect of the encasement (Highway Research Board, 1961; Davidson, 1961). An alternative description of the mechanism uses a skeletal framework structure in which the clay lumps are enmeshed but the individual lumps are also stabilised by the migration of lime from the hydrating cement into the clay (Stocker, 1963). A third mechanism describes the cement grains as being suspended in the clay and these hydrate to form "protruding arms" of secondary cementitious products forming a skeleton structure (Herzog, 1963). As in the second mechanism these products are derived from the lime-clay reaction described in Section 2.4.2.

The strength development of cement-cohesive soil mixes depends to a large extent on the clay mineralogy. If the lime-clay reaction is slow, as in the case of kaolin and to

a lesser extent illite, then sufficient lime is available to promote hardening of the primary cementitious compounds. Hence higher strengths are obtained than with cement stabilised expansive clays. In the latter case lime depletion, due to faster lime-clay reactions, leads to a retardation of the hardening of the cement paste and consequently inferior cementitious compounds. For these clays, lime stabilisation or dual stabilisation (involving treatment of soil with lime prior to cement addition) may be more suitable (McNulty, 1985).

With the stabilisation of cohesive materials it is important to break down the clay aggregations as much as possible, as a higher degree of pulverisation leads to higher strengths (Grimer and Ross, 1957) "Clause 805 Soil Cement" in the current specification (Department of Transport, 1977) covers the use of these materials, and the specification includes both grading requirements (minimum coefficient of uniformity) and plasticity limits.

2.6 Factors Affecting the Performance of Cement Stabilised Soils.

The main criteria for assessing the performance of soil cement mixes are generally compressive strength and durability. In the past durability has been measured in a variety of ways including resistance to the effects of; immersion, cyclic freezing and thawing, cyclic wetting and drying and prolonged freezing. Detailed critiques of durability criteria have been presented elsewhere (Packard and Chapman, 1963; McNulty, 1985).

The performance of a cement stabilised material is dependent on the characteristics of the mix, such as; soil type, density, cement content, etc. Careful control of the mix is vital to ensure a strong and durable material.

2.6.1 Type of Soil

The role played by clay minerals, organic matter and sulphates in cement stabilisation has already been discussed. Whereas the presence of organic matter and sulphates result in a reduction in strength and durability, a small quantity of clay may be beneficial by producing cementitious compounds by reaction with the calcium hydroxide (Sherwood, 1968). Together with the chemical benefits of the pozzolanic activity, small amounts of clay may have physical benefits. The dry density of a sand mix may be increased by adding a proportion of clay, resulting in increased strength (Davidson *et al*, 1962). The increased density may be due to a pore filling role (Williams, 1972). High contents of clay, however, may reduce the dry density with an adverse effect on strength. Optimum clay contents of the order of 25% have been suggested for sand-clay mixes (Reinhold, 1955). Generally, beyond the optimum clay content, increases in cement content are required to attain sufficient strength.

A heavy clay presents mixing problems if an intimate cement-clay matrix is required as a higher degree of pulverisation will be necessary (MacLean *et al*, 1952). Clays of high sensitivity are more susceptible to moisture effects and may create a lime depleted environment.

The influence of grading on the properties of a stabilised material are such that the strength decreases as the grading becomes finer (McLaren *et al*, 1960). This is probably due to a combination of reduced dry density and increased surface area (Highway Research Board, 1961).

Particle strength will obviously have an effect on the cemented materials if it is below the strength of the cement fines mortar.

2.6.2 Dry Density

The relationship between dry density and the strength of soil cement mixtures is well established (Grimer, 1958; Larnach, 1960; Sherwood, 1968) and the following form of relationship has been presented (Grimer and Broad, 1958):

$$S = KD^n$$

S = unconfined compressive strength

D = dry density

K = a constant

n = a dimensionless constant

The value of n is independent of cement content and it has been suggested that n is an inverse function of moisture content (Sherwood, 1968).

The quality of stabilised materials improves dramatically as higher dry densities are achieved (Felt, 1955; West, 1959). The importance of achieving proper compaction is reflected in the specifications controlling the use of stabilised materials (Department of Transport, 1977), current practice being that moisture content is selected to achieve the maximum dry density.

2.6.3 Moulding Moisture Content.

The moulding moisture content has two main roles: a) to aid compaction; and b) to provide water for the hydration of cement. It is possible for these two aims to conflict, the optimum moisture water content for maximum dry density not satisfying the requirements for complete hydration of the cement (Davidson *et al*, 1962). In clay cement mixes the absorption of moisture by the clay fraction may

result in an internal depletion of moisture and thereby prevent the complete hydration of the cement. In sand cement mixes the moisture needed for compaction is not readily absorbed by the sand particles and may result in a relatively high water cement ratio thereby reducing strength.

The moulding moisture content has a more pronounced affect on durability than it does on strength. The use of a moisture content above the optimum for compaction produces a material more resistant to the effects of immersion, freeze-thaw cycling and wet-dry cycling (Felt, 1955; Highway Research Board,1961; Road Research Laboratory, 1966; Lightsey and Callihan, 1970; McNulty, 1985; Thomas, 1985). The effects of excess moisture are more profound in fine-grained materials with high clay mineral contents. The increased durability is partly due to the increased cement hydration achieved in fine-grained soils with excess compaction moisture but other mechanisms include reduced swelling of clay minerals and reduced interparticle swelling (McNulty, 1985). These swelling potentials are reduced since with the increased moisture the absorption, and associated swelling, commences before compaction so there is a decreased potential for subsequent swelling.

2.6.4 Cement Content

Previous studies have shown that the strength of soil cement mixes increases with increasing cement content at least up to a cement content of around 40% (Sherwood, 1968; Highway Research Board, 1961; McLaren *et al*, 1960; Maclean *et al*, 1952; Felt,1955). This assumes that sufficient moisture is available for hydration which is not always the case at high cement contents (Sherwood, 1968). Linear relationships between strength and cement content have been suggested (Sherwood, 1968) for materials of all gradings, through the range of 0 - 12%

cement for sands and up to 40% for heavy clays.

Cement contents are usually governed by economics, in that the soil cement must remain a viable alternative to more traditional road building materials.

2.6.5 Type of Cement

The majority of soil stabilisation in the U.K has been carried out using Ordinary Portland Cement. Many other cements are available and may be more suitable in certain circumstances. High early strength cements speed up the hardening of soil cement (Felt, 1955) and it has been suggested (Clare and Farrar, 1956) that fine cements may reduce the cost of the final material due to reduced cement content. Super rapid hardening cements also promote high early strength in soil cement. These cements also have a beneficial effect when used with organic soils (Clare and Pollard, 1951) due to a presence of about 2% calcium chloride added during manufacture. The additional calcium ions react with the organic matter preventing a depletion of the calcium hydroxide liberated during hydration.

High-alumina cement can significantly increase early strength in soil cement (Clare and Pollard, 1951) but it is susceptible to conversion and strength loss in humid conditions (Neville, 1981). This, together with its relative high cost, prohibits its use in most soil stabilisation applications.

Sulphate-resisting cement may be used advantageously where high sulphate groundwaters are encountered. However, its effectiveness in stabilising sulphate contaminated clayey soils is highly questionable (see Section 2.4.3).

Pozzolanic cements are more likely to improve the durability of stabilised sulphate

bearing soils due to the reaction of the pozzolan with the lime liberated during the hydration to form relatively stable calcium silicates.

2.6.6 Preparation of Specimens.

The preparation of laboratory specimens can play a major part in determining the performance of the stabilised soil. The condition of the raw material in terms of moisture content, the degree of pulverisation achieved by mixing, mixing duration, time between mixing and compaction, method of compaction, size and shape of test specimen and curing regimes can alter the strength and durability of the hardened specimen (Felt, 1955; Highway Research Board, 1961; West, 1959; Grimer, 1958; Symons, 1965). The effects of these variables on laboratory specimens are similar to their effects on cement stabilised structures in the field.

If the object of a laboratory study is to assess the suitability or predict the performance of materials to be used on site then it is important to simulate the production techniques used on site.

2.6.7 Age

The strength of cement stabilised materials increases with age assuming suitable curing conditions (i.e. constant moisture content and temperature). During the first few months the relationship between strength and the logarithm of time is approximately linear (Grimer and Krawczyk, 1963; Dumbleton, 1962; Circeo *et al*, 1962). Soil cements are more likely to retain this linearity for longer periods than clay cements. The latter exhibit increases in the slope of the relationship resulting in proportionately higher strengths. This is probably a result of the long-term pozzolanic reactions between lime and clay minerals (see Section 2.4.2).

2.6.8 Temperature

The rate of strength development of cement stabilised soils is greater at higher temperatures up to around 50°C (Dumbleton, 1962; Clare and Pollard, 1954). For stabilised cohesive soils there is an amplification in the rate of increase of strength with rising temperature. This opposes the log (maturity) law of concrete (Plowman, 1956). The increased rate is not noticeable for stabilised sands and it would appear to be due to pozzolanic lime-clay reaction which is temperature dependent.

2.7 Summary of Cement Stabilisation

The factors contributing to the mechanism of cement stabilisation and the performance of cement stabilised materials are complex and variable. As a result, it becomes difficult to study the subject as a whole. While recognising the importance of all these variables it is not possible to examine all their individual contributions in a single study.

3. MINESTONE

3.1 Introduction

Coal in Britain is mined from the Coal Measures in the Carboniferous System. Coal seams occur in sequence with other Coal Measure rocks and a typical sequence, or cyclothem, will contain coal, mudstone, shale, siltstone, sandstone, seatearth and occasionally limestone. One such sequence is shown in Figure 3.1. Most of the coal is separated from the non-coal rocks and minerals in a washery plant. The coarse discard is settled out and tipped. The fine discard, or colliery tailings, remain in suspension and are either dewatered or settled out in lagoons.

Colliery spoil tips are composed mainly of the shales, mudstones and seatearths of the roof and floor of the seam but also include rocks incorporated in the seam and other rocks associated with the driving of drifts or shafts. This material is referred to as minestone (Rainbow, 1982) and is basically a heterogeneous mixture of rock fragments and rock products. The general composition of minestone is largely controlled by the geographical location of the mine and the geological setting of the seam but considerable variations may be encountered within an individual tip.

3.2 Physical Properties of Minestone

The particle size distribution of the material within a given tip is largely dependent on the degree of weathering and the mineralogy of the particular minestone (Taylor and Spears, 1970). The processes of excavation and crushing both prior to washing and during compaction in the tip are sufficient to ensure that there are very few

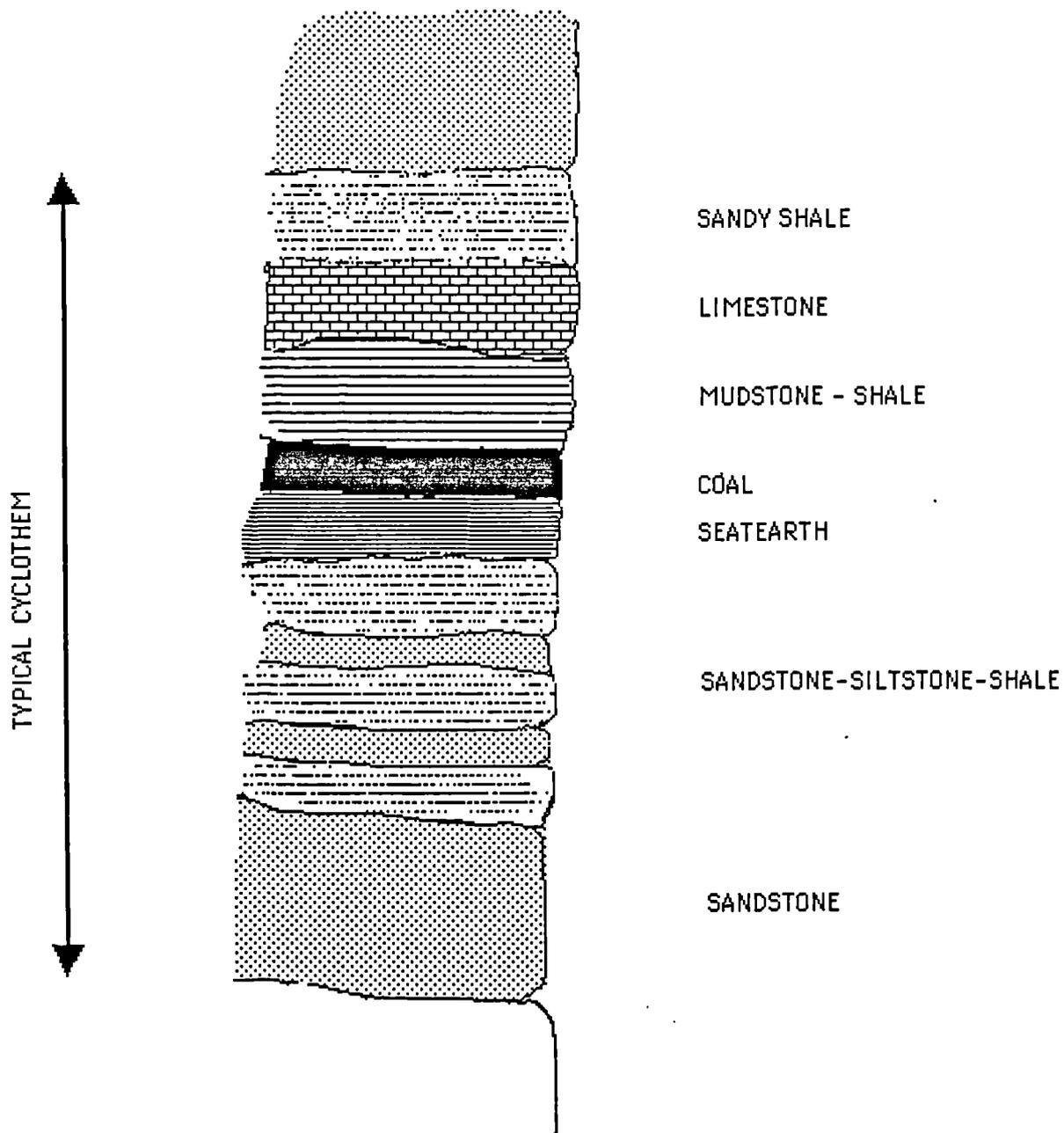


Figure 3.1 Coal Measure Rocks.

particles in excess of 200mm present (Rainbow, 1983). The fine fraction of minestone is generally moderately plastic, although, some minestones are non-plastic. In the majority of minestones, the fine fraction can be classified as a silty-clay of medium to low plasticity.

Specific gravities of minestone are generally low with values ranging between 1.77 to 2.76 (Rainbow, 1983). The mineral densities of the common rock types found in minestones are possibly in excess of 2.7 (Morton *et al*, 1984) and the lower specific gravity of the material taken as a whole is thought to reflect its coal content. A relationship has been established between the specific gravity and the loss on ignition of minestone (Rainbow, 1983). A good correlation exists, although the loss is not necessarily a true reflection of coal content as many other minestone minerals undergo weight loss at high temperatures.

Other physical properties such as compaction characteristics, shear strength, consolidation and permeability have been measured for a large range of minestones, and, whilst they are not relevant to this study, the data are readily available (Rainbow, 1983).

3.3 Chemical Composition of Minestone

The chief chemical constituents of minestone have been reported (Taylor and Spears, 1970; Spears *et al*, 1971; Collins, 1976; Rainbow, 1983) as:-

<u>Element</u>	<u>Oxide</u>	<u>Range %(for oxide)</u>
Silicon	SiO ₂	28 - 67
Aluminium	Al ₂ O ₃	15 - 27
Iron	Fe ₂ O ₃ + FeO	3 - 10
Free Carbon		5 - 20

The free carbon represents the organic content, measured either by ignition loss at 950°C and corrected for oxidation of ferrous iron and pyrite (Spears *et al*, 1971) or by first removing tars and carbonates followed by heating at 1000°C and collecting the CO₂ produced (Collins, 1976).

Other elements in smaller quantities include potassium, calcium, magnesium, sodium, titanium, phosphorous, manganese and sulphur.

Of all the chemical compounds in minestone the sulphate fraction has caused the most concern for the engineer. The sulphates present may attack adjacent concrete structures or lead to disruption of cement stabilised minestone. The broad family of sulphur compounds present in minestones include iron sulphide, sulphates of calcium, iron, potassium, magnesium and sodium together with organic sulphur compounds. The total sulphur content of minestone is usually less than 5% (expressed as SO₃) but has been reported (Rainbow, 1983) as high as 12% in some cases. These percentages refer to the amount of sulphate precipitated as barium sulphate and are expressed as a percentage of the oven dry mass of material used for gravimetric analysis. Total sulphate contents are typically less than 1% (as SO₃) but may be 2 or 3 times higher (Rainbow, 1983).

The pH of fresh minestone is normally neutral or slightly alkaline but the weathering of sulphides produces sulphuric acid which may result in an increasingly acid environment (see Section 3.5.2). A range of 2.7 - 9.6 has been reported (Rainbow, 1983).

3.4 Mineralogical Composition of Minestone

Early optical microscopy studies (Dixon *et al*, 1964) on the mineralogy of inorganic matter associated with coal seams gave quartz, degraded illite and a kaolin type mineral as the chief components. X-Ray diffraction techniques for determining clay mineralogy (Shultz, 1964) have been used on colliery tailings (Taylor and Spears, 1970) and spoil tip borehole samples (Spears *et al*, 1971). The principal clay minerals were reported as kaolinite and illite. Subsidiary chlorite may make a contribution to the 7Å peak and an expandable mixed-layer clay was evident as a tail on the low angle side of the 10Å illite peak and this last was separated and determined by ethylene glycol treatment. The mineralogy of the tailings was thought to reflect the composition of the coarse discard (Taylor and Spears, 1970) and a degree of variation in the clay mineralogy of different spoils was suggested.

A method has been proposed (Collins, 1976) for the study of minestone mineralogy. The total clay content is calculated following quantitative analysis of quartz and other minerals using internal standards. X-Ray diffraction of orientated specimens were used for clay mineral analysis (Shultz, 1964) together with chemical analyses to provide quantitative data. The results from eight minestones collected from around the U.K. show the major minerals to be:

<u>Mineral</u>	<u>Range %</u>
Quartz	15 - 24
Total Clay	52 - 66
Kaolinite	3 - 38
Illite	7 - 36
Chlorite	2 - 7
Mixed Layer	6 - 17
Carbonaceous Matter	7 - 28

Montmorillonite has not yet been recorded as a separate phase but often occurs as a mixed-layer illite-montmorillonite (Taylors and Spears, 1970; Collins, 1976). The mixed layer component is, therefore, likely to be the most expansive of these minerals especially if sodium is the interlayer cation (Gillot, 1968). The carbonaceous matter represents combustible matter that was not separated in the washery plants. The carbonates, calcite, siderite and ankerite; the feldspars, both orthoclase and plagioclase, and the sulphur bearing minerals; jarosite, pyrite, gypsum and alunite in various proportions may contribute typically between 2 and 10% of the minerals in minestone, together with traces of many other minerals (Collins, 1976).

3.5 The Weathering of Minestone

Once excavated, minestones undergo weathering processes resulting in the breakdown of particles. There are principally two main types of weathering; physical and chemical. The breakdown of minestones within spoil tips is reported to be chiefly the result of physical weathering (Taylors and Spears, 1970) although as degradation takes place a greater surface area is made available to chemical reactions which may intensify such breakdown.

3.5.1 Physical Weathering

The physical disintegration of minestones occurs immediately following removal from the rock mass, beginning with the formation of fractures perpendicular to the bedding planes. Although, these cracks may be assigned to stress-relief mechanisms (recovery of elastic strain), the absence of such cracks in fresh samples immersed in water suggest negative pore pressures following desiccation to be the cause (Kennard *et al*, 1967). Further weathering may reduce shales and mudrocks to

gravel size aggregate and the degree of disintegration is thought to be influenced by the sedimentary structures, textural features and mineralogy of the parent rock (Taylors and Spears, 1970).

Many shales and mudrocks tend to virtually disintegrate when immersed in water (Badger *et al*, 1956) whereas the carbonaceous and silty mudstones appear to be more stable. The more unstable shales and mudrocks are often associated with low-rank coals (Badger *et al*, 1956; Raybould, 1966). The rapid breakdown of shales and mudstones has been attributed to slaking phenomena, slaking being loosely defined as "the crumbling and disintegration of earth materials when exposed to air and water" (American Geological Institute, 1976). Many mechanisms have been proposed to explain the phenomena of shale disintegration in water and these are discussed below.

3.5.1.1 Air Breakage

Air breakage is due to the entrapment of air in the pores by water drawn into the rock by capillary action. Compression of the air results in tensile forces on the rock particles leading to disruption (Terzaghi and Peck, 1967). Increased resistance to slaking has been reported for minestones tested following removal of the air from the pores by vacuum (Taylor and Spears, 1970; Berkovitch *et al*, 1959) confirming the role played by this mechanism. Reduced slaking durability of desiccated shales has been suggested as further support for this mechanism in the breakdown of minestone (NCB, 1964). However, the air breakage mechanism has failed to explain the behaviour of shales that disintegrated more rapidly when tested *in vacuo* (Badger *et al*, 1956; Nakano, 1967). In these cases, the removal of air is thought to increase the accessibility of the shale to water enhancing the effects of ionic dispersion.

3.5.1.2 Ionic Dispersion

Colloidal matter, usually clays, is surrounded by adsorbed cations which may be disassociated in a dispersing liquid leaving the clay particles negatively charged. Consequently, there is a net repulsive force between the colloids which may result in interparticle swelling. Ionic dispersion is influenced both by the potential of the dispersing fluid to permit ionisation (as measured by its dielectric constant) and by the adsorbed cation (monovalent sodium clays dispersing more easily). Disintegration of minestones has shown to increase with both the exchangeable sodium ion content of the clay and dielectric constant of the slaking fluid (Badger *et al*, 1956). It was concluded from this study that neither the total clay colloid content or the clay mineralogy were responsible for the variation in shale disintegration, the exchangeable cation and porosity of the shale being the influencing properties. The porosity of shales may be dependent on geological maturity partly explaining the correlation between rate of disintegration and coal rank. However, it has been suggested (Taylor and Spears, 1970) that with the use of organic liquids (for low dielectric constants) and electrolytes, the surface tension is also affected, resulting in reduced capillarity. This would decrease the tendency of disintegration due to air breakage as well as ion dispersion. The same authors also hypothesised that the minestones with high sodium ion concentrations may derive some of the sodium ions from the acid leaching of interlayer sites in montmorillonite. The high sodium content may be a measure therefore, of expansive mixed-layer clays leading to intraparticle and not necessarily, interparticle swelling.

3.5.1.3 Ion Adsorption

Ion adsorption is the hydration at clay surfaces due to the hydrogen bonding of newly

adsorbed water molecules with the existing molecules in the adsorbed layer (Terzaghi and Peck, 1967). Water within the adsorbed layer has an effectively increased viscosity closer to the clay surface and displays some of the properties of a solid. Consequently, further adsorption of water molecules leads to an increase in the effective solid volume of the clay. The adsorbed layer also may initiate osmotic pressures due to the reduced vapour in the smallest pores. Water from larger pores, is "sucked" in by the osmotic pressure causing interparticle expansion (Hudec, 1983). Clay minerals may also swell due to a different osmotic mechanism. Here the double layer water imbibes water in order to dilute its ion concentration towards the concentration of the bulk water (Gillot, 1968). This differs from the adsorption of ions into the first few monolayers where hydration and chemical effects dominate. Ion adsorption has been proposed as a mechanism for the expansion of cement stabilised minestones exposed to fluctuations in moisture content (McNulty, 1985).

3.5.1.4 Intraparticle Swelling

Intraparticle or intracrystalline swelling is the volume increase within a clay colloid caused by the uptake of water between the unit layers of the crystal structure (Gillot, 1968). This mechanism is prevalent in Na-montmorillonite clays. Montmorillonite occurs in the mixed-layer component of minestone (Taylor and Spears, 1970; Collins, 1976). The influence of this mechanism in the breakdown of minestones with high expansive clay mineral contents has been confirmed by the rapid disintegration of such minestones when exposed to moisture (Taylor and Spears, 1970) in contrast to the stability of shales from northern coalfields which are kaolinite dominated, in coal preparation plants (Raybould, 1966). Intraparticle swelling may explain the tendency for minestones associated with low rank coals to disintegrate rapidly (Badger *et al*, 1956) as montmorillonite

clays may be excluded by the diagenetic processes leading to high rank coals (Grim, 1953).

3.5.1.5 Removal of Cementing Agents

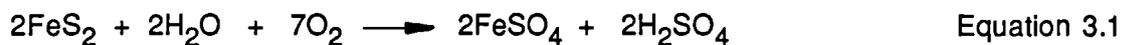
Cementing agents in shales, siltstones and mudrocks may be leached out by the dissolving action of the bulk water. This is principally a chemical weathering process but is included here as it has been proposed (Moriwaki, 1975) as a slaking mechanism. Carbonaceous sediments may be vulnerable to the action of acidic groundwaters, however, such cements in minestone are not common (Taylor and Spears, 1970). Clay may be described as a binding agent of mudrocks (Badger *et al*, 1956) and its removal due to dispersion in water has been described as the loss of a cementing agent.

3.5.1.6 Summary of Physical Weathering

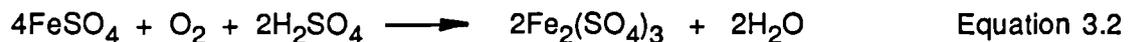
The initial breakdown of minestone on excavation from the Coal Measures is controlled largely by geological structure. Sandstones and siltstones degrade into particle sizes governed by joints and bedding planes (Taylor and Spears, 1970) and these particles are resilient to further physical effects. Mudstones and shales, however, continue to degrade when subjected to fluctuations in moisture content. The mechanisms of air breakage and intraparticle swelling are considered (Taylor and Spears, 1970) to be of primary importance with the effects of interparticle swelling and chemical weathering becoming more important with time and increasing surface area.

3.5.2 Chemical Weathering

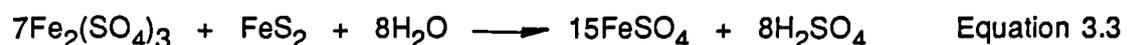
The action of chemical weathering is governed by the surface area available for chemical reactions. Chemical decomposition increases with time due to disintegration of the particles and, therefore, can be seen to be controlled by physical breakdown (Taylor and Spears, 1970). The detrital minerals of minestone have undergone at least one cycle of weathering during their formation and mineralogical changes due to further weathering are unlikely, with the exception of the formation of isomorphs of clay minerals due to interlayer cation substitution. The only significant mineralogical changes occur to the small non-detrital minerals present in the minestone. Pyrite and other iron sulphides are such minerals. When exposed to moist air these iron minerals oxidise to form ferrous sulphate and sulphuric acid. The oxidation of pyrite can be represented as follows:-



Further oxidation of the ferrous sulphate may occur;



This reaction can not proceed chemically in an acid environment (Penner *et al*, 1970) but at lower pH the reaction is due to the action of autotrophic bacteria of the ferrobacillus - thiobacillus group (Temple and Delchamps, 1953). The ferric sulphate itself is a strong oxidising agent which may attack further pyrite;



Equation 3.3 can be explained as the combination of two reactions. Firstly the strictly chemical oxidation of pyrite;



followed by further oxidation of the sulphur;



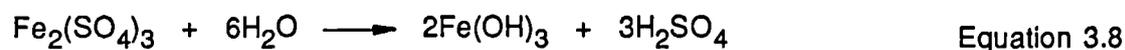
However, it has been suggested that the oxidation of the elemental sulphur may be due to Thiobacillus - thio-oxidans (Temple and Delchamps, 1953);



this would result in ferric sulphate being left available for hydrolysis (Hawkins and Pinches, 1984) yielding yet more sulphuric acid;



or;



The ferric hydroxide is common in the liquid discharge from colliery spoil (Henderson and Norton, 1984). The oxidation process is complex but would eventually lead to a low pH environment in which bacterial activity flourishes (pH 2 to 4) though there is evidence that the system self buffers at about pH1 (Lowson, 1982).

Completion of this outlined weathering process of the exposed pyritic shales is unlikely as the reaction products may combine with other components present or be removed in solution. However, the reactions are a common phenomena in coal mining shales and it is probable that pyrite is present in the various stages of alteration. In calcareous shales the calcite may combine with the sulphuric acid to produce gypsum;



Limestone has been suggested as a possible source of calcium ions (Dougherty and Barsotti, 1972) but if insufficient calcite is available then the clays present in minestone may provide a source of calcium ions. The mineral jarosite $[\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6]$ is another common product formed under these acid conditions, the potassium probably resulting from the degradation of illitic clay minerals.

The sulphates produced form between the laminations and cleats of the shales and, due to the volume increases associated with their formation, accelerate the degradation of the rock particles. A volume increase of a factor of two has been suggested for the formation of gypsum from calcite (Hawkins and Pinches, 1984), an increase of 115% for pyrite to jarosite and 170% for pyrite to ferric sulphate (Penner *et al*, 1971). Other sulphate minerals may also contribute to shale weathering. For example thenardite (sodium sulphate) has been observed in the fissures of minestones from the southeast of England (Thomas, 1985). The mineral ankerite $[\text{CaCO}_3(\text{Mg Fe Mn})\text{CO}_3]$ may provide cations for the formation of further sulphates (Taylor and Spears, 1970) and other carbonates such as siderite are also present in minestone.

Although the chemical weathering of minestones due to the oxidation of pyrite is deemed to be slow (Taylor and Spears,1970), studies of pyrite shales have indicated a more rapid reaction. A black pyritic mudstone foundation suffering from heave, in the U. K. was found to have sulphate contents increasing from 2.20% to 4.15% (as SO_3) over a sixteen month period (Hawkins and Pinches, 1984). In the same material water soluble sulphate levels were found to more than double over a 4 week period. A coal shale fill from South Africa having an initial sulphide content of around 3% (as FeS_2) was found (Caldwell *et al*, 1984) to weather at such a rate that the sulphide content was below 2% after one year.

Other forms of chemical weathering are active in minestone to a lesser degree. These include the hydration of feldspars and the removal of soluble sulphates, chlorides and carbonates.

3.6 Summary

Raw minestones have been utilised in a wide range of engineering applications (NCB, 1984) and the role of both physical properties and chemical composition in determining the suitability of minestone for a given use is well established (Rainbow, 1982; 1983). The physical and chemical breakdown of North American shales used in the construction of embankments and building foundations is well reported (Bailey, 1976; Deen, 1981; Penner *et al*, 1970; Quigley and Vogan, 1970). However, this study is concerned with cement stabilised minestones and the influence of the physical and chemical properties of the raw material on the CSM together with the engineering implications of further weathering following stabilisation are discussed in subsequent chapters.

4. CEMENT STABILISED MINESTONE (CSM)

The major area for the utilisation of cement stabilised minestone is in the construction of road pavements (Rainbow and Sleeman, 1984). The design of pavements incorporating cement bound materials is usually carried out in accordance with Road Note 29 (Department of the Environment, 1970) and the construction is controlled by the Requirements of the Department of Transport's Specification for Road and Bridge Works (Department of Transport, 1977).

4.1 Specifications for CSM

Three categories of cement stabilised materials are currently included in the Specifications and these are referred to as Soil Cement (SC), Cement Bound Granular Material (CBGM) and Dry Lean Concrete (DLC). However, minestone is normally considered for use as either as a soil cement or a cement bound granular material (Rainbow, 1982) as it is unlikely to meet the requirements for lean concrete. The Specification's requirements for these two materials (SC and CBGM) can be summarised as follows, and they cover both the material to be stabilised and the resulting mixed material:-

1. The total sulphate content shall not exceed 1% (as SO_3) for granular or 0.25% for cohesive minestones.
2. Grading limits are provided for the raw materials used both as Cement Bound Granular Material and Soil Cement. In addition materials to be used in Soil Cement must have a liquid limit less

than 45% and a plastic limit less than 20%.

3. The mixing moisture content must not be below the optimum for compaction nor more than 2% above the optimum, these figures are based on the Vibrating Hammer Compaction Test in BS1924 (British Standards Institution, 1975a).

4. Soil Cement or Cement Bound Granular Material should have an average 7 day crushing strength in excess of 3.5 MPa for cubical specimens compacted at field density or 2.8 MPa for cylindrical specimens with an aspect ratio of 2. In addition, the strength results of 5 successive batches of 5 test specimens must display sufficient uniformity such that the root mean square value of the coefficient of variation does not exceed 40% for SC and 25% for CBGM.

5. For SC or CBGM used within 450 mm of the surface the material should not be frost susceptible.

Requirements for 1 and 2 are assessed using the relevant procedures of BS 1377 "Methods of Test for Soils for Civil Engineering Purposes" (British Standards Institution, 1975b), requirements for 3 and 4 by BS 1924 "Methods of Test for Stabilised Soils" (British Standards Institution, 1975a) and the frost susceptibility is determined by the TRRL Frost Heave Test (Croney and Jacobs, 1970).

4.2 The Use of CSM in Pavement Structures

The earliest use of minestone was as a replacement for the diminishing supplies of

burnt spoil in bulk fill applications (Tanfield, 1978; Fraser, 1974). Once the risk of spontaneous combustion had been eliminated by adopting suitable compaction techniques (Lake, 1968) its use was encouraged by the Ministry of Transport (1968).

Early use of CSM was restricted to relatively undemanding roles such as colliery roads and car parks (Ingle, 1956; Kettle and Williams, 1969). During this period laboratory data were collected on the behaviour of CSM and some of the results were very encouraging with compressive strengths in excess of 3.5 MPa achieved for minestone from the Kent Coalfields stabilised with less than 11% cement. The elastic moduli and tensile strengths of the CSMs included in this study were considered satisfactory compared to other cement stabilised materials (Kettle and Williams, 1969). Following this success, the NCB laid trial areas of CSM from a second Kent colliery (Tanfield, 1978) using 10% cement. The main purpose behind this field trial was to assess whether CSM could be prepared and laid using standard construction techniques and the project clearly demonstrated that mixing, laying and compaction of the material could be performed satisfactorily and the CSM achieved the required strength at field density (Kettle and Williams, 1978; Kettle, 1978). Recommendations were made to the effect that the minestone was suitable for use as a stabilised material in pavement construction (Tanfield, 1978).

Following improvements in the availability of mix-in-place and continuous mixing plant, the NCB utilised CSM in many construction applications including hardstandings, coal stacking areas and haul roads (Tanfield, 1978; Rainbow, 1982; Sleeman, 1984). CSM has since been used in construction projects outside the coal industry including car parks, car stacking areas and public roads. Continuous mixing plants have been in operation at Wardley (NE region) and Snowdown (Kent) Collieries, the latter being installed by a private contractor in agreement with the

NCB. Two schemes utilising these mixing plants have been well documented (Sleeman, 1984; Kettle, 1983) these being a lorry park at Horden Colliery (NE region) and the Thannington Diversion for the Canterbury By-pass (Kent). Tests made during construction indicated the suitability of both Wardley and Snowdown minestone for use as both Soil Cement and Cement Bound Granular Material. Sampling and testing of *in situ* material in the Thannington Diversion almost two years after construction provided evidence of service life durability (Kettle, 1983).

4.3 The Strength of CSM

Although most CSMs are capable of achieving the strength for soil cement specifications (Department of Transport, 1977), many require cement contents which may not prove economically viable. Earlier studies (Kettle and Williams, 1969) suggested difficulties in meeting strength requirements with less granular minestones and it would appear that the appropriate cement content is a function of the grading and lithology of the raw minestone.

The effects of clay mineralogy and organic matter on the hardening of cement gel products have been discussed in Chapter 3. Deleterious organic matter is not a common problem in CSM and the current strength requirements are sufficient to detect its presence (Sherwood, 1962b). The presence of reactive clay minerals can result in calcium hydroxide depletion leading to inhibited cement hydration and strength reduction. Mixing and compaction are also adversely affected by high clay contents which increase plasticity and higher cement contents are needed to overcome this problem (Rainbow and Sleeman, 1984). This is controlled by using raw materials that comply with the plasticity requirements of the specification (Department of Transport, 1977). Pretreatment with lime prior to cement

stabilisation may modify the influence of the clay fraction (Kettle and McNulty, 1981) by reducing plasticity and the risk of calcium hydroxide depletion. However, it is doubtful whether the benefits outweigh the increased costs to provide a satisfactory material.

High clay contents are not always detected in grading analyses due to clay aggregations behaving as larger particles. The clay size fraction is also not necessarily composed entirely of clay minerals. Consequently, it is possible for a minestone to have a fine grading and low plasticity. In these cases an increased cement content may be required to overcome the higher surface area of the raw material.

4.4 The Durability of CSM

The fulfilment of strength criteria is not, in itself, an adequate guarantee of long-term performance. Resistance to the likely environmental conditions encountered in practice is a necessary quality of all construction materials. A number of CSM pavements have suffered deformation attributed to expansion (Byrd, 1980; Morton *et al*, 1984) despite the apparent "suitability" of the raw minestone.

The durability of cement stabilised materials is usually assessed in terms of their resistance to fluctuations in moisture content and to temperature changes within the environment. Although current specifications (Department of Transport, 1977) only require these materials to be resistant to frost action it is thought that future specifications will include proven resistance to the effects of moisture (Rainbow and Sleeman, 1984).

4.4.1 Performance of CSM in the Immersion Test

The resistance of cement bound materials to the effects of increased moisture may be assessed by the Immersion Test of BS1924 (British Standards Institution, 1975a) and it is anticipated (Rainbow and Sleeman, 1984) that future specifications will require these materials to record an Immersion Ratio of at least 0.8 following this test. The purpose of including this test is to detect the presence of sulphates and expansive clay minerals likely to cause disruption of the CSM (Rainbow and Sleeman, 1984; Sherwood, 1958).

It was concluded in 1969 (Kettle and Williams, 1969) that some minestones may not produce a cement stabilised material with satisfactory resistance to immersion in water. The resistance of CSM has since been related to the grading of the raw minestone (Kettle and Williams, 1978) and it was proposed that materials having a sub-75 microns content in excess of 30% would be unsuitable for cement stabilisation. A detailed study of CSM durability (McNulty, 1985) suggested that the Immersion Ratio was not a sufficient estimate of performance as it failed to "indicate the extent of any deterioration" or "demonstrate if such deterioration has ceased or is continuing", and alternative criteria based on volume increase and retained strength were proposed. This study agreed with other work (Rainbow and Sleeman, 1984) in detecting no simple relationship between the expansive clay mineral content and performance in the immersion test. This led McNulty (1985) to propose interparticle swelling mechanisms as the chief source of short-term expansion in CSM. These mechanisms were discussed as possible causes of the breakdown of minestone within spoil heaps in Chapter 3.

This test may be considered as too harsh for pavement materials as the pavement is rarely inundated and a test in which specimens absorb moisture by capillary action

through moisture contact at their bases has often been used (Kettle and Williams, 1978; Kettle and McNulty, 1981) in its place. The wet-dry test based on the ASTM procedure (ASTM, 1980a) has been used to assess the durability of CSM (McNulty, 1981) but was also considered to be too severe and was not recommended as suitable for CSM.

4.4.2 Frost Resistance of CSM

Frost heave tests have been carried out on a number of raw and cement stabilised minestones (Kettle and Williams, 1976; 1977). Most raw minestones can be classified as non-frost susceptible as defined by the TRRL Frost Heave Test (Croney and Jacobs, 1970), the exceptions are, generally, the fine-grained minestones. The addition of 5% cement is usually sufficient to reduce the heave of these materials provided the fines content is not excessive (Kettle and McNulty, 1984). It has also been suggested (Kettle and McNulty, 1984) that those CSMs which attain the specified compressive strength are likely to meet the frost heave resistance criteria. Tensile strength has been proposed (Packard and Chapman, 1963) as an alternative criterion for estimating frost resistance in cement stabilised materials. Positive heave in excess of 1% generally results in a complete loss of tensile strength in CSM (Kettle and Williams, 1978) and, consequently, any related criterion would further restrict the use of many minestones.

Conditions of prolonged freezing are likely to be experienced by sub-base materials in severe winters, hence, frost heave criteria are appropriate. However, road-base materials used in this country are more likely to be subjected to cyclic freezing and thawing in most winters and this has led to the development of suitable testing procedures.

4.4.3 Resistance of CSM to Freeze-thaw Cycling

A freeze-thaw test based on the ASTM procedure (ASTM, 1980b) has been developed for CSM (McNulty, 1985). Many criteria are available for assessing the deterioration of specimens subjected to this test (Packard, 1962; Packard and Chapman, 1963). The relative merits of volume stability, mass changes, compressive strength indices and retained compressive strength for determining the performance of CSM in the freeze-thaw test have been examined (McNulty, 1985). As a result of this study, durability criteria were proposed for CSM which were more acceptable than the restrictive compressive strength requirement suggested by Packard and Chapman (1963) which would preclude the use of most CSMs. McNulty (1985) also proposed different mechanisms for the behaviour of CSM in this test. The exposure of cement stabilised materials to excess moisture during the thaw cycle and the resulting expansion due to interparticle swelling and sulphate attack is considered more critical in determining the deterioration of CSM than the mechanisms established as occurring during the freezing cycles (Packard and Chapman, 1963), such as ice growth. Consequently, the raw material properties controlling the performance of CSM in the immersion and freeze-thaw tests should be the same.

4.5 Summary

The success of CSM as used in many pavement structures enhances its potential as a road building material. However, the extreme variability of the stabilised material necessitates the rigorous testing of each separate sample prior to utilisation. The need for establishing critical parameters of both raw and stabilised minestone capable of predicting the performance of CSM has existed since the earlier studies (Kettle and Williams, 1969).

The strength of CSM can be controlled by cement content, although this relationship is a function of the grading and mineralogy of the raw minestone. Unfortunately the strength requirements of the specification (Department of Transport, 1977) are not sufficient to ensure the long-term performance of CSM and the need for durability criteria is well established (McNulty, 1985). Recognised durability tests are available and criteria suitable for CSM have been proposed. However, all these tests suffer from the limitation of insufficient duration. The continued expansion of CSM during periods of prolonged exposure (Kettle and Williams, 1969; Thomas, 1985) together with long-term disruption of CSM pavements (Morton *et al*, 1984) suggests the presence of mechanisms adversely affecting durability which are not apparent in short-term testing. It is not feasible to subject cement bound materials to durability tests of 1 or 2 years duration prior to acceptance and consequently the mechanisms that determine long-term durability must be identified, in order to establish the appropriate raw material limits to prohibit the use of unsuitable minestones.

5. EXAMINATION OF DISTRESSED PAVEMENTS

A number of pavements have suffered distress during the period of this work and these have afforded the opportunity to examine the material on site. The various observations and results of subsequent tests are reported here but there is often a lack of detail concerning the mix design, construction techniques and various environmental parameters (e.g. subgrade type, drainage, trafficking). The examination whilst not, therefore, rigorous provides a useful basis on which to formulate a hypothesis to explain the failure mechanisms involved.

5.1 Pavements Examined.

Four pavements have been examined, one from northeast England and three from Kent. The minestone used in these structures had been screened at 50mm prior to use.

In the northeast, the lorry park at Horden Colliery, constructed using minestone from the Wardley colliery tip, was examined. The parking area was constructed in two phases each of a 150mm CSM layer with a wearing course of tarspray and chippings. The Wardley minestone had been extensively examined (Berry,1981) and was considered suitable for use as CSM. A cement content of 8% produced a material with a mean 7 day crushing strength of 5.75MPa (Sleeman, 1984), the root mean square of the strengths being 11.9%. Despite the apparent suitability of the material the pavement showed some distress at the construction joint between the two phases after some twelve to eighteen months.

In Kent, the three sites comprise a small school playground, a larger industrial car

park and the temporary Thannington Diversion. In each case the minestone from Snowdown colliery was employed, with the addition of some 30% waste sand in the first two structures but with no sand in the last. The school playground, with the benefit of 8-10% cement, performed adequately for some eighteen months before rapidly developing signs of distress during the early summer. The larger industrial car park, having a similar cement content, was constructed in two distinct phases. After approximately twelve months the latter phase showed distress whilst the earlier phase still performed adequately. The sub-base of the Thannington Diversion was constructed with Snowdown CSM at cement contents of 6 and 8% and overlaid with a flexible roadbase. Snowdown minestone has been extensively examined (Kettle and Williams, 1978) and the conclusions from these studies together with tests performed on site (Kettle, 1983) during construction gave evidence of the material's suitability for use as CSM. A year or so following construction circumstances provided an opportunity to sample the *in situ* material (Kettle, 1983). The sampled CSM was then deemed to have acceptable durability. Some of these samples had been stored in water and were available for examination although considerable deterioration had occurred by the time of this study.

Samples were excavated from these sites (with the exception of the Thannington site which had been previously sampled) in the form of intact slabs or cores and transported to the laboratory for a more detailed investigation. As many samples dried following excavation, they developed a white crystalline efflorescence. This was particularly noticeable with the Snowdown CSM's.

Further sites have been visited where pavements have deteriorated rapidly following periods of two or more years satisfactory service.

5.2 Nature of Distress.

A diagrammatic representation of the nature of the distress seen at a construction joint on the lorry park at Horden colliery is shown in Figure 5.1. The failure although possibly promoted by poor construction techniques (joints should be cut back vertically and perhaps were not) is consistent with the expansion of one or both of the CSM layers adjacent to the joint with subsequent movement across the joint.

The school playground and the car park constructed from Snowdown minestone suffered visible disruption in the form of asphalt ridges often 50 mm high in the wearing course, Plate 5.1. The school playground is subdivided into smaller bays by concrete drains and Plate 5.2 shows asphalt override at a safety drain which occurred during early summer, some 18 months after construction. In places, these concrete drains were fractured and the mechanism as seen is presented in Figure 5.2. Where cores were cut through the ridge on the car park, Plate 5.3, the material was no longer intact having a failure plane of around 45° running from the ridge and the failure was compatible with the mechanism shown in Figure 5.1. In many cases the inclined plane, along which movement between the slabs occurs, may be the result of badly finished construction joints. However, evidence of fractured particles in some failure planes indicates a fracture in the CSM. In these cases the mechanism for failure would appear to be internal expansion of the CSM layer.

5.3 Laboratory Examination of Pavement Samples

In the laboratory the following tests were made on some or all of the CSM samples:-

1. Cutting of cubical or cylindrical specimens for density and

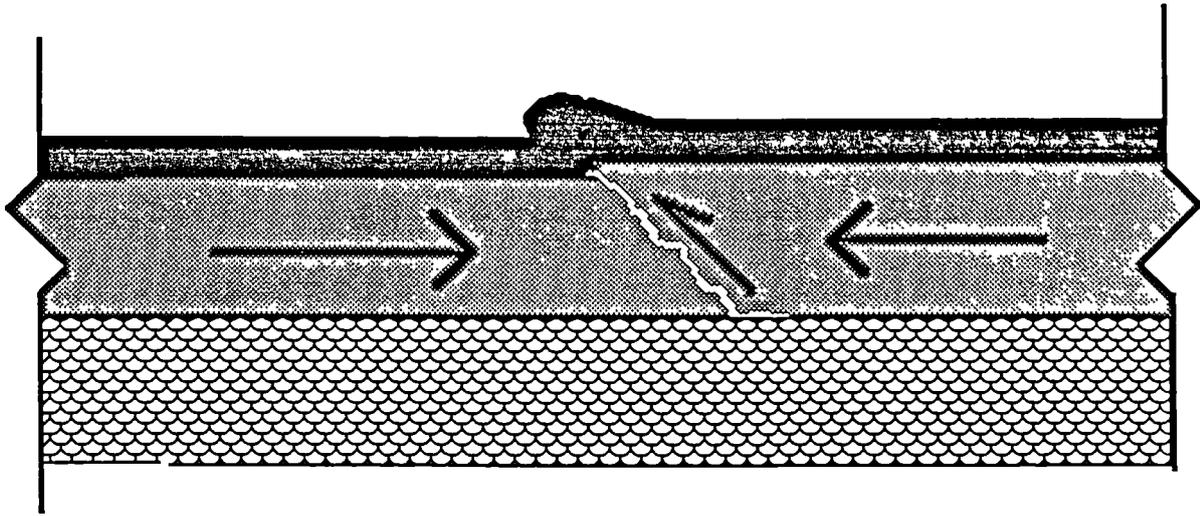


Figure 5.1 Mode of Failure in Wardley CSM - Horden Lorry Park.

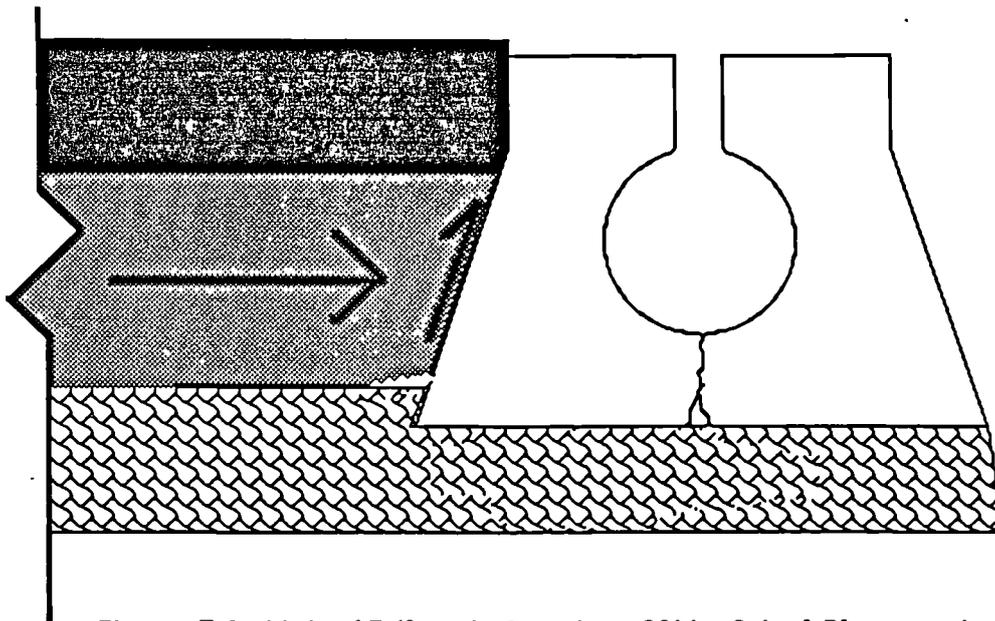


Figure 5.2 Mode of Failure in Snowdown CSM - School Playground.



Plate 5.1 Asphalt Ridge on Snowdown CSM



Plate 5.3 Core taken through Snowdown CSM at the Location of Disruption



Plate 5.2 Asphalt Override on Snowdown CSM at School Playground

strength determinations. Effects of immersion on strength and volume stability were also carried out,

2. Determination of total sulphur and acid soluble sulphate content,
3. Preparation of a water extract for pH and water soluble sulphate determination,
4. Thin section preparation and examination by optical microscopy,
5. Materials were crushed to pass 75 μ m and glass slide smears examined by X-Ray diffraction (XRD),
6. Removal of crack infill material and efflorescence for examination by XRD,
7. Examination of crack surfaces by scanning electron microscopy (SEM).

Additional details on the test methods are given in Chapter 6. The numerical results of tests 1, 2 and 3 are given in Table 5.1.

5.3.1 Strength.

The Horden Lorry Park retained strength in excess of the specified requirement (Department of Transport, 1977) and no strength loss due to immersion was apparent. However, the equivalent cube strengths were lower than the strengths reported for the CSM at the time of construction (Sleeman, 1984) and, therefore, the CSM has suffered a loss of strength during its service life. In the case of the two Snowdown CSMs tested, strengths were below the required 3.5 MPa and the specimens were vulnerable to the affects of immersion. Strength data for the material at 7 days were not available but a recent study (Thomas, 1985) on the effects of sand addition on Snowdown CSM found that sand contents of 20% were sufficient to achieve the required 3.5 MPa minimum. Thus, the CSM, remote from

Table 5.1 Results from Samples taken from CSM Pavements.

Site	Forms of Sulphur (as SO ₃)		pH	Compressive Strength (MPa) (corrected to equivalent cubes)	
	Total	Water Soluble Sulphate		As sampled	After 28 days Immersion
Horden	1.21	0.40	11.0	4.56	4.97
Thannington	2.01	0.71	10.7	-	-
Playground	2.80	0.58	10.3	2.65	2.17
Car Park	3.64	0.63	10.1	2.38	2.01

the failure sites of both pavements, had probably deteriorated to some extent.

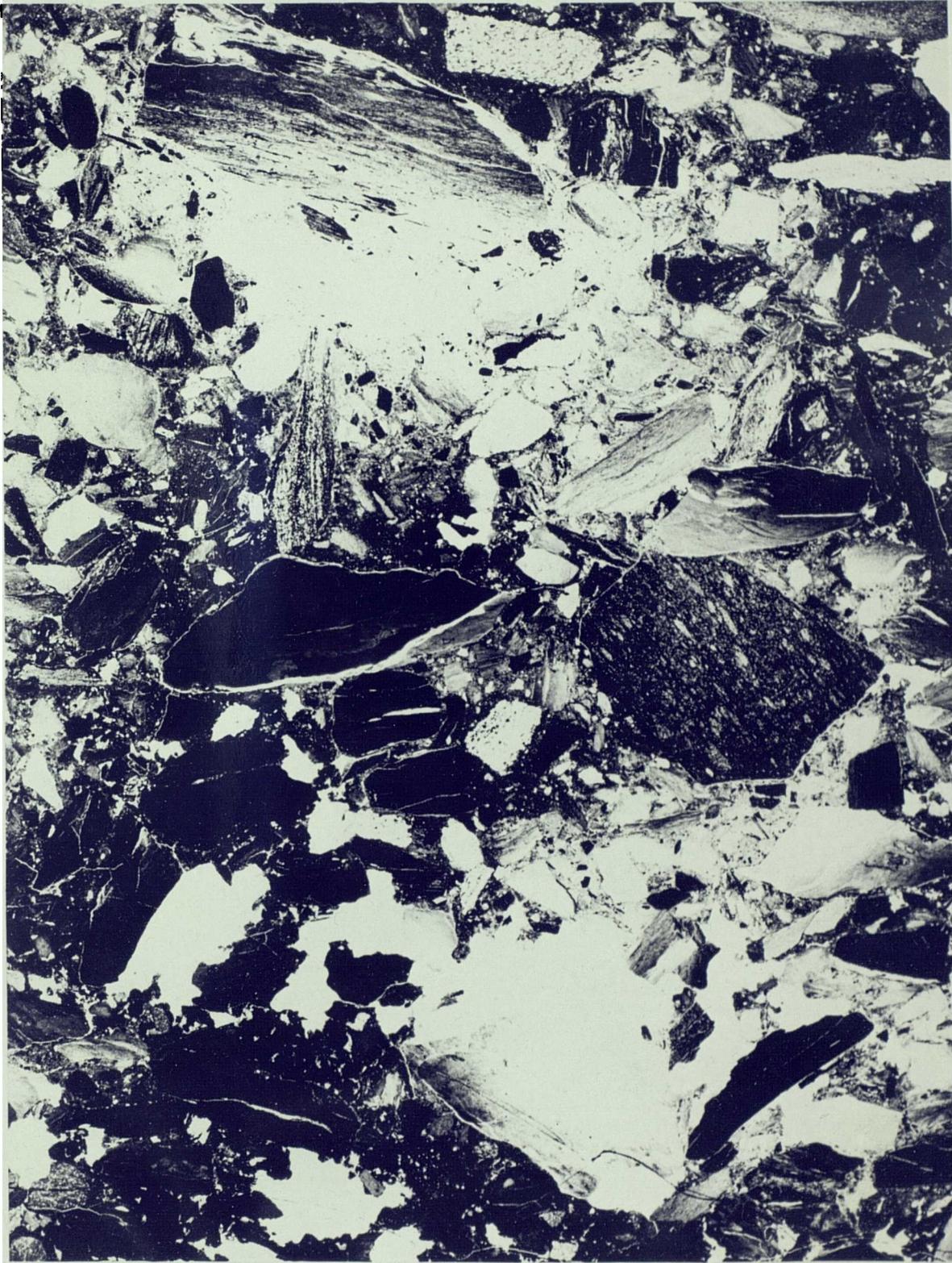
5.3.2 Chemistry.

The total sulphate content of the Horden CSM was 0.4% (as SO_3) which, even after correcting for the approximate 0.25% contribution of the cement, is considerably higher than other reported values (Berry, 1981; Sleeman, 1984). The pyritic sulphur content was not determined but it may be estimated from the total sulphur and sulphate contents by assuming that 10% of the non-sulphate sulphur is organic (Henderson and Norton, 1984). The pyritic sulphur content of the raw minestone is calculated as being approximately 0.5% (as SO_3) in contrast to 0.96% determined for the minestone prior to stabilisation (Sleeman, 1984).

Sulphur content data were not available for the raw minestones used in the three Kent pavements under examination. The pyritic and sulphate (total and water soluble) sulphur contents of these three CSMs were considerably higher than the CSM from Horden lorry park. The pH of the water extract from the Kent CSMs were lower than the northeastern CSM.

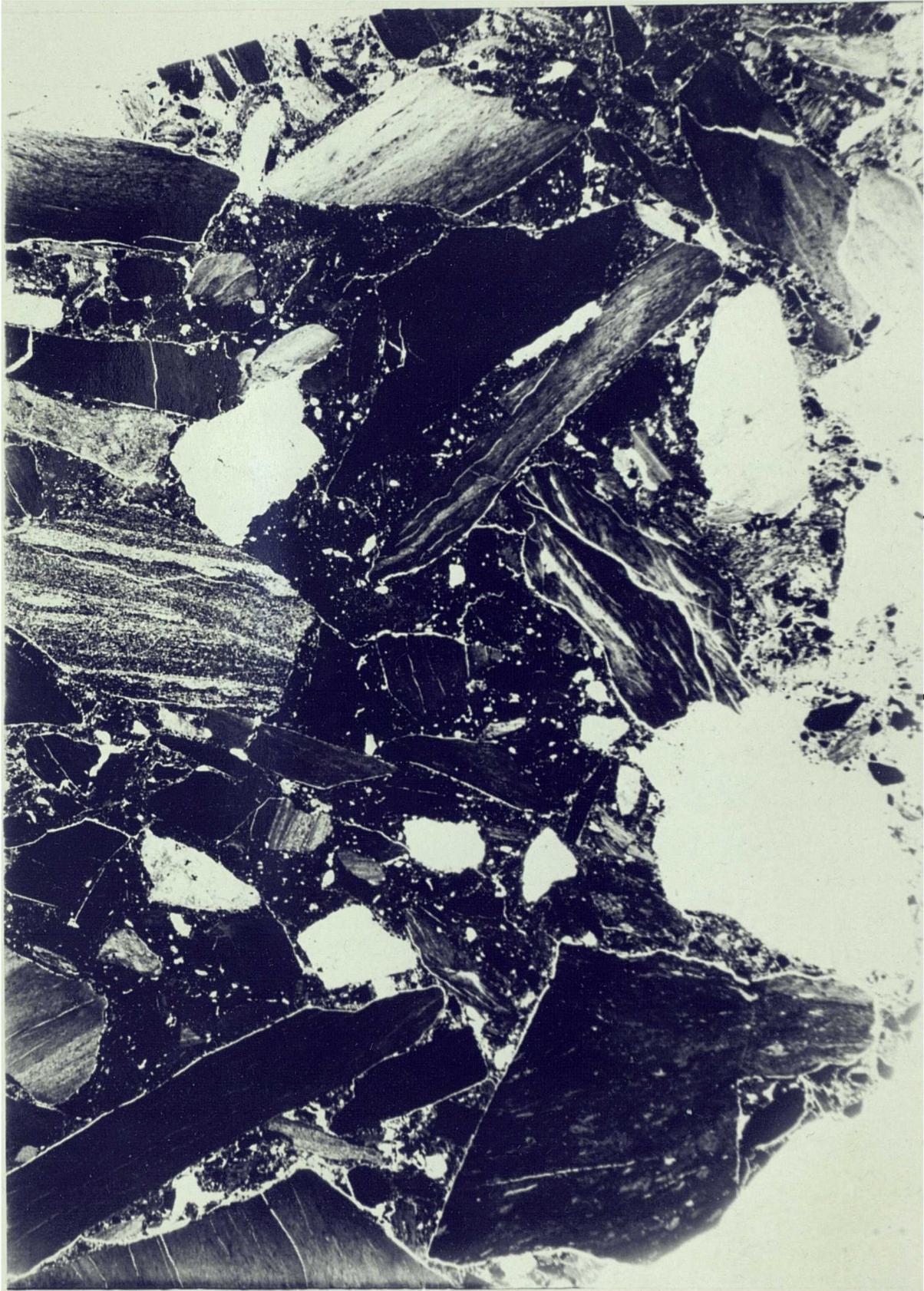
5.3.3 Thin Sections

Photomicrographs for Horden Lorry Park and Thannington Diversion are shown in Plates 5.4 and 5.5 respectively. During preparation of these it was noticeable that some of the particles were surrounded by cracks infilled with traces of mineral deposits. Unfortunately due to the method of preparation, which necessitated cutting and grinding in water after impregnation with an epoxy resin, most of the crack infill material was lost as it was either soft and/or soluble and could not be



5 mm

Plate 5.4 Photomicrograph from Horden Lorry Park



3mm

Plate 5.5 Photomicrograph from Thannington Diversion

positively identified by optical microscopy.

Plate 5.4 shows a typical section of the Wardley CSM where the total crack width across a linear traverse is of the order of 1%. Some of the internal cracks in the aggregate may be due to the effects of compaction and rebound at the time of placing but close observation of the larger marginal cracks, (e.g. the dark sulphide rich particle centre left) suggests a reaction at the particle surface.

Plate 5.5 shows a similar photomicrograph from the Thannington site constructed with Snowdown minestone. Here, the total crack width in linear traverse is of the order of 4%. It is perhaps more obvious in this example that the wider cracks are more strongly associated with the dark sulphide rich particles.

5.3.4 XRD Analysis

X-Ray diffractograms of sample smears revealed little information with the principal peaks being associated with quartz and the various clay minerals present. Portlandite [$\text{Ca}(\text{OH})_2$] was not in evidence but small calcite (CaCO_3) peaks suggested a degree of carbonation had occurred. Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and ettringite ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O}$) peaks were discernable but semi-quantitative analysis was not possible.

X-Ray diffractograms of the efflorescence proved more successful. The Wardley coating gave the diffraction peaks of calcite. This suggests a calcite saturated pore fluid which, on drying of the material, precipitates the carbonate at the surface. The analysis of the efflorescence on the dried surfaces of the Snowdown CSMs showed

diffraction peaks corresponding to thenardite (Na_2SO_4) with traces of halite (NaCl) and calcite. The origin of the soluble sodium salts is thought to be due to saline groundwater from the sub-sea level mining or original connate brine.

Plate 5.6 shows a cut surface through the CSM used in the playground. A large pore can be seen in the centre of the plate and this has been partially filled with a white crystalline material. The infill mineral was successfully removed from this pore and analysed by XRD. The mineral was principally a combination of gypsum and ettringite with small traces of thenardite, halite and calcite. The low solubilities of gypsum and ettringite suggest that these minerals are found at the site of their formation.

A similar mineral combination was removed from some of the larger cracks in the Snowdown CSM used in the construction of the car park. The presence of these minerals in the pore spaces and cracks of the CSM is thought to indicate a chemical reaction within the material after placement.

5.3.5 SEM Analysis

The pore infill material exhibited in Plate 5.6 was examined by scanning electron microscopy and a photomicrograph is shown in Plate 5.7. A dispersive X-Ray analysis gave silicon, aluminium, calcium, chlorine, sulphur, potassium, iron and sodium as the main elements. Silica and alumina are the principal chemical oxides of colliery shale. The remaining elements confirm the presence of minerals proposed from the XRD analysis. Iron and potassium may be present either in the clay minerals or sulphate minerals such as jarosite and melanterite ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$). By closer inspection of this material the mineral ettringite can be separately



Plate 5.6 Section Out Through Snowdown CSM at School Playground

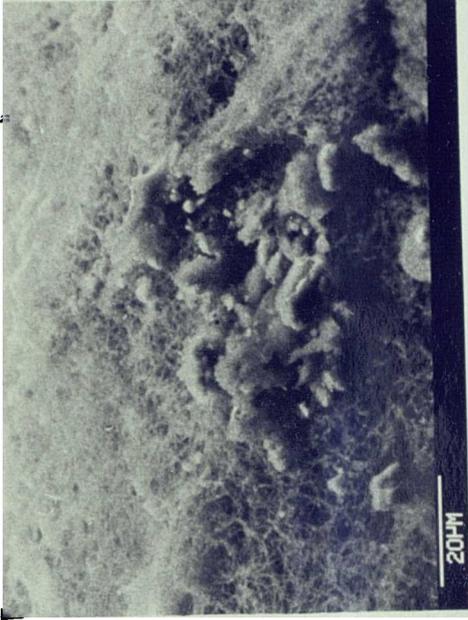


Plate 5.7 SEM Photomicrograph (x 1000) of Pore Infill Material in Snowdown CSM

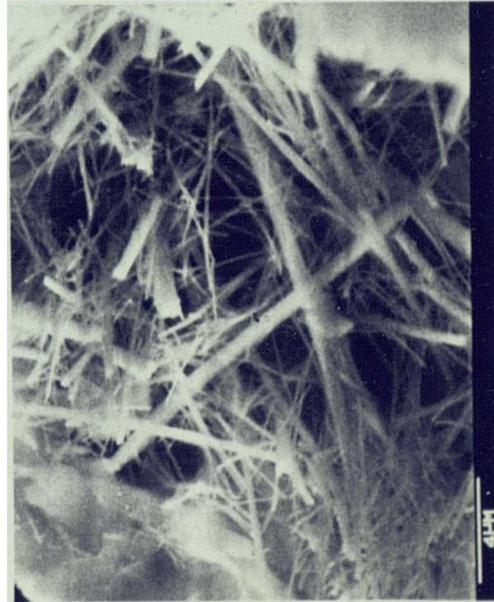


Plate 5.8 SEM Photomicrograph (x 5000) of Pore Infill Material in Snowdown CSM

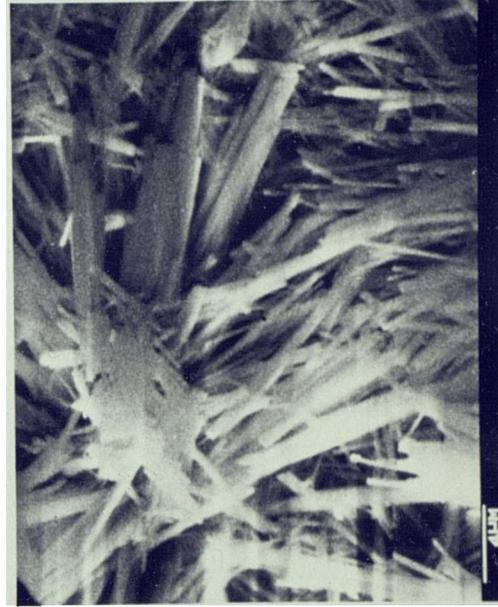


Plate 5.9 SEM Photomicrograph (x 5000) of Crack from Thannington Diversion

identified, Plate 5.8. The long thin needles and the elemental constituents (calcium, sulphur and aluminium) are consistent with ettringite.

A micrograph of a crack surface in the material from Thannington Diversion, Plate 5.9, also confirms the presence of ettringite. In this case the mineral gypsum can be seen as the more tabular crystals in association with the long thin ettringite needles.

5.4 Discussion.

The four pavements examined were all constructed using tried and tested colliery shales. The rigorous testing employed prior to the acceptance of the CSM's, indicated that the materials were suitable for such construction. The evidence from visual examination of the modes of failure suggest that the pavements all suffered disruption attributable to expansion of the CSM layer. Restraints to lateral expansion result in either movement along badly finished construction joints or shear failure of the CSM material and subsequent movement along the failure plane. It is assumed that vertical expansion also occurs but no monitoring to confirm this has ever been carried out.

Results from strength testing confirm that the material away from the failure zone has retained its integrity. However, the residual strength of the Snowdown CSM's were below the required (Department of Transport, 1977) 3.5 MPa . In addition, the measured *in situ* strength for the Wardley CSM was approximately 80% of the reported 7 day strength for laboratory specimens (Sleeman, 1984).

The thin sections show a high degree of internal cracking within the CSMs. It is suggested that the wider cracks are more closely associated with sulphide rich

particles. Further evidence of this is given by the larger crack width of 4% across a linear traverse of the Snowdown material used at Thannington as opposed to 1% for the Wardley CSM. This Snowdown material has a higher potential sulphide content of 1.1% compared with 0.5% for the Wardley CSM. (Potential sulphide approximately calculated as the difference between total sulphur and sulphate making due allowances for organic sulphur).

XRD and SEM analyses confirm the presence of sulphate minerals within the pore spaces and cracks of the CSM material. The textural and mineralogical setting of gypsum and ettringite indicates that these secondary minerals were produced by reactions between the pore fluid and adjacent solids at the site of the reaction. Their production is certainly post-construction and may result as the action of the more soluble sulphates (magnesium, sodium, potassium) on either the products of cement hydration or the clay minerals in association with free lime. Alternatively the continued oxidation of the sulphides present in colliery shale would result in a continuous production of sulphate minerals with or without the interaction of hydrated cement minerals. There is evidence that the pyritic sulphur content of the Wardley CSM had decreased from its initial value. Gypsum and ettringite are both known to develop sufficient crystallisation pressures to disrupt concrete (Lea, 1956) which may be as much as a factor of ten times the strength of CSM.

Both these hypotheses are based on rather inconclusive and, to some extent, subjective findings. These tentative suggestions must, therefore, be tested in a laboratory controlled experiment. First and foremost perhaps, is the need to establish the degree to which sulphide minerals oxidise within CSM and the engineering implications of this process.

6. LABORATORY INVESTIGATION OF THE DURABILITY OF CEMENT STABILISED MINESTONE

Many CSMs suffer from serious volume increase and strength loss when exposed to moisture. Though many mechanisms have been conjectured (e.g. McNulty, 1985), no single mechanism satisfactorily explains these swelling phenomena. This study compares the short-term durability of sixteen different CSMs with various physical and geochemical characteristics of the raw material.

Two methods of rapidly assessing the effects of increased moisture have been developed. The first involves rapid saturation of CSM specimens *in vacuo*. The second is a modified slaking test performed on raw minestones. The results of these rapid tests have been correlated with the existing durability criteria.

The possibility of sulphide alteration in CSM may have serious engineering implications. A study of the long-term geochemical and engineering stability of CSM was set up to determine:-

- 1) whether sulphide minerals oxidise in CSM,
- 2) the role played by micro-organisms,
- 3) the extent to which the oxidation products disrupt the CSM due to their:-
 - a) crystallisation pressures
 - b) attack on products of cement hydration.

6.1 Materials Used

Minestones were sampled from a variety of colliery tips around the U.K. to give a

wide range of properties and not necessarily to identify a material suitable for cement stabilisation. The minestones were collected in two phases and were:-

First Phase - Sampled July/August 1984

<u>Sample Number</u>	<u>Colliery</u>	<u>Coalfield (Region)</u>
31	Littleton (old)	Staffordshire
32	Littleton (fresh)	Staffordshire
41	Coppice	Staffordshire
51	Bentinck (old)	Nottinghamshire
52	Bentinck (fresh)	Nottinghamshire
61	Wardley I	North East
71	Snowdown	Kent
81	Chislet	Kent

Second Phase - Sampled March/April 1985

62	Wardley II	North East
72	Tilmanstone	Kent
73	Betteshanger	Kent
91	Roseheyworth	South Wales
92	Desford	Nottinghamshire
93	Cardowan	Scotland
94	Prince of Wales (old)	Yorkshire
95	Prince of Wales (fresh)	Yorkshire

Minestone 31 was sampled from a tip of at least 60 years of age whereas 32

represents current arisings from the same colliery. Similarly minestones 51 and 52 and 94 and 95 represent old and fresh material. However, 51 and 94 were only approximately 20 years old and 94 was deliberately sampled at least 2 metres beneath the surface of the tip. All remaining samples were taken from 0.3 to 0.6 metres below the surface of tips between 5 and 20 years old.

Throughout the experimental investigations a single supply of typical Ordinary Portland Cement was used, its chemical composition is given in Appendix A, and all the mixes were prepared with double distilled water.

6.2 Classification Tests on Raw Minestones

6.2.1 Standard Tests

The following standard classification tests were carried out:-

Test	BS1377 (British Standards Institution, 1975b)
Particle Size Distribution	7(A) and 7(C) when required
Plastic Limit	2(A)
Liquid Limit	3
Specific Gravity	6(A)
pH Value	10(A)

The above tests were carried out in conjunction with the suggested modifications of "Application of British Standard 1377:1967 to the Testing of Colliery spoil" (National Coal Board, 1971). A grading index was calculated to provide a numerical

representation of the grading curve of each minestone. It is calculated from the proportion of each minestone that falls within selected particle size intervals, the index for a particular minestone being the sum of the products of the mean size of each interval and the proportion of the minestone within it, thus higher indices are obtained for coarser minestones (Hale, 1979). The details are presented in Appendix B.

6.2.2 Total Sulphur Content

The total sulphur content of the minestones was determined by the "Eschka Method" of Test 8 in BS1016:Part 6, "Analysis and Testing of Coal and Coke" (British Standards Institution, 1977a). This method is suitable for the combination of sulphur compounds found in minestone such as iron sulphides, inorganic sulphates and organic sulphur. This method has been employed by the National Coal Board for the determination of total sulphur content of minestone (Berry, 1981).

6.2.3 Pyritic Sulphur Content

Two methods for the determination of pyritic sulphur are given in Test 7 of BS1016:Part 11, "Analysis and Testing of Coal and Coke" (British Standards Institution, 1977b). Both methods involve the "simultaneous" extraction of "non-pyritic" iron (by hydrochloric acid) and "total acid-soluble" iron (by nitric acid) on two separate samples. The pyritic iron is then found by difference and converted to the equivalent sulphate content (expressed as SO_3). Iron content is used in preference to barium sulphate precipitation to avoid erroneous results due to nitric digestion of organic sulphur compounds (Powell, 1920).

The "colorimetric" procedure was adopted for the analysis of the minestones. It has been shown to be as accurate as the volumetric method (Edwards *et al*, 1957) and has the advantage of being quicker and avoids possible errors due to iron precipitation. This method has been employed by the National Coal Board for pyritic sulphur analysis of colliery shales (Berry, 1981).

6.2.4 Sulphate Content

Acid and water soluble sulphate contents were determined using the techniques in Road Research Laboratory Report No. LR324 (Sherwood and Ryley, 1970) which had been developed for testing colliery shales.

6.2.5 Organic Sulphur Content

The organic sulphur content was calculated as:

$$S_o = S_t - (S_s + S_p)$$

Where; S_o = organic sulphur

S_t = total sulphur

S_s = sulphate sulphur

S_p = pyritic sulphur

6.2.6 X-Ray Diffraction Analysis

6.2.6.1 Whole Sample

For the whole sample analysis sub-samples of each minestone were crushed to pass 75 microns. A sample smear on a glass slide was prepared (Gibbs, 1971) and analysed by X-Ray diffraction, generally in the range of d-spacings 1.6 Å to 20 Å. Detailed accounts of the theory and methodology attached to X-Ray diffraction can be found elsewhere (Nicol, 1975).

6.2.6.2 Clay Minerals

Clay minerals can be separated into two basic classifications from the whole sample analysis:

- 1) d-spacing 10 Å - probably illite and mixed-layer illite-montmorillonite,
- 2) d-spacing 7 Å - kaolinite and chlorite

and the preparation of orientated specimens was deemed necessary for further separation of the minerals.

The XRD analysis of the clay minerals was performed on the "clay size" fraction (sub-2 microns) of the minestones. In order to separate this fraction from the bulk sample a clay suspension was prepared by the following method. A 5g sample of crushed minestone was placed in a measuring cylinder with 1 litre of water and shaken end over end to fully disperse the material. The suspension was then left standing for a period of time to allow the greater than 2 microns fraction to settle.

A sample of the clay suspension was then taken by pipette.

A ceramic tile mount was chosen to facilitate heat treatments (Kinter and Diamond, 1956). A sample from the clay suspension was drawn through the tile by vacuum leaving a clay film on the upper tile surface. The process was repeated until an adequate clay film thickness was achieved. This method can provide a precise and accurate representation of the clay minerals (Gibbs, 1965) providing the liquid can be drawn through the tile with sufficient speed to avoid mineral segregation due to differential settling times of the constituent minerals.

The purpose of conducting a semi-quantitative clay mineral analysis was to provide a comparison between the minestones. Many methods of varying complexity are available for differentiating individual clay mineral content (Schultz, 1964, Weir *et al*, 1975, Gibbs, 1967). Most of these methods are time consuming and, a simplified method was chosen for its suitability for routine analysis (Griffin, 1971).

Three basic assumptions are made in this procedure;

1. the clay minerals comprise 100% of the sample,
2. the refracting ability of the clay minerals is consistent,
3. the relationship between the ratio of the 3.58 Å kaolinite peak to the 3.54 Å chlorite peak is a 1:1 linear relationship.

Two treatments are made to the sample;

1. Ethylene glycol treatment. Samples are placed in a sealed desiccator with a reservoir of ethylene glycol for a period of

24 hours at 20°C. This treatment results in the swelling of the expansive clay minerals separating them from the 10Å peak.

2. Heating to 180°C for 1 hour, which partially dehydrates the expansive clay minerals collapsing their crystal lattice to a d-spacing of 10Å.

Diffractograms are obtained for the untreated sample and immediately after the two treatments. The relative proportions of the minerals are then determined from the following equations:-

$$\% (K + C) = \frac{\frac{h_{7\text{Å}}(180^\circ)}{2.5}}{h_{7\text{Å}}(180^\circ) + h_{10\text{Å}}(180^\circ)} \times 100\%$$

$$\%K = \frac{h_{3.59\text{Å}}(180^\circ)}{h_{3.59\text{Å}}(180^\circ) + h_{3.54\text{Å}}(180^\circ)} \times \% (K + C)$$

$$\%C = \% (K + C) - \%K$$

$$\% (I + M) = \frac{h_{10\text{Å}}(180^\circ)}{\frac{h_{7\text{Å}}(180^\circ)}{2.5} + h_{10\text{Å}}(180^\circ)} \times 100\%$$

$$\%I = \frac{h_{10\text{Å}}(\text{EG}) \times \frac{h_{7\text{Å}}(180^\circ)}{h_{7\text{Å}}(\text{EG})}}{h_{10\text{Å}}(180^\circ)} \times \% (I + M)$$

$$\%M = \%(I + M) - \%I$$

Where; %K, %C, %I, %M = percentage of kaolinite, chlorite, illite and montmorillonite respectively.

$h_{x\text{\AA}}(180^\circ)$, $h_{x\text{\AA}}(\text{EG})$ = the heights of the diffraction peaks at d-spacings of $x\text{\AA}$ following heating at 180°C and treatment with ethylene glycol respectively.

Pure montmorillonite is not common as a separate phase in minestone (Collins, 1976) and the quantity %M is likely to be representative of the mixed-layer illite-montmorillonite.

6.3 Slake Durability Test

The Slake Durability Test was originally designed to evaluate the weathering resistance of fissile clay bearing rock when exposed to variation in water content (Franklin, 1970). The standard test method (Franklin and Chandra, 1972) uses a sample of 10 shale particles with a total mass of approximately 500g. These are rotated for 10 minutes in a brass mesh drum which is semi-submerged in water. The material is oven dried at 105°C after each cycle. The Slake Durability Index is calculated as the percentage of dry rock retained following two such cycles.

Apparatus was constructed according to the recommended specifications (Franklin and Chandra, 1972) and the equipment is shown in Plate 6.1. The standard Slake Durability Index was determined for all sixteen minestones. The method used and the results are presented in Appendix C. The test procedure was incapable of ranking the minestones in any consistent order. The shales associated with lower rank coals

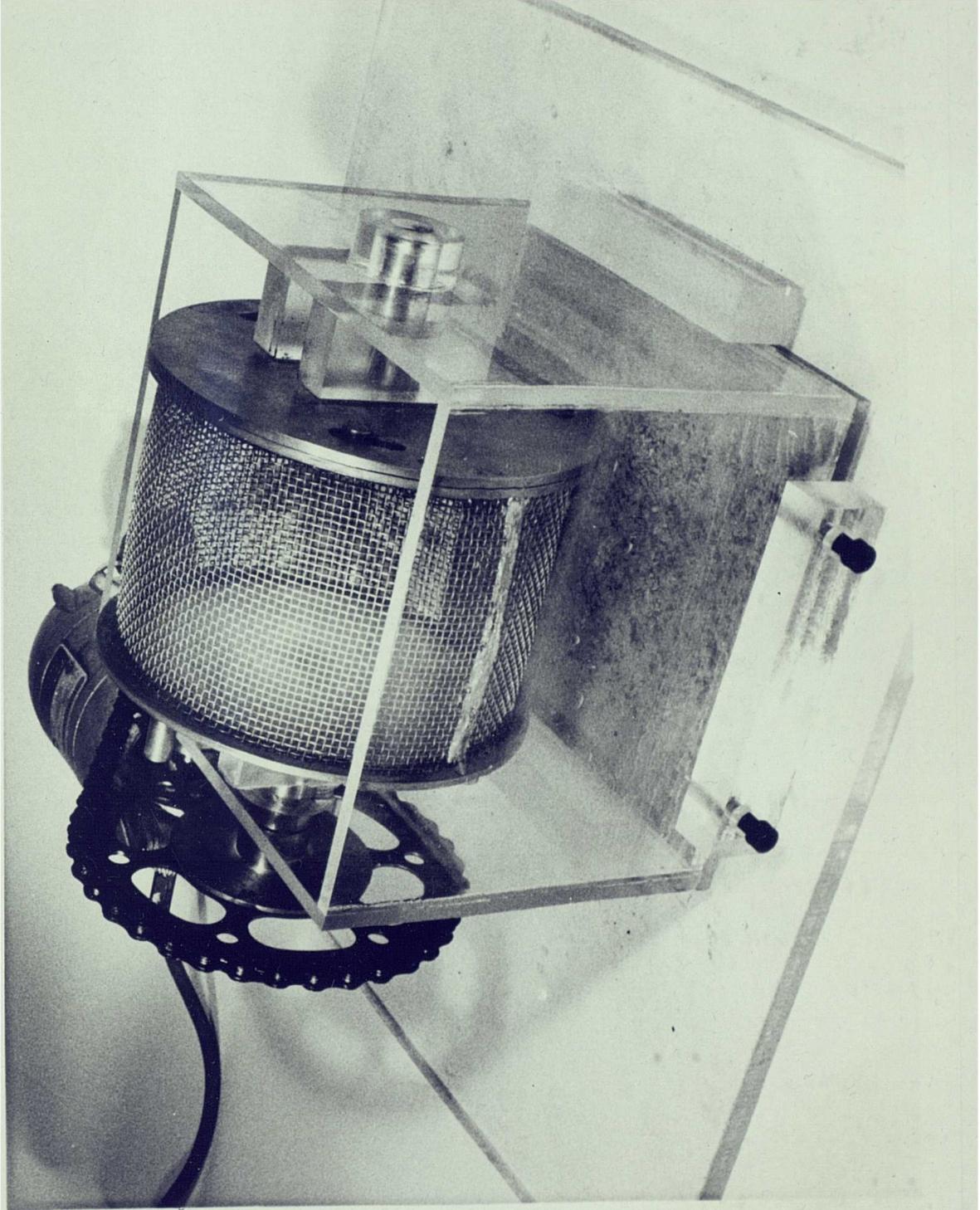


Plate 6.1 Slake Durability Apparatus

recorded high durability which is uncharacteristic (Badger *et al*, 1956). The use of large shale lumps (approximately 50 g each) is considered to be the cause. The well weathered minestones, especially those of low rank, are unlikely to have many clay bearing rocks in this size range (Taylor and Spears, 1970). Consequently, this fraction will be dominated by the more resilient limestones and sandstones.

Modification of the standard procedure to better represent all lithologies was undertaken and this necessitates smaller particle sizes. The mesh size of 2 mm restricts the minimum particle size and a lower limit of 5 mm was set arbitrarily. As the proposed testing programme involved the manufacture of CSM specimens from minestone crushed to pass a 10 mm sieve and since correlation of the slake durability index and the resistance of CSM specimens to moisture effects would be required, it was decided to use the same crushed material for the slaking test. Hence the modified test incorporated a 500 g crushed sample in the size range 5 to 10 mm. The actual method of testing used followed the guidelines of Hopkins and Deen (1984). Oven drying the material at 105°C prior to testing can result in increased slake durability due to alteration of mineral structures (Hopkins and Deen, 1984) and therefore air dried material was used in conjunction with a moisture content determination on a similar sample. A single 60 minute cycle was chosen to provide a greater distinction between shales (Hopkins and Deen, 1984). Immediately following the 60 minute cycle the drum and wet shale are oven dried at 105°C to constant moisture content. The modified slaking index, MSI, is then given by:-

$$\text{MSI} = \frac{m_2 \times \frac{(100 + w_1)}{100}}{m_1} \times 100\%$$

Where; m_1 = mass of air dried sample before test
 m_2 = mass of oven dried sample after test
 w_1 = water content of original sample (%)

The moisture content of the material retained by the drum was also calculated.

6.4 Preparation of CSM Specimens and General Test Procedures.

6.4.1 Raw Material Preparation

A sub-sample of approximately 50 kg was obtained for each minestone by quartering the bulk sample collected from the colliery. The material was spread out and allowed to dry at room temperature to a constant moisture content. Once air dry, material coarser than 10 mm was removed and crushed in a pug mill mixer to pass a 10 mm sieve. The crushed material was then returned to the sub-sample. The crushing was carried out to enable all lithologies to be present in subsequent tests without the need to include oversize particles. The increased surface area would also facilitate geochemical reactions. The crushed minestones were stored in sealed plastic bins until use. The moisture content of the air-dry material was determined in accordance with Test 1 (A) of BS1377 "Methods of Tests for Soils for Civil Engineering Purposes" (British Standards Institution, 1975b).

6.4.2 Mix Design

Compaction tests were performed on a mix of minestone plus 10% cement (by mass of dry shale) in accordance with Test 5 of BS 1924 "Methods of test for stabilised soils" (British Standards Institution, 1975a).

A mix design was then produced to provide a mix sufficient to manufacture eight cylinders (50 dia. x 100 mm) of CSM at optimum moisture content and 10% OTC. A dry density of 95% maximum dry density was chosen as the target density. The reduced density was chosen to avoid difficulties in the compaction of the smaller specimens leading to variability in compacted specimen density. Such variability can result in a considerable variation in the strength of otherwise identical CSMs (McNulty, 1985). The number of cylinders per mix was kept low in order to ensure the specimens could be compacted within 15 minutes of mixing. Longer delays can cause strength reduction in CSM (Thomas, 1984). The criterion for selecting cement content was to try to ensure that the more plastic, finely graded soil had sufficient strength whilst maintaining a practical stabiliser content. A maximum cement content of 10% has been suggested to maintain economic viability (Kettle and Williams, 1978) although it may be possible in some instances to use larger proportions (Kennedy, 1979).

The reduced dry density produced a more open textured material through which moisture and air movements were fairly unrestrained. The rate of geochemical alteration will rely on the rapidity of pore fluid movements and it was hoped that specimens manufactured at 95% of maximum dry density would help to accelerate the effects of the chemistry involved.

6.4.3 CSM Specimen Preparation

For each mix the mass of minestone required was obtained by successive riffing of the whole sub-sample to ensure representative mixes. The minestone and cement were mixed in a twin-bladed pug mill mixer for 2 minutes prior to the addition of the required distilled water. Mixing then continued for a further 3 minutes. A

more intimate mix is expected from this type of mixer than from a conventional open pan mixer (Kettle and McNulty, 1981). A total mixing time of 5 minutes is thought to produce an adequate degree of dispersion of the cement grains throughout the soil (Sherwood, 1968).

The CSM mix was removed from the mixer and sufficient material was weighed into the 50 dia. x 100 mm cylindrical moulds to produce specimens to the predetermined dry density. Compaction was achieved by simultaneous insertion of the end plugs using a vibrating hammer. Nine mixes were made for each CSM. Following extrusion, all specimens were placed in individual self-sealing polythene bags and stored for 7 days at 20°C.

6.4.4 Unconfined Compression Tests

7 day and 14 day unconfined compression tests were each performed on 3 specimens from all sixteen CSMs in accordance with Test 11 of BS 1924 (British Standards Institution, 1975a).

6.4.5 Effects of Increased Moisture

The standard immersion test, Test 12 of BS 1924 (British Standards Institution, 1975a), was carried out on 3 specimens from each CSM. In addition to measuring strength, dimensional changes across the diameter were monitored throughout the 7 day immersion period. The method of dimensional measurement is shown diagrammatically in Figure 6.1.

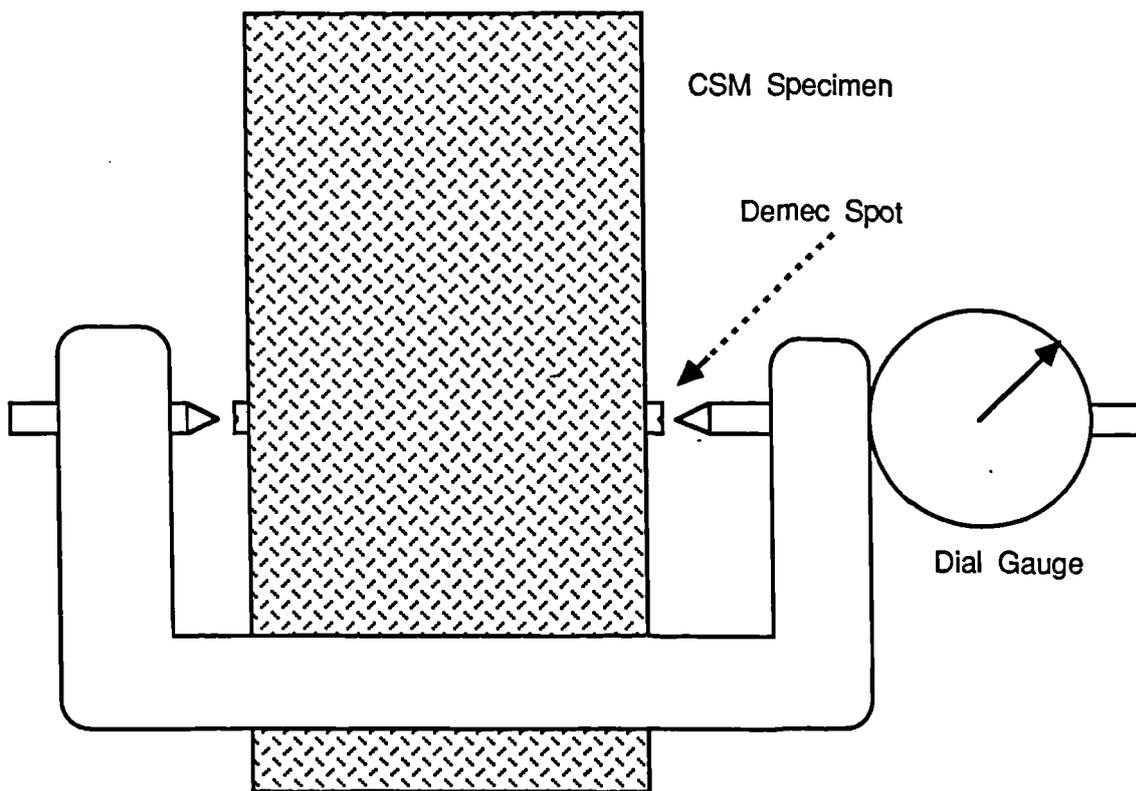


Figure 6.1 Dimensional Measurement using Length Comparator.

6.4.6 Equivalent Cube Strength

A number of 100mm cubes were prepared using CSM mixes from the uncrushed First Phase minestones screened at 20mm. The specimens were compacted at optimum moisture content with 10% OTC and to the maximum dry density. Strength tests were carried out at 7 days, 14 days and for immersed cubes using the testing procedures outlined above. These results could then be compared to the strengths obtained for cylindrical specimens of crushed minestone compacted to 95% maximum dry density.

6.5 Vacuum Saturation Test.

The vacuum saturation test has been used to rapidly assess the freeze/thaw resistance of cement stabilised soils (Dempsey and Thomson, 1973). It is hoped that the same test may be utilised to predict resistance to immersion of CSM. The vacuum saturation test was performed on CSM specimens after 7 days curing. The apparatus developed for this purpose is shown in Figure 6.2.

One day prior to testing two demec spots were attached across the diameter of each specimen. The specimens were then returned to the polythene bags to prevent moisture loss. Immediately before testing, the specimens were removed from the bags, weighed and measured in the length comparator. For the test they were placed on a gauze plate in the vacuum vessel and the chamber evacuated to 610 mm Hg for 30 minutes. After this period the vacuum was maintained from the top whilst water was permitted entry from the base. Once the specimens were fully covered the vacuum was removed and the specimens were soaked for one hour at atmospheric pressure.

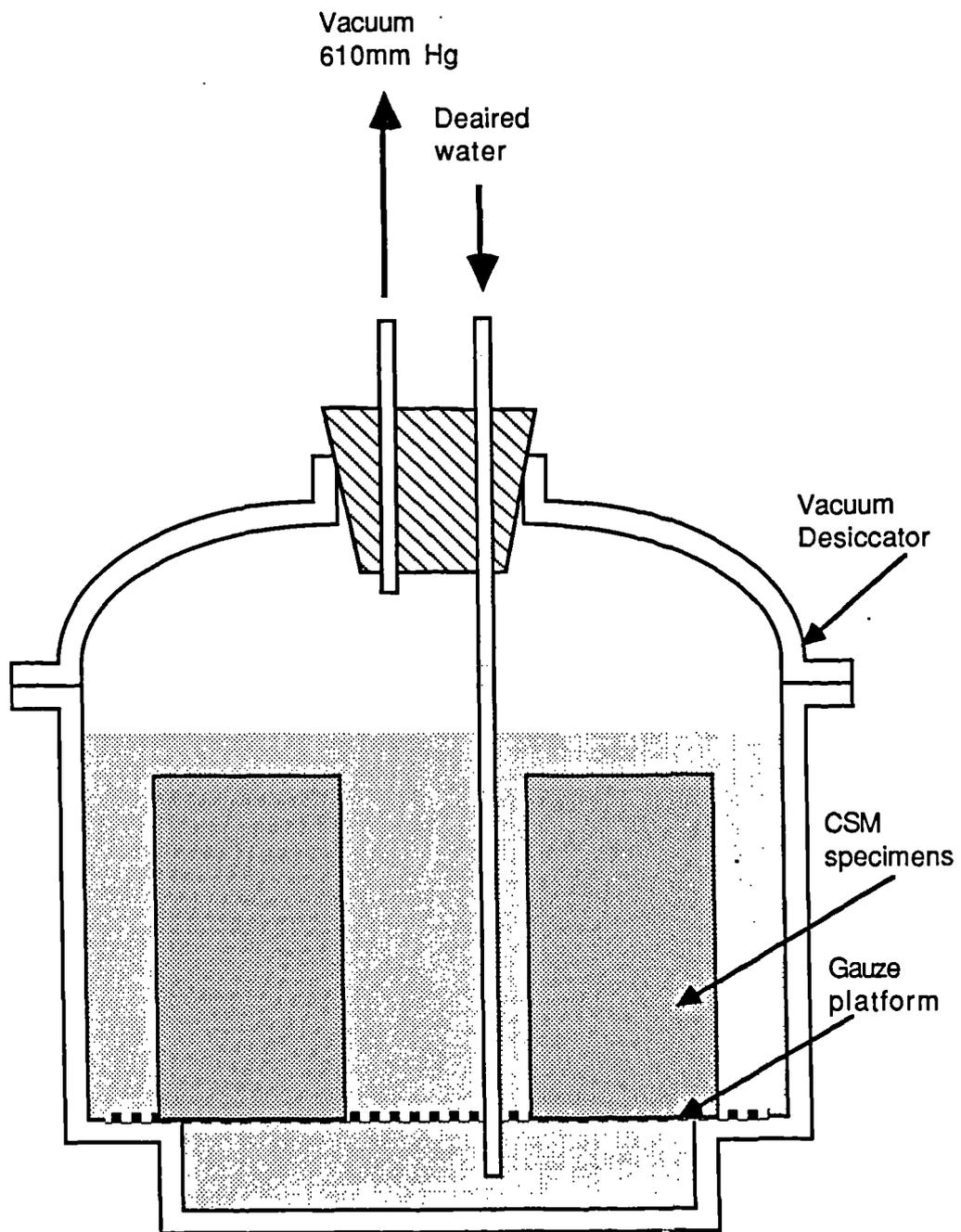


Figure 6.2 Vacuum Saturation Apparatus.

Following inundation the specimens were removed and the free surface water was removed with an absorbant cloth. The soaked specimens were weighed, dimensionally measured and their strengths determined in accordance with Test 11 of BS 1924 (British Standards Institution, 1975a).

The Vacuum Saturation Ratio is defined by:-

$$\text{VSR} = \frac{\text{Vacuum saturated strength}}{\text{Normal 7 day strength}} \times 100\%$$

6.6 CSM Testing for Long-term Durability.

6.6.1 Selection of Environmental Regimes

The weathering processes and the effects of sulphates on cement minerals, discussed in earlier chapters, depend on the availability of water and oxygen. Two different conditions of moisture supply and a datum of constant moisture content were therefore selected and these were:-

- 1) Polythene wrapped and stored at 30°C
- 2) Immersed in distilled water at 30°C
- 3) In airtight containers at 30°C with capillary access to distilled water through porous plates.

An elevated temperature was chosen to accelerate chemical reactions without retarding microbiological action (Leathen *et al*, 1955; Penner *et al*, 1973). A temperature of 30°C represents a condition likely to exist below the asphalt of a

real pavement structure during the summer.

The remaining 57 CSM specimens of the 72 prepared from each minestone (section 6.4.1) were used for this study. Following a 7 day curing period at 20°C and constant moisture content, demec spots were fitted to each specimen. All specimens were weighed and the dimensions (between demecs) recorded, as in Figure 6.1. Nineteen specimens from each of the CSMs were then placed in each of the three environments.

6.6.2 Monitoring Engineering Performance

The dimensional changes of all specimens were obtained at regular intervals throughout the study. Periodically samples of the CSMs were taken from each environment on which an ultimate crushing strength test was performed in accordance with Test 11 of BS1924 (British Standards Institution, 1975a).

6.6.3 Monitoring Geochemical Stability

Various geochemical analyses were performed on the sixteen raw minestones. In the long term investigation only the CSMs prepared from the minestones of the First Phase (Section 6.2) were monitored for geochemical alteration, the reason being purely a time constraint.

The material for the analyses was taken from the CSM specimen used for the strength determination. The whole specimen was crushed in a "tama" mill to pass 75µm before sub-samples were taken for the following:-

1. Total Sulphur Content

Section 6.2.2

2.	Pyritic Sulphur	Section 6.2.3
3.	Acid and Water Soluble Sulphates	Section 6.2.4
4.	XRD - analysis	Section 6.2.6
5.	pH determination	Section 6.2.1

6.6.4 Investigation of Secondary Phases

Secondary phases refer to deposits that were initially identified by visual examination of the specimens. Where cracks or fissures were seen to be opening in the stabilised specimens these were often associated with secondary mineral deposits. Where possible a sample of the mineral was removed for analysis by XRD leaving part of the fracture surface undisturbed for examination by scanning electron microscopy.

6.6.5 Examination of the Role of Bacteria

The role of autotrophic bacteria in the weathering of sulphides in coal and the Coal Measure rocks was described in Chapter 3. The bacteria involved belong to the Ferrobacillus-Thiobacillus groups. Thiobacillus-thiooxidans is mainly capable of oxidising elemental sulphur released by the chemical oxidation of ferrous ions (equation 3.4). Thiobacillus-ferrooxidans has been identified as the autotroph responsible for oxidising iron (Temple and Colmer, 1951). The role of a second bacterial species, Ferrobacillus-ferrooxidans in the ferrous to ferric iron transfer, has been proposed (Leathen and Braley, 1954). In order to establish the presence of autotrophic bacteria in the CSM materials, samples were sent to the Department of Pharmaceutical Sciences at Aston University.

A ferrous iron-silica gel medium (Leathen *et al*, 1951) was used to promote the

growth of the iron oxidising bacteria. Sample scrapings were taken from CSM specimens where visual degradation was evident. The scrapings were used to inoculate the growth medium. Occurrence of bacterial oxidation is normally established by a yellow to red-brown staining of the medium and further confirmed by microscopic examination.

7. ANALYSIS AND DISCUSSION OF RESULTS FROM THE SHORT-TERM DURABILITY INVESTIGATION

7.1 Introduction

The performance of the sixteen CSMs was correlated with various physical, chemical and mineralogical characteristics of their component raw minestones including plasticity, grading, air-dry moisture content, resistance to slaking, expansive clay mineral content and level of sulphate. In addition a vacuum saturation test was examined as a means of providing a rapid assessment of the immersion resistance of CSM.

The materials used throughout the study varied only by minestone type. The quality and quantity of cement used in the manufacture of CSM specimens remained constant. All specimens were made to the appropriate optimum moisture content and 95% of the maximum dry density. Consequently any variation in the engineering properties of the stabilised material may be seen only as a function of the properties of the raw minestone.

7.2 Physical Characteristics of Raw Minestone

The particle size distributions for the minestones studied are given in Table 7.1 together with the specified upper grading limit for Soil Cement (Department of Transport, 1977). Whilst all sixteen minestones may be considered, by their grading, as suitable for use as Soil Cement, the grading envelope shown in Figure 7.1 indicates substantial variation between the samples. Other physical properties, listed in Table 7.2, also show substantial variation (e.g. plasticity and slaking

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characteristics).

Where weathered and fresh samples were taken from a colliery (31/32, 51/52, 94/95) the latter are more coarsely graded, this being a result of the reduced exposure to the processes of weathering. The grading change is particularly noticeable between minestones 31 and 32. The former, having been on the tip for over 60 years, has a sub-63 microns content of 44% in contrast to a mere 5% for the more recently excavated minestone 32. However, minestone 94, sampled well below the tip surface, does not appear to have undergone much more physical degradation than the fresher minestone.

The plasticity characteristics of the minestones exhibit similar contrasts to the grading. Minestones from the North Eastern coalfields (61 and 62) and some of the Kent coalfields (71 and 72) are, on the one extreme, granular and cohesionless, whereas minestones 31 and 41 from Staffordshire and 92 from Nottinghamshire are highly plastic with a considerable proportion of material finer than 63 microns. The plasticity of the minestones appears to be a function of the grading rather than the clay mineralogy in agreement with previous studies (McNulty, 1985). A regression analysis on the data in Table 7.2 gives a positive correlation coefficient, r , of 0.815 between the plastic limit and the proportion of material passing the 63 microns sieve. This is further demonstrated by samples 31 and 32 which have similar clay mineralogy, as might be expected for minestones from the same colliery, but show significant disparity in their plasticity characteristics and sub-63 microns content.

The minerals kaolinite and illite are present in significant proportions in all the minestones. Montmorillonite was not identified as a separate phase and the mineral identified by the symbol M in Table 7.3 refers to the mixed-layer mineral assumed

to be principally illite-montmorillonite. The mineral chlorite is present in small proportions in all sixteen minestones. Generally there is little contrast in clay mineralogy between the minestones with the exception of minestone 93. This minestone, from the Scottish region, has a kaolin content more than twice that of any other minestone and as a corollary, the proportion of illite and mixed-layer clay is reduced. This feature of Scottish minestones conforms with an earlier study involving more complex analytical XRD techniques (Collins, 1976).

The air-dry moisture content is a function of both the plasticity ($r=0.834$ for plasticity index) and sub-63 microns content ($r=0.796$) of the minestone. The reliability of the correlations is due to the increased affinity for moisture of a minestone with a large surface area and clay activity .

The grading index, which is calculated from the particle size distribution across the whole size range, does not appear to correlate reliably with other soil parameters. This confirms that the physical and engineering properties are controlled by the silt/clay size content (Rainbow and Sleeman, 1984) rather than the actual distribution of material in the larger, sand and gravel, sizes.

The modified slaking index (MSI) ranges from 30 to 93% and three distinct classes of minestone can be drawn from the data. Minestone 31, having an index of 30, was totally isolated from the other minestones. Those with indices between 50 and 70 are all from the Staffordshire, Yorkshire or Nottinghamshire Coalfields. These minestones are associated with lower rank coals than the minestones from the North Eastern, Kent and South Wales regions, which have indices in excess of 70. The modified index is, therefore, capable of distinguishing between minestones and the results suggest that the slaking durability of minestone is related to the associated coal rank, concurring with a previous study using a Shale Disintegration Test

(Badger *et al*, 1956). The MSI has a strong negative correlation with the plasticity ($r=-0.771$) and sub-63 microns content ($r=-0.732$) of the minestone despite the test being performed on a separate size fraction, in that the more cohesive minestones with high fines content are less durable. As with an earlier study (Hopkins and Deen, 1984), the modified slaking index is related to the air-dry moisture content ($r=-0.702$), durability decreasing with increasing moisture. It has been suggested that the slake durability is strongly related to clay content and mineralogy (Deen, 1981) but this relationship has not been identified in this study, perhaps partly as a result of the relatively consistent mineralogy of the minestones. The moisture content of the material retained in the drum after the slaking cycle was a good indicator of slake durability ($r=-0.858$), higher indices being achieved for minestones that absorbed less moisture. A similar relationship between the modified slaking index and the "soaked" moisture content has been proposed (Hopkins and Deen, 1984) for shales.

The results in Table 7.1 and 7.2 show that considerable physical similarities may exist in samples from the same tip (minestones 61 and 62) and to a lesser extent between samples from different collieries in the same geographical region (minestones 71, 81, 72 and 73). The physical properties of minestones 51/52 and 94/95 suggest that minestones of different ages from the same colliery may have a degree of similarity. However, although some uniformity exists the possibility of encountering vast diversity between two samples from the same colliery (minestones 31 and 32) highlights the problems of material selection.

7.3 Chemical Properties of Raw Minestone

The chemical properties determined in this investigation are displayed in Table 7.3. The various forms of sulphur suggest further disparity among minestones, e.g.

Sample	pH	Forms of Sulphur		% SO ₃		Rem.	K	Clay	Mineralogy	% - age :-	
		Pyritic	Acid sol.	Water sol.	---					C	I
		Total									
31	2.9	9.45	5.68	2.35	0.7	1.42	14	5	53	28	
32	7.7	1.66	1.42	0.08	0.05	0.16	16	8	54	22	
41	6.9	0.35	0.25	0.04	0.03	0.06	15	6	45	35	
51	7.6	1.88	1.63	0.11	0.08	0.14	14	8	48	30	
52	7.8	3.29	2.96	0.05	0.03	0.28	12	9	54	26	
61	7.5	1.31	0.97	0.29	0.13	0.05	19	10	44	27	
71	4.1	2.1	0.99	0.96	0.39	0.15	9	7	63	22	
81	6.7	2.15	1.1	0.8	0.31	0.25	13	5	52	30	
62	6.9	1.77	1.26	0.45	0.23	0.06	22	8	43	27	
72	8.9	1.39	1.15	0.26	0.06	-0.01	8	6	56	30	
73	5.1	0.88	0.44	0.4	0.17	0.04	8	4	60	28	
91	7.8	1.58	1.4	0.07	0.02	0.11	17	9	53	21	
92	6.6	8.08	5.53	1.89	0.19	0.66	23	6	50	21	
93	7.5	5.5	5.4	0.14	0.07	-0.04	47	14	25	14	
94	6.3	5.69	4.82	0.44	0.22	0.44	16	8	44	32	
95	6.9	5.02	4.52	0.24	0.12	0.26	17	9	43	31	

TABLE 7.3 CHEMICAL AND MINERALOGICAL PROPERTIES OF RAW MINESTONES.

minestone 32 appears to be the complete antithesis of its older counterpart, minestone 31. The contrasts in the contents of sulphur can not, in this particular instance, be explained by the result of geochemical weathering. Minestone 31 contains more pyritic and sulphate sulphur than the current arisings (minestone 32). These two materials probably are the result of mining two different seams since the sheer magnitudes of both their chemical and physical differences would indicate two totally different materials.

Minestones 51 and 52, however, lend themselves as an example of pyrite oxidation. The fresh sample contains nearly 3% pyrite (as SO_3) and negligible sulphate minerals. The weathered sample has a reduced pyrite content of 1.63% and a sulphate content of 0.11%. Minestone 94 is geochemically similar to the more recently excavated minestone 95 confirming earlier suggestions (Glover, 1984) that pyrite oxidation is inhibited below the surface of a well compacted tip. Although minestones 61 and 62 exhibit uniformity within a single tip, the minestones from the Kent Coalfield (71, 72, 73 and 81) indicate that the chemistry may vary within a single region, total sulphur ranging from 0.88 to 2.15% in the samples studied.

The pH of minestone is controlled by the sulphuric acid production which is a consequence of pyrite alteration and, therefore, the pH will depend upon the initial pyritic sulphur content and the environmental conditions within the tip (Henderson and Norton, 1984). To some extent the pH will fall as sulphate is produced and a degree of negative correlation ($r=-0.719$) can be seen between the pH and sulphate content data presented in Table 7.3. However, sulphuric acid may be leached from a tip, whereas insoluble sulphate minerals can not and sulphuric acid may react with other minerals to produce sulphate salts, and consequently sulphate levels may increase without a corresponding decrease in pH.

7.4 XRD Analysis of Raw Minestones

The results from the semi-quantitative clay mineral analyses are presented in Table 7.3 and discussed in Section 7.2 where relevant to the physical soil parameters. As mentioned in Chapter 5 the diffractograms from the whole sample smears were dominated by quartz and clay peaks. However, peaks of trace minerals could be identified in some cases. The main peaks for pyrite occur at 1.63\AA and 2.71\AA . These reflections are weak and usually hard to observe in colliery spoil (Collins, 1976). Discernable peaks were identified in minestones 31, 51 52, 92, 93, 94 and 95. In other minestones, peaks may be tentatively resolved from the background with the exception of minestones 41 and 73 where no trace of pyrite was evident.

A relatively substantial gypsum peak at 7.56\AA was identified in minestone 31 and to a much lesser extent in the Kent minestones (71, 72, 73 and 81). Jarosite and alunite peaks at 3.08 and 3.04\AA respectively were identified in these and other minestones. No sulphate mineral traces were defined for minestones 32, 41 and 52. Intrinsically, the presence of trace minerals observed in the whole sample smears followed earlier findings (Collins, 1976) with various carbonate minerals being identified alongside the sulphates and pyrite. The minestones from the Staffordshire region (31, 32 and 41) exhibited better defined carbonate peaks than the other minestones. Only minestone 31 had a well defined calcite peak and the reaction of this mineral with sulphuric acid may be the source of gypsum in this minestone.

Minestones were transported and stored in polythene bags prior to their utilisation in the laboratory study. During this period minestones 31, 71 and 81 developed an efflorescence where sharp minestone fragments had pierced the bags and thus been exposed to the atmosphere. In all three cases the efflorescence was identified by XRD

as the mineral thenardite (sodium sulphate) and had undoubtedly been precipitated at these sites as a result of the migration and evaporation of pore fluid from the bagged minestone. The mineral thenardite was not identified as a phase by the X-Ray analysis performed on whole sample smears due to the masking effects of the more abundant minerals. It is possible that many other minerals may be present in the minestones but in such small quantities to render them undetectable by XRD methods.

7.5 Effect of Raw Material Properties on Cement Stabilised Minestone

7.5.1 Suitability of Raw Minestone Properties for Cement Stabilisation

Although all the raw minestones meet the grading requirements of the specification for soil cement (Department of Transport, 1977), only seven have acceptable plasticity characteristics. These are:-

32	Littleton "Fresh"
61	Wardley I
62	Wardley II
71	Snowdown
72	Tilmanstone
91	Roseheyworth
93	Cardowan

With the exception of minestone 32 these minestones all have modified slaking indices in excess of 70.

Only samples 31 and 92 have sulphate contents in excess of the imposed limit of 1%

(as SO_3) for "granular" soils. All the minestones may be classed as granular with respect to clause 601 of the specification.

7.5.2 Performance of CSM

For the purpose of the short-term study of CSM the strength and resistance to immersion were used to assess the engineering performance of the stabilised specimens. The current specification requires a 7 day cube strength of 3.5 MPa for soil cement. The specification is currently under review and it is anticipated that the revision will include a proven resistance to immersion. It is likely that test specimens will be required to have an immersion ratio, as defined by Test 12 of BS 1924 (British Standards Institution, 1975a), of not less than 80% (Rainbow and Sleeman, 1984).

7.5.3 Compaction Characteristics of CSM

The physical properties of the CSMs are shown in Table 7.4 and comparisons with raw material indices are shown diagrammatically in Figure 7.2. The optimum moisture content (OMC) increases with increasing plastic and liquid limit, verifying established relationships (Lo and Lovell, 1983), but the best prediction of OMC can be made from the air-dry moisture content of the raw minestone. Figure 7.3 shows the relationship with a positive correlation coefficient of 0.935. As OMC increases the dry density decreases and the relationship is presented in Figure 7.4. This relationship is well established for other materials and reliable predictions of dry density can be made from the OMC (Lo, 1980). It is possible to estimate the compaction characteristics of CSM from the Atterberg Limits, the air-dry moisture content or a combination of both with a reasonable degree of accuracy for

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preliminary determinations. However, the reliability of these predictions is unlikely to be sufficient to replace the need for standard compaction tests at the design stage.

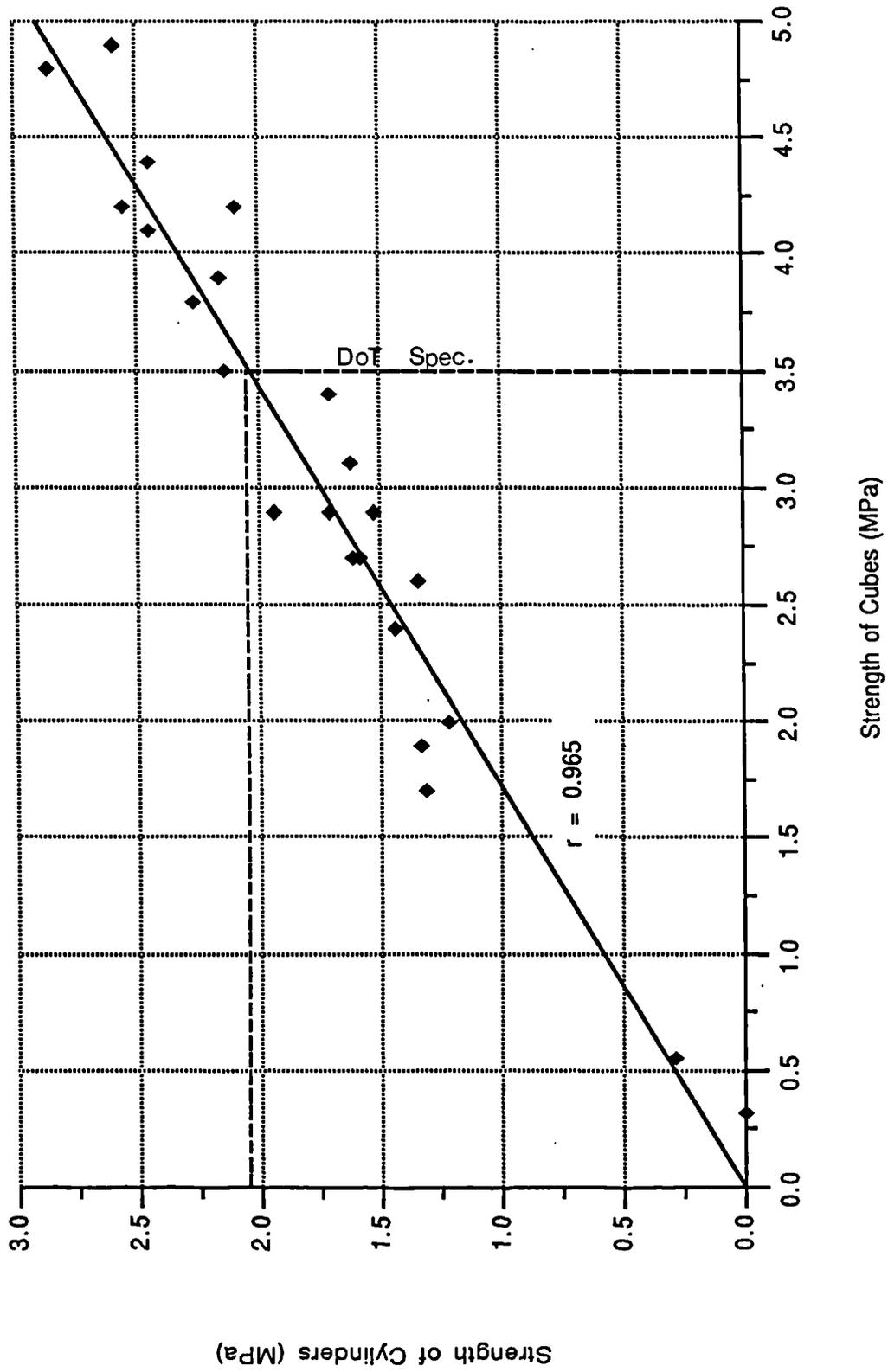
The compaction characteristics of the stabilised minestone are also compatible with the grading and specific gravity of the raw minestones (Road Research Laboratory, 1966) and confirm an observation reported in an earlier study of minestone (McNulty, 1985). Typically, the materials with the higher silt/clay fraction tend to have lower dry densities and higher optimum moisture contents than the coarser grained minestones. Where weathered and fresh minestone samples were available for comparison, it was possible to infer that the weathering processes produced a material with a higher moisture requirement for compaction and a lower dry density. This change is clearly apparent for minestones 31 and 32, but barely noticeable with 94 and 95, where the degree of weathering was less marked due to the deeper burial of the weathered minestone.

Minestones 61 and 62 are very similar in compaction characteristics, and three of the four Kent Minestones (71, 71 and 73) also exhibit similarity. Minestone 81 has, however, a higher OMC and lower dry density than the other Kent materials. This minestone was also the most plastic of all the Kent minestones, and has the highest fines content and air-dry moisture and the lowest specific gravity. Predictions based on Atterberg Limits and air-dry moisture contents, therefore, seem capable of detecting slight regional variations in compaction characteristics.

7.5.4 Compressive Strength of CSM

The relationship between the compressive strength of the cylindrical specimens and that of cubical specimens compacted to maximum dry density is shown in Figure

Figure 7.5 Relationship between the Strength of Cubical and Cylindrical CSM Specimens.



7.5, all specimens were stabilised with 10% cement. The required cube strength of 3.5 MPa can be converted into a target strength of 2.03 MPa for the cylinders, using the gradient of the linear regression line. This value is significantly below the suggested 2.8 MPa for cylinders with an aspect ratio of 2 emphasising the influence of compacted dry density on the compressive strength, as the cylindrical specimens have dry densities measuring 95% of the dry density of the equivalent cubes. The deliberate introduction of the additional 5% air voids results in a strength reduction of 27.5% from the expected strength of the cylinders. This is in close agreement with the 6% reduction in the compressive strength of concrete for every 1% of air introduced (Neville, 1981).

The relationship between the strength and durability of CSMs and other properties of both the raw and stabilised materials are presented diagrammatically in Figure 7.2. There is a tendency for the coarser, less plastic minestones to achieve higher compressive strengths, as can be seen from the detailed results in Table 7.4. The CSMs prepared from the seven minestones (32, 61, 62, 71, 72, 91 and 93) regarded as suitable by the specification (Section 7.5.1) all achieved strengths in excess of 2.03 MPa. The following CSMs also have 7 day compressive strengths in excess of this value:-

73	Betteshanger
94	Prince of Wales Old
95	Prince of Wales Fresh

An examination of the plasticity characteristics of the raw minestones (Table 7.2) shows that these three minestones only exceed the plastic limit constraint by 2%.

Minestones containing high proportions of fines and/or active clay fractions

require high moisture contents for compaction and achieve correspondingly low dry densities. The reduced dry density alone is sufficient to reduce the strength of the stabilised material (Grimer, 1958). Further consequences of high fines content and plasticity on the strength of CSM are:-

1. Mixing and compaction problems due to clay aggregations and increased surface area. With highly plastic or fine material an intimate mix with cement is hard to achieve. A greater degree of pulverisation (Grimer and Ross, 1957) or increased cement contents (Gillot, 1968) are required to overcome this problem.
2. Colloidal aggregations are formed within the mix resulting in a skeletal framework of clay lumps bound by cement matrix (Lilley, 1979; Davidson, 1961). These aggregations may be stabilised by secondary cementitious products due to migrating lime (Stocker, 1963; Herzog, 1963) but invariably this leads to regions of weakness (McNulty, 1985).
3. Lime depletion, caused by the pozzolanic reaction between lime and clay, retards the formation of primary cementitious products (Croft, 1967).

A combination of these phenomena may adversely affect the strength of CSM. The more coarse-grained materials have higher dry densities with a more conventional cementing action. The reduced surface area permits a higher proportion of particles to be coated by cement grains, strength being derived by bonding at the points of particle contact. These materials generally achieve greater strength than the more cohesive minestones.

If the target cube strength of 3.5 MPa (or 2.03 MPa for the cylindrical specimens at reduced dry density) is required then the limiting plasticity requirements appear reasonable for cement contents of 10%. The proportion of material passing 75 microns has been suggested as an index for assessing the ability of CSM to achieve sufficient strength at similar cement contents, a limit of 20% has been proposed (McNulty, 1985). A lower value would be required to preclude minestone 81 from acceptability. However, the plasticity characteristics and fines content are not sufficient, by themselves, to predict the strength of stabilised materials. Minestones 94 and 95 failed both criteria and achieved strengths considerably higher than 2.03 MPa.

A more statistically significant relationship can be found between 7 day compressive strength and the modified slaking characteristics. A positive correlation coefficient of 0.721 was calculated for a linear regression analysis between the parameters 7 day strength and slake index, and a negative coefficient of 0.770 was found between the strength and the moisture content of the material after slaking. Both these test statistics are significant at the 1% level (Caulcutt, 1983).

The slaking characteristics are designed to measure the resistance of rocks to the effects of moisture. It is evident that the more resilient, harder minestones produce CSMs of greater strength. As discussed earlier, the slaking index reliably correlates with both the sub-63 microns content and the plasticity characteristics. Thus a relationship between this index and strength would be expected. The increased significance of this relationship is, perhaps, due to the ability of the slaking test to measure other properties relevant to strength. It is probably the individual strength of minestone particles that has an effect on both these parameters. Weak, fissile particles being lower strength aggregates lead to lower compressive strengths and degrade more readily in the slaking test and during

compaction. Particles broken during compaction also introduce uncemented surfaces in the CSM producing lower strengths.

In summary, the initial strength of CSM depends upon the grading, plasticity and hardness of the raw minestone and the dry density achieved. Although a significant amount of intercorrelation exists between these variables their individual importance is evident in the results. It is suggested that these parameters are the most important with regards to early strength, although, other soil properties may be influential. In fact, criteria can be selected from these raw minestone indices to solely preclude the six CSMs that failed to achieve a crushing strength of 2.03 MPa at 7 days. For example these might be:

- | | | |
|----|------------------------|------------------|
| 1. | Modified slaking index | greater than 55% |
| 2. | Plastic limit | less than 22% |
| 3. | Plasticity index | less than 15% |
| 4. | Sub-63 microns content | less than 25% |

7.5.5 Resistance to Immersion

The Immersion Ratio (IR) ranges from 0% for minestone 31 to 99% for minestone 72. Samples prepared from minestone 31 were deemed to have lost all strength since, despite being able to support their own self weight, the specimens collapsed on being placed in the loading machine. Seven of the CSMs have shown IRs in excess of the proposed 80% (Rainbow and Sleeman, 1984) and these are :-

- | | |
|----|----------------|
| 52 | Bentinck Fresh |
| 61 | Wardley I |
| 62 | Wardley II |

- 72 Tilmanstone
- 73 Betteshanger
- 91 Roseheyworth
- 93 Cardowan

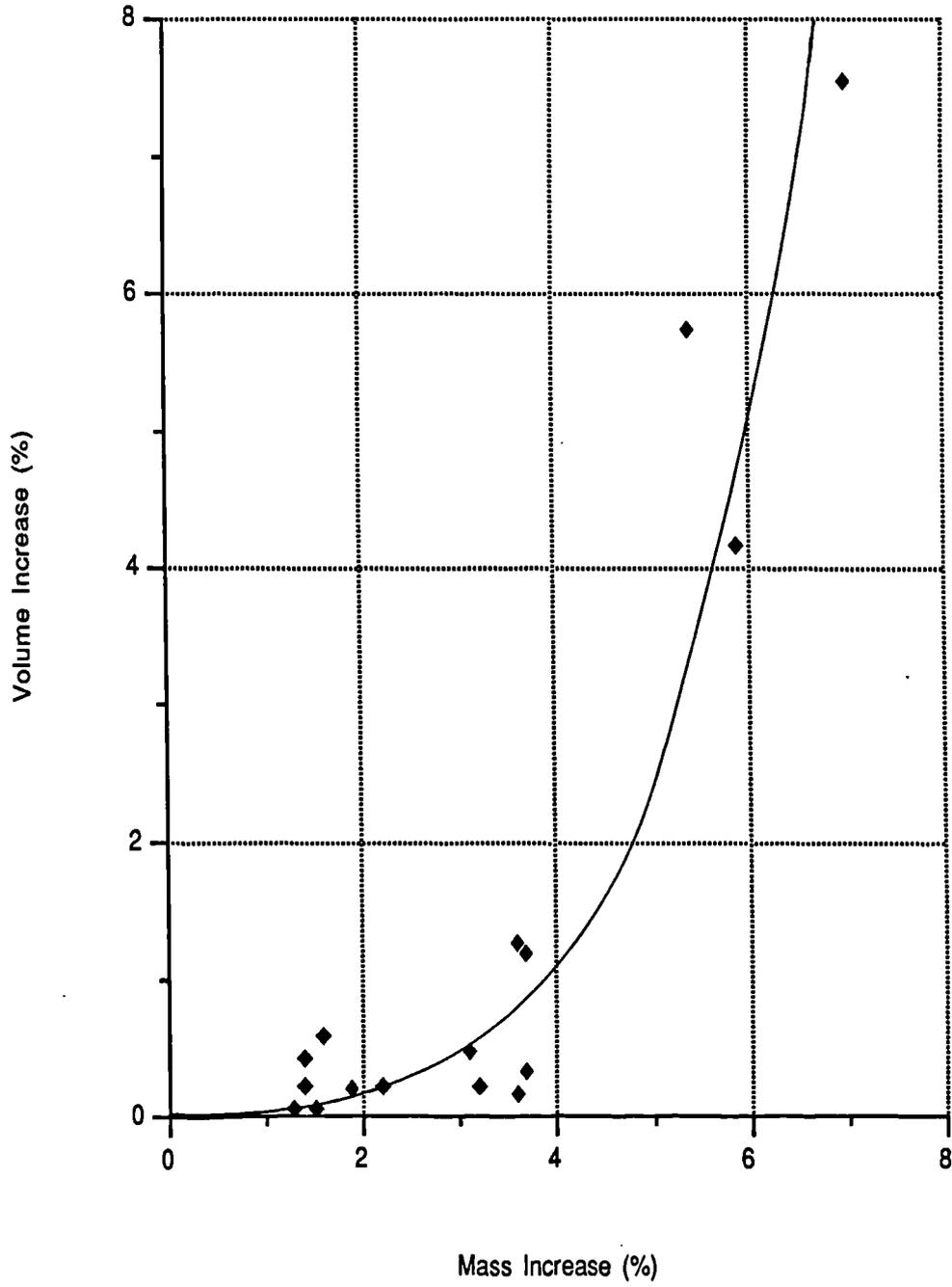
Only the following four CSMs gained strength during immersion (i.e. immersed strength greater than 7 day strength);

- 51 Bentinck Old
- 52 Bentinck Fresh
- 72 Tilmanstone
- 93 Cardowan

but none of these CSMs achieved strength gains equal to the equivalent specimens cured for 14 days at constant moisture content.

All specimens took up water into the matrix and exhibited volume increase, but the individual mass increases and volume changes showed substantial variation. The percentage volume increase (calculated from the linear dimensional changes) is related to the percentage mass increase of the samples as shown in Figure 7.6. The relationship is not linear, with large volume increases only occurring in specimens taking up at least 4% water. As the specimens were produced to 95% of their maximum dry density at least 5% (by mass of compacted specimen) water can be accommodated within the voids. A severe change in the volume increase was brought about by water uptake in excess of 5%. Beyond a certain value the swelling may no longer be contained by the specimen and, consequently, there was an overall increase in volume. A further explanation of this phenomenon may be that the majority of the swelling in soil cement occurs as a result of the saturation of the

Figure 7.6 Relationship between Volume Increase and Mass Increase for Immersed CSM Specimens.



less accessible voids (George, 1968) of the fines/cement matrix. This leads to surface adsorption and interlayer absorption, the mechanisms of which are discussed below.

The swelling of the stabilised specimens results in disruption of the cement bonds and degradation of the minestone particles leading to a loss in strength. The relationship between strength loss (as defined by Immersion Ratio) and the dimensional increase across the specimen diameter (during 7 days immersion) is shown in Figure 7.7. The properties of the minestone which influence the swelling potential of the CSM when exposed to water similarly affect the degree of strength loss of the specimens.

Approximately 50% of the total expansion due to the 7 day immersion period occurs in the first 24 hours, Figure 7.8. This value is somewhat lower than the previous findings (McNulty, 1985) and this may be due to the lower dry densities used in this study, the higher air void content enabling some of the initial expansion to occur within the matrix. However, the high correlation coefficient of 0.989 of the simple regression line in Figure 7.8 appears to confirm the proposal (McNulty, 1985) that the initial expansion (after 24 hours) may be used to predict subsequent behaviour. However, CSMs 71 and 81 exhibit 7 day expansion in excess of four times the 24 hour expansion.

All CSMs can be placed into two groups according to expansion following 24 hours immersion and Immersion Ratio (IR):-

- | | |
|--------------------------------|------------------|
| 1. Expansion less than 0.2% | IR exceeds 60% |
| 2. Expansion greater than 0.4% | IR less than 40% |

Figure 7.7 Relationship between Immersion Ratio and Swelling During Immersion for CSM.

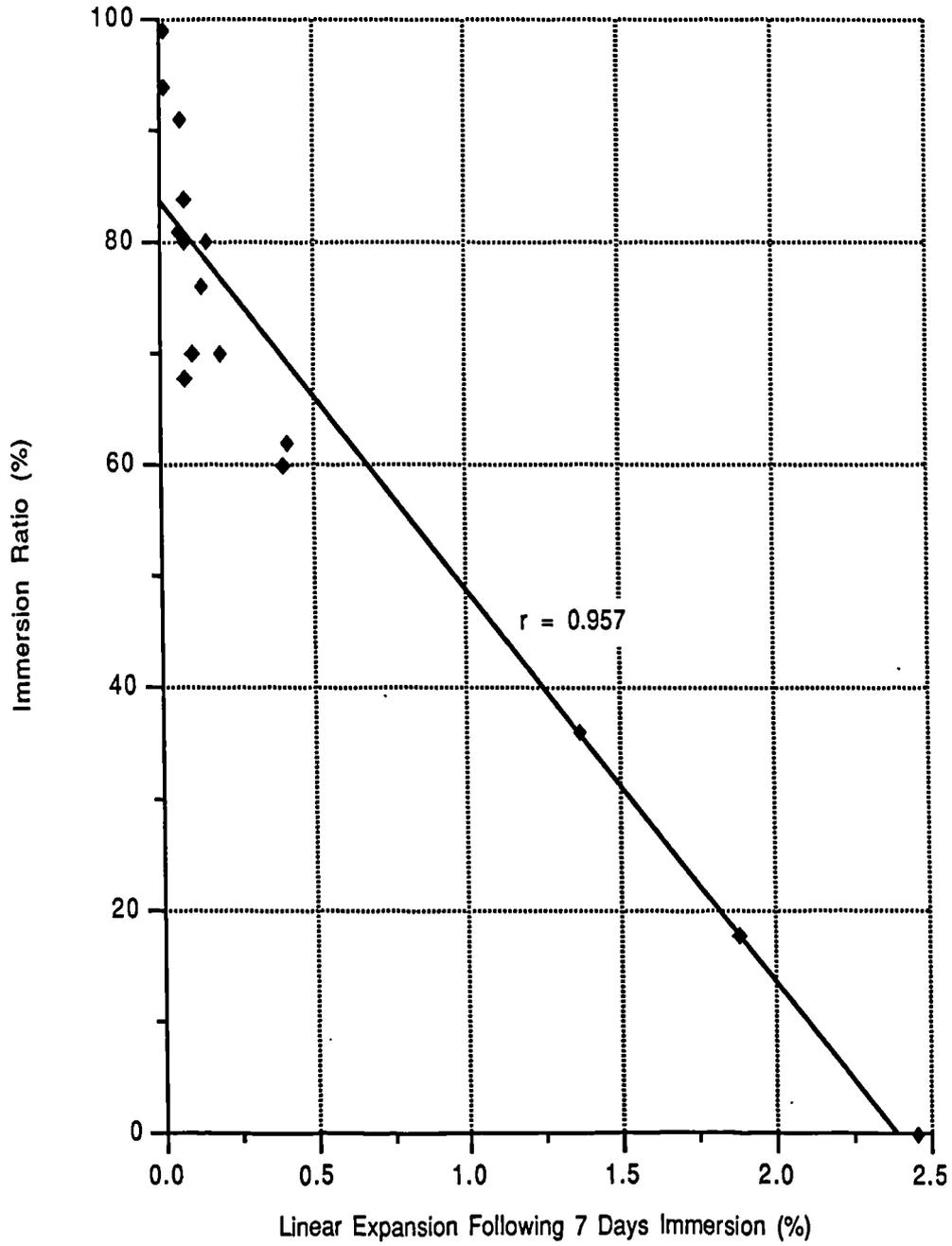
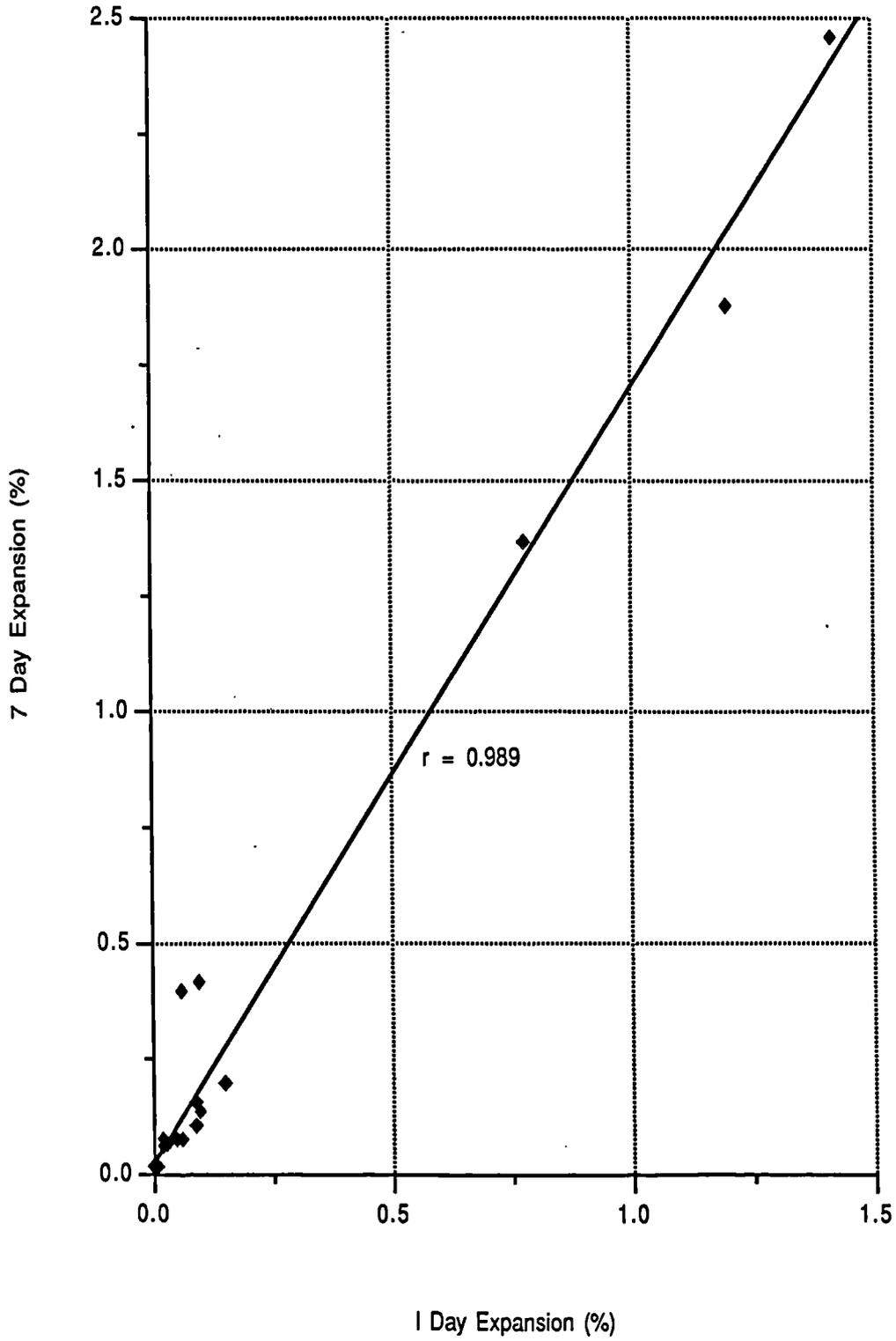


Figure 7.8 Relationship between 7 day and 1 day Expansion of Immersed CSM Specimens.



In contradiction to the findings of the earlier study (McNulty, 1985), none of the CSM specimens had ceased to expand at the end of the 7 day immersion period confirming an earlier study by the author (Thomas, 1985), in which CSM specimens of Wardley minestone continued to expand beyond 140 days continuous immersion. In addition, specimens were still increasing in mass at the end of the immersion period albeit at a much reduced rate. Most of this mass increase is associated with the increase in specimen volume but some water may still be required to fully saturate the smaller voids. McNulty (1985) proposed that CSM specimens attain their saturation moisture content after 24 hours immersion. The saturation point was determined by calculation using the specific gravities of the CSM constituents and dry densities to determine air voids. However, the specific gravities used were considerably lower than mineral grain densities (Morton *et al*, 1984) and consequently the micro-voids within minestone particles were not considered in the calculation of the saturation moisture content.

The causes of swelling in cement stabilised minestones are complex and to date several mechanisms have been proposed, and these are:-

1. Swelling of expansive clay minerals (Sherwood, 1968)
2. Sulphate attack on cement and/or clay minerals (Sherwood, 1968; Sherwood, 1962a),
3. Breakdown of mudstones due to slaking mechanisms (McNulty, 1985)

Although a well defined relationship between compressive strength and immersion resistance was not established, it appears that the soil properties which influence the former have a similar but more profound effect on both swelling during immersion and the immersion resistance. Relationships exist between the IR

and the sub-63 microns content, plasticity and slaking resistance and these are shown in, Figures 7.9, 7.10 and 7.11 respectively. No relationship is apparent between immersion resistance and the measured proportions of expansive clay minerals, confirming earlier findings (Rainbow and Sleeman, 1984). However, in this study the mineral percentages were calculated from the sub-2 microns fraction of the minestone and, since no account was taken of the total clay content, these do not represent actual proportions.

It is possible to surmise that the coarse-grained, less plastic minestones with high slake durabilities produce CSMs with a higher resistance to the effects of immersion in water than do the finely graded, plastic and "soft" minestones. Due to the high intercorrelation between these variables it is not possible from simple regression analysis to determine the most influential parameter.

The fact that the minestones with the highest fines contents tend to suffer the greatest expansions and strength losses is not necessarily an indication of the presence of swelling clay minerals. These minestones have usually undergone substantial degradation prior to stabilisation. With minestones having a high proportion of mudrock this breakdown may largely be due to air breakage (Taylor and Spears, 1970). Air breakage may, to some extent, be inhibited in a pre-wetted minestone. However, following cement stabilisation there is competition between the minestone and cement for the available moisture. If the moisture contents of any mudrocks fall below their hygroscopic requirements then the possibility of air breakage is reintroduced when more moisture is made available. These processes are often referred to as "slaking" (Terzaghi and Peck, 1967) and the resistance of a minestone to this kind of degradation may be evaluated by a suitable slaking test (Franklin and Chandra, 1972). The relationship between the modified slake index and the Immersion Ratio is shown in Figure 7.11. The relationship is statistically

Figure 7.9 Relationship between Immersion Ratio and Sub-63 Microns Content.

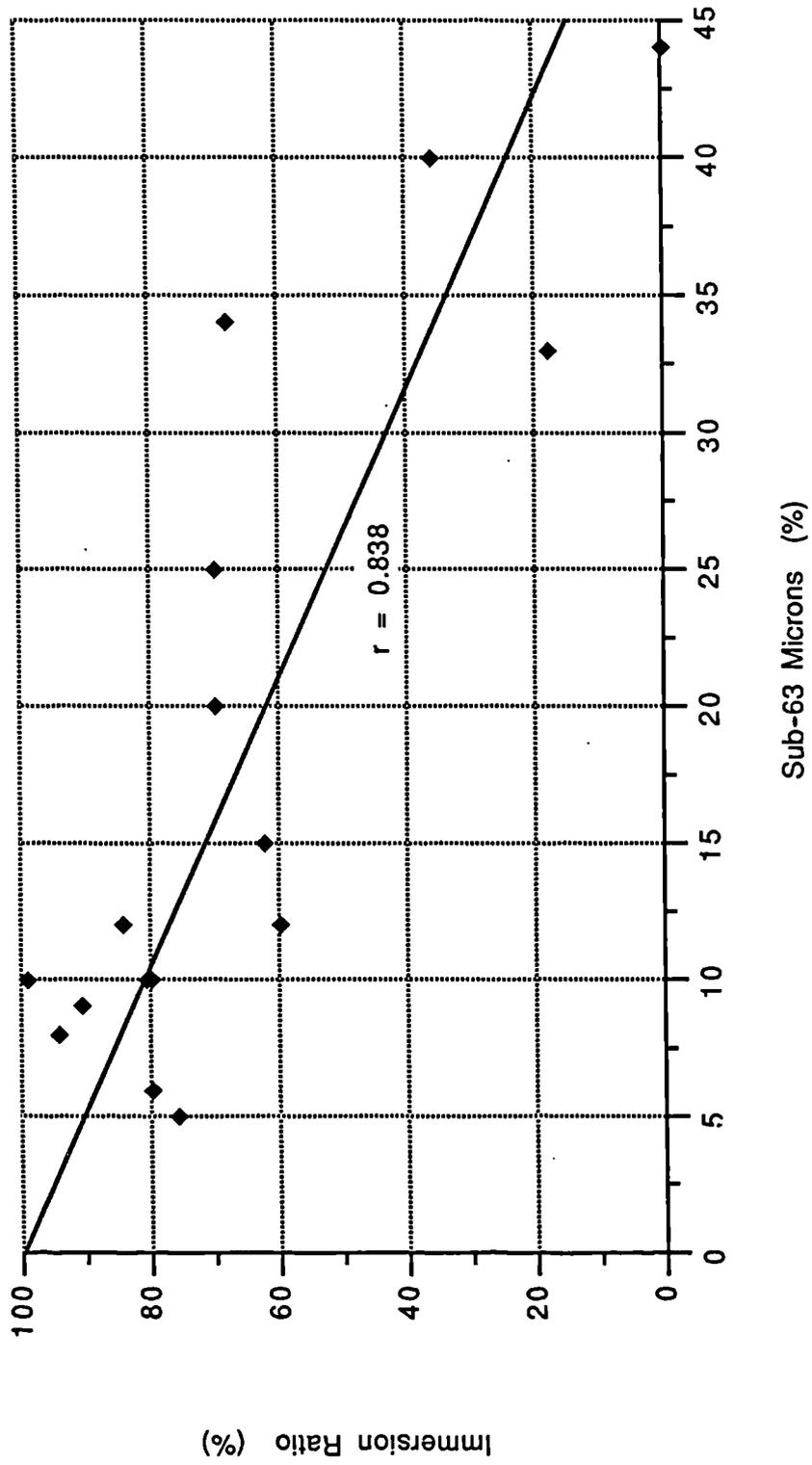


Figure 7.10 Relationship between Immersion Ratio and Plastic Limit.

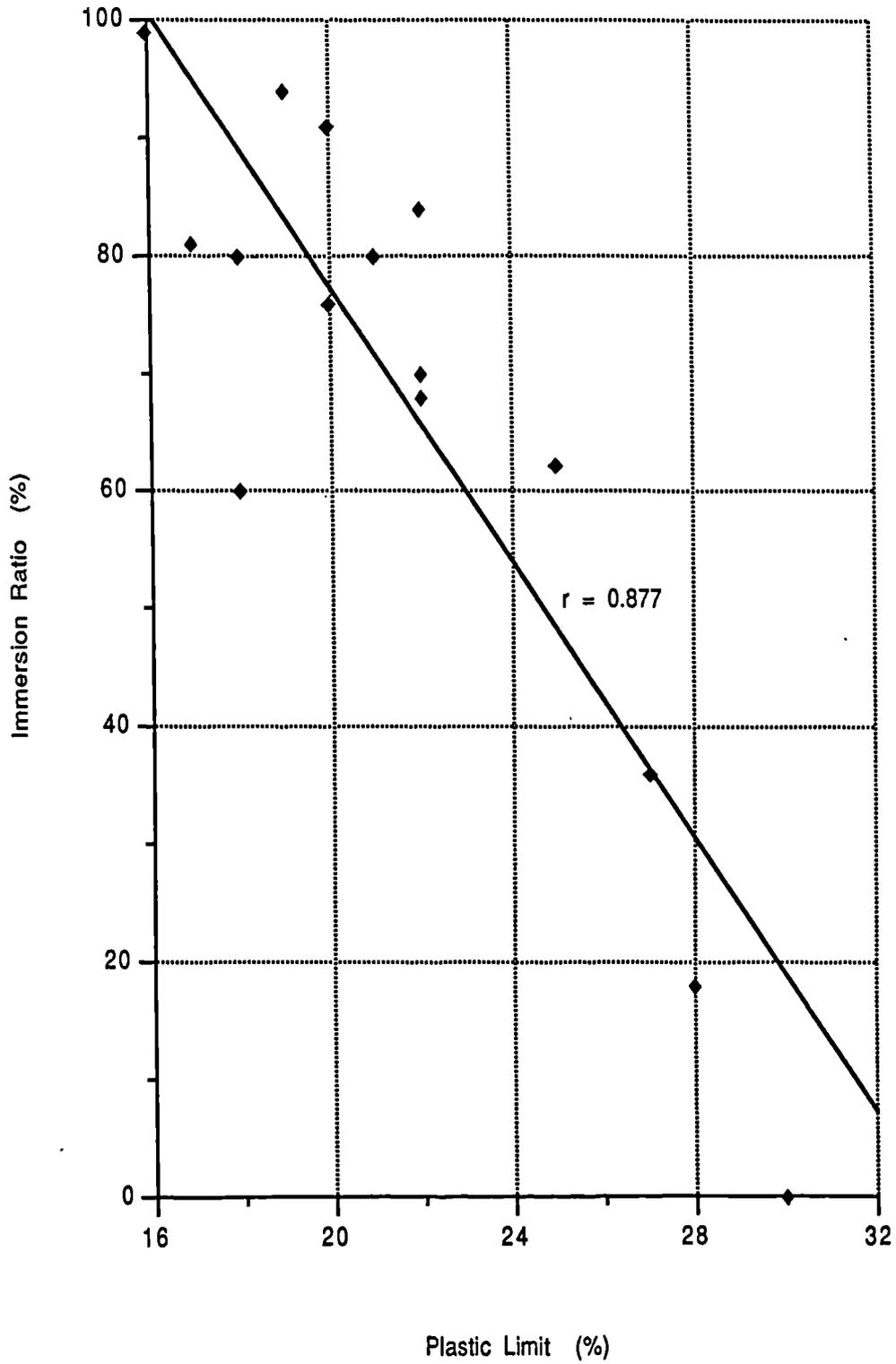
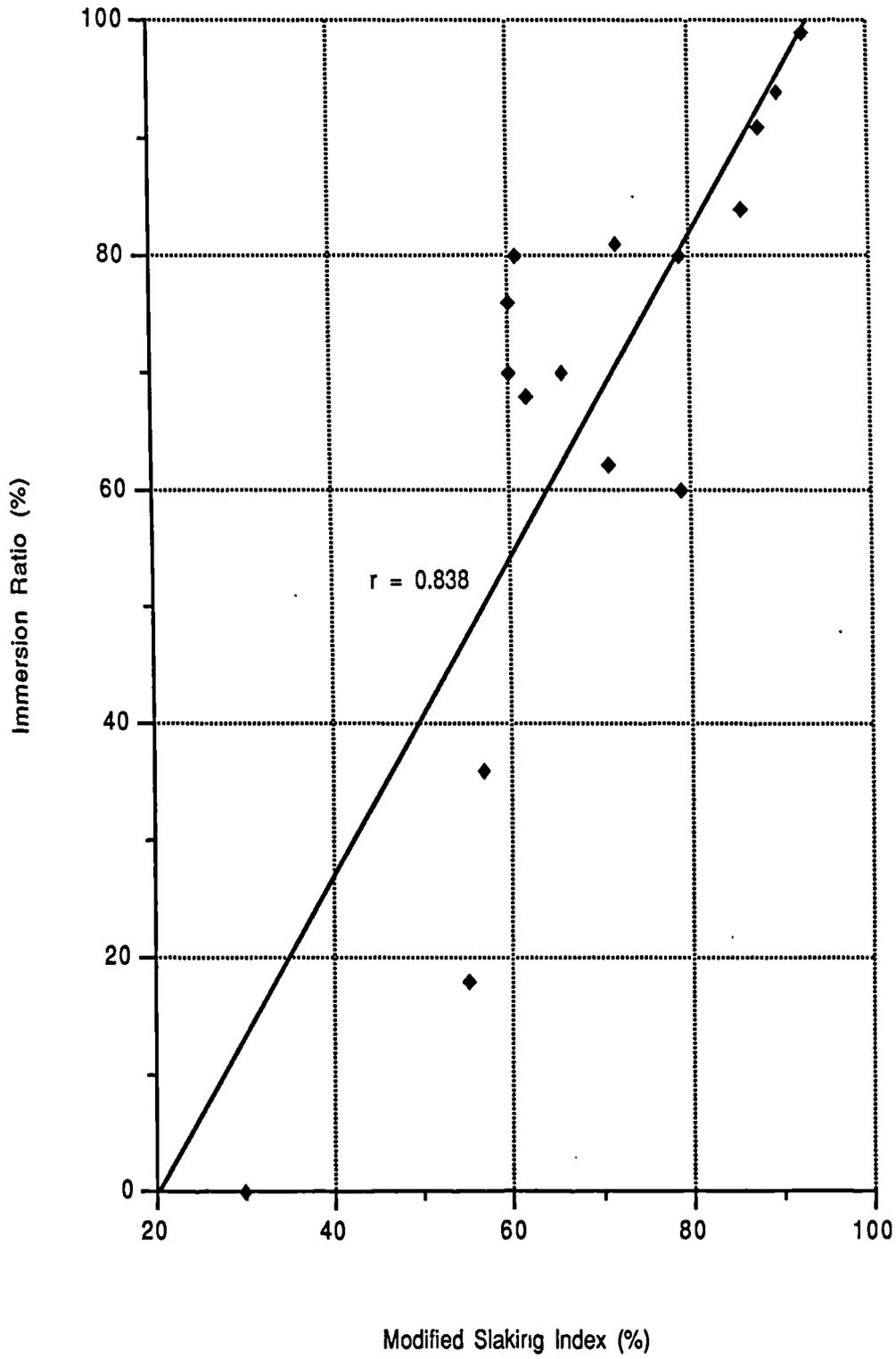


Figure 7.11 Relationship between Immersion Ratio and Modified Slaking Index.



significant at the 1% level with a correlation coefficient of 0.838. The slaking resistance of minestone 31 is considerably lower than all other minestones and slaking was probably responsible for the complete loss of strength of CSM 31, which is unique, despite other raw material similarities with 51, 52 and especially 92. Whereas the slaking characteristics of minestone are apparently important in determining the resistance of CSM to immersion they are not sufficient to accurately predict the IR. This is probably due to a combination of the mechanical properties of the sub-5 mm fraction (excluded from the slake test) and chemical properties of the raw minestone.

The material passing the 5 mm sieve is classified as being of sand, silt and clay size. These particles may behave similarly to the larger particles when subjected to fluctuations in moisture content. However, the more plastic, fine materials are likely to have clay/silt aggregations or clay flocs incorporated in the soil cement structure (see Section 2.5.2). The surface area within these flocs is substantial, hence, the adsorbed substances (cations and water molecules) play an important role in determining the mechanical properties of the flocs (Terzaghi and Peck, 1967). The abundance of calcium ions in a soil cement mix may result in base exchange with monovalent cations in the adsorbed layer, reducing the volume of the flocs. The hydration of cement, requiring up to 50% of its own weight of water (Neville, 1981), may result in the depletion of water molecules in the adsorbed layer. When excess moisture is made available the free water molecules may be attracted by the negatively charged surfaces of the flocs causing an increase in thickness of the adsorbed layer creating interparticle swelling. If the flocs contain expandable crystal lattices (probably mixed layer illite-montmorillonite in minestone) free water may penetrate the sheets creating volume increase due to intraparticle (or intracrystalline) swelling.

The surface activity plays a greater role as the particles get smaller and approach a colloidal state (Terzaghi and Peck, 1967). Hence the proportion of colloidal material together with a measure of colloidal properties is likely to give an indication of the effects of surface activity. The sub-2 microns content of minestone does not necessarily reflect the clay content, as non-clay minerals may be present in this size fraction. However, the plasticity does provide an indication of the activity of the material in the sub-425 microns fraction which is controlled by the content and mineralogy of the clay. Therefore, the use of a fines content and plasticity index together provide both an indication of the proportion of clay-size material and a measure of the clay properties.

Fine particle analyses were only performed for those minestones with more than 10% material passing 63 microns. Consequently sub-2 microns contents were only determined for eight of the minestones. However, the correlation between the sub-63 and sub-2 microns contents, where available, is high having a correlation coefficient of 0.939. Hence the sub-63 microns content may be used to provide an estimate of the proportion of clay-size material present in minestones. Relationships between IR, sub-63 microns content and plastic limit are shown in Figures 7.9 and 7.10 respectively.

In summary, the physical properties of the coarse particles that affect immersion resistance may be measured by the modified slaking index while the appropriate properties of the fine fraction may be assessed through a combination of plasticity and fines content. None of these indices alone is capable of selecting minestones with adequate durability when stabilised with cement. However, for each of the relationships, Figures 7.9 - 7.11, it is possible to propose a limiting value for each index to achieve an IR of 80%. These would be:-

- | | |
|---------------------------|------------------|
| 1. Sub-63 microns content | less than 20% |
| 2. Plastic limit | less than 25% |
| 3. Modified slaking index | greater than 60% |

The minestones satisfying these criteria are:-

- | | |
|----|----------------|
| 52 | Bentinck Fresh |
| 61 | Wardley I |
| 71 | Snowdown |
| 62 | Wardley II |
| 72 | Tilmanstone |
| 73 | Betteshanger |
| 91 | Cardowan |
| 93 | Roseheyworth |

With the exception of Snowdown all of these produced a CSM, at 10% cement, capable of achieving an Immersion Ratio of 80%. Although Snowdown minestone was physically comparable with the other minestones listed above an examination of the chemical properties listed in Table 7.3 shows that it has total and water soluble sulphate contents at least twice those of the other "accepted" minestones. It is thus suggested that its sulphate content of 0.96% is responsible for the greater swelling and strength loss of CSM 71 compared with CSMs produced from physically "alike" minestones. Thus for the coarse-grained, hard minestones the swelling during immersion would appear to be related to the total sulphate content. The relationship between the expansion following 7 day immersion and total sulphate for the eight CSMs listed above is shown in Figure 7.12. The relationship has a correlation coefficient of 0.914 and is statistically significant at the 1% level. The relationship between water soluble sulphate content and 7 day expansion is shown in

Figure 7.12 Relationship between Expansion following 7 days Immersion and Sulphate Content for Coarse-grained CSM.

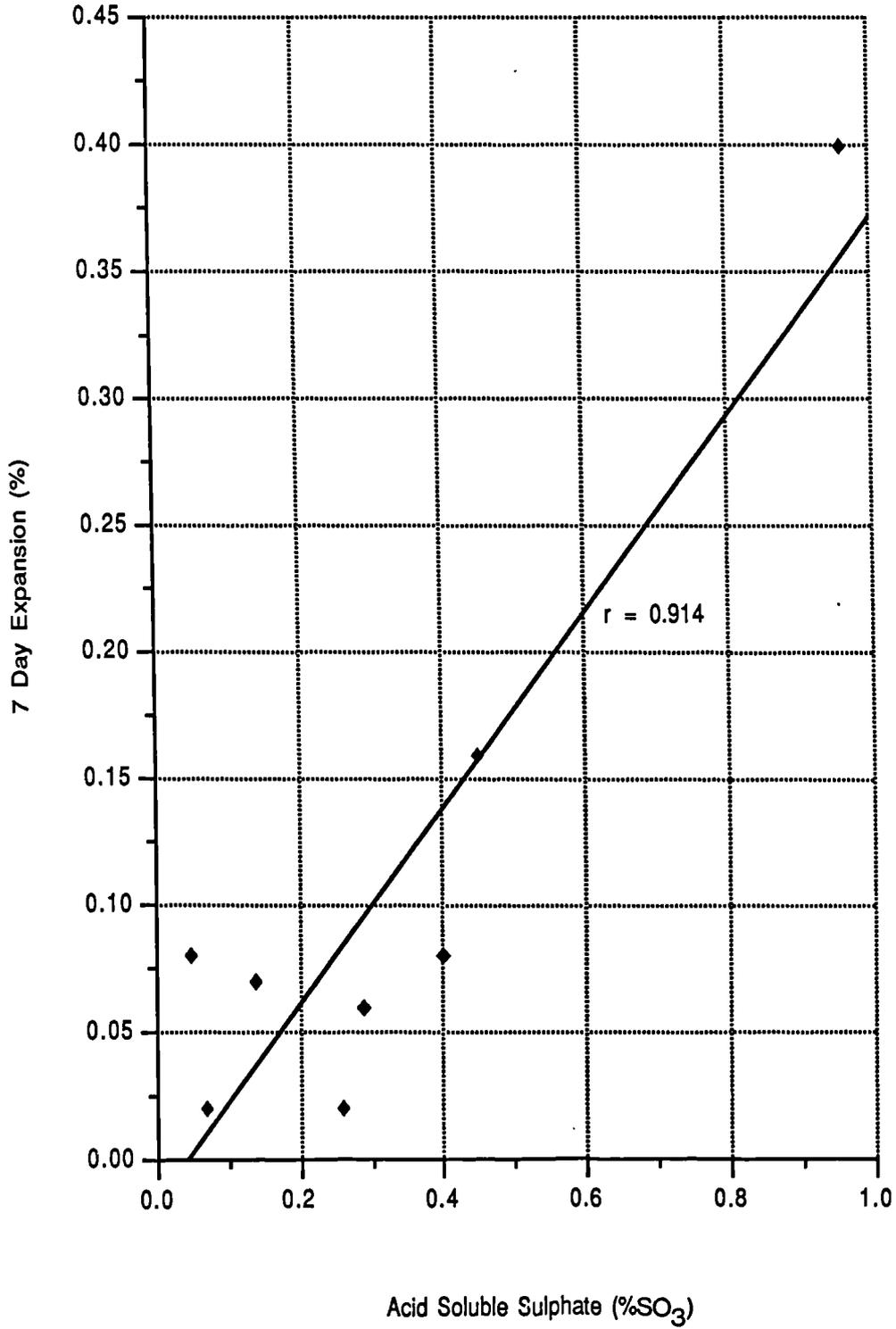


Figure 7.13. A slightly higher correlation coefficient of 0.924 was calculated for this regression line. The rate of sulphate attack will depend on the solubility of the sulphate minerals available (Sherwood and Ryley, 1970). During a 7 day exposure period it is likely that the water soluble sulphates will control the degree of expansion due to ettringite and gypsum formation (see Section 2.4.3). The high correlation between total sulphate and expansion reflects the high intercorrelation between acid and water soluble sulphate contents.

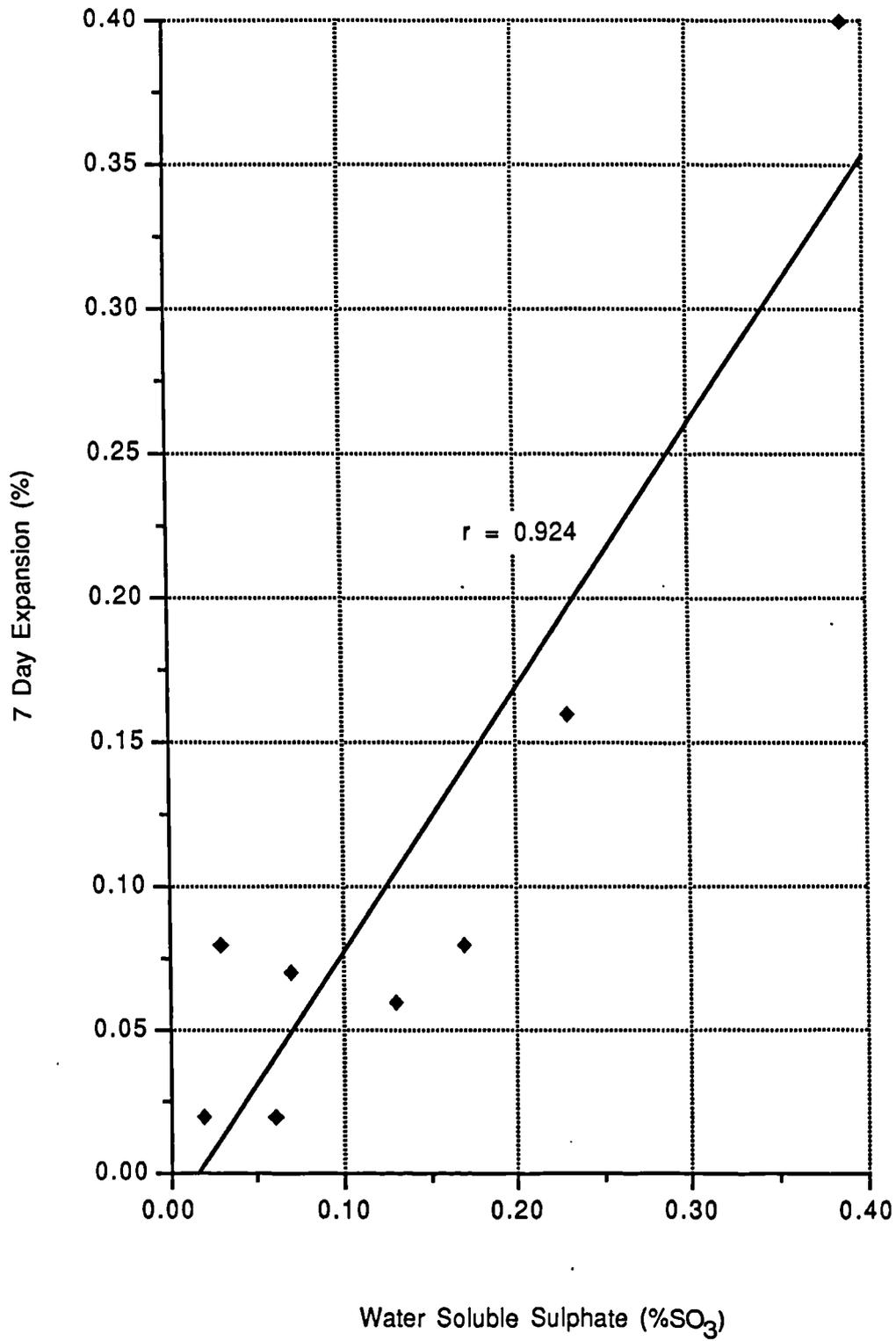
The expansion of CSM 71 following 24 hours immersion gave no indication of the expected total expansion. This CSM and CSM 81 both had actual 7 day expansions in excess of the predicted value from Figure 7.8 based on initial 24 hour expansion. Thus, the effects of sulphates on CSMs can not be detected by short periods of immersion . Indeed the full consequences are not necessarily experienced following 7 day soaking (Morton *et al*, 1984) and an investigation of long-term durability is required if the full effects of chemical attack are to be determined.

7.5.6 Prediction of Immersion Ratio from Raw Material Indices

Many single soil parameters may be used to predict the Immersion Ratio with limited accuracy. In order of decreasing correlation coefficient these are:-

<u>Index</u>	<u>Correlation Coefficient (r)</u>
Plastic limit	- 0.877
Liquid limit	- 0.860
Moisture content after slake test	- 0.850
Sub-63 microns	- 0.838
Modified slake index	0.837
Optimum Moisture Content	-0.837

Figure 7.13 Relationship between Expansion following 7 Days Immersion and Water Soluble Sulphate Content for Coarse-grained CSM.



A multiple regression was performed on the data presented in Tables 7.1 to 7.4. The first independent variable was chosen to give the greatest percentage fit ($100r^2$) and gives the following relationship:-

$$IR = 196 - 5.94 PL \quad 77.0\% \text{ fit}$$

where PL = plastic limit

The second independent variable was selected to give the greatest increase in the percentage fit:-

$$IR = 105 - 3.87PL + 0.663MSI \quad 83.4\% \text{ fit}$$

where MSI = modified slake index

The null hypothesis, that the immersion ratio is not dependent on the slake index, can be rejected at the 10% significance level. No other parameter offers a more statistically significant dependence. The third selection of the variable follows the same procedure as the second and results in the relationship:-

$$IR = 115 - 3.62PL + 0.529MSI - 34.3 WS \quad 87.0\% \text{ fit}$$

where WS = water soluble sulphate (as % SO_3)

Again the null hypothesis can be rejected at the 10% significance level. No further parameter can be added to the model in order to statistically increase the percentage fit at the 10% significance level.

The "best" equation satisfactorily explains 87% of the variation and is in agreement with the argument presented in Section 7.5.5. The plastic limit and modified slake index represent the sensitivity of a CSM to the effects of the physical swelling mechanisms in the fine and coarse fraction respectively whereas the water soluble sulphate content provides an indication of the expansion due to sulphate attack.

7.6 The Vacuum Saturation Test

The performance of the sixteen CSMs in the Vacuum Saturation Test is recorded in Table 7.4 with the other properties of the stabilised material. All specimens imbibed water and suffered a degree of expansion during the test and the relationship between mass increase and dimensional increase is shown in Figure 7.14. During this test, specimens absorbed on average 70% of the weight of water taken up during the 7 day immersion test, the relationship is shown in Figure 7.15. Either the vacuum pressure or the soaking period would need to be increased if the test specimens are to achieve the same degree of saturation as specimens immersed for a 7 day period. This contradicts earlier findings (Dempsey and Thompson, 1973) which suggest that a pressure of 610 mm Hg and a soaking period of one hour are sufficient for soil cement specimens to reach saturation.

A study of the data presented in Tables 7.1 to 7.4 evinces the correlation of the vacuum saturation swelling with the raw material properties plasticity, grading and slake durability. It has already been established that the swelling of specimens in the Immersion Test can be correlated with these properties. However, the expansion of CSM specimens subjected to the Vacuum Saturation Test represents, on average, less than 20% of the expansion following 7 day immersion (Figure 7.16). As discussed in Section 7.5.5 much of the water absorbed in the first instance has little associated expansion as it largely filled the voids and promotes only a small

Figure 7.14 Relationship between Expansion and Mass Increase following Vacuum Saturation of CSM.

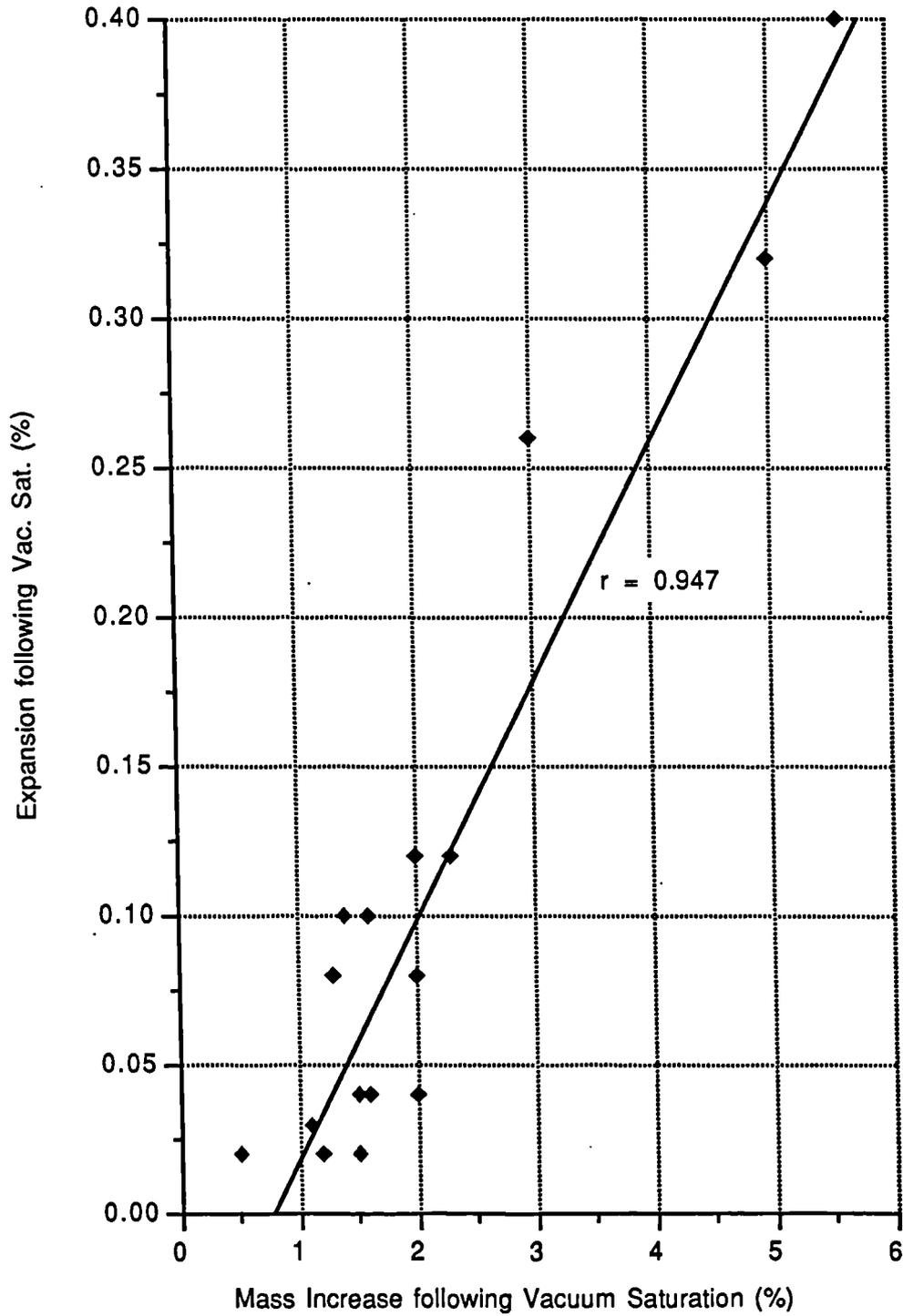


Figure 7.15 Relationship Between Mass Increase due to Immersion and Vacuum Saturation Tests.

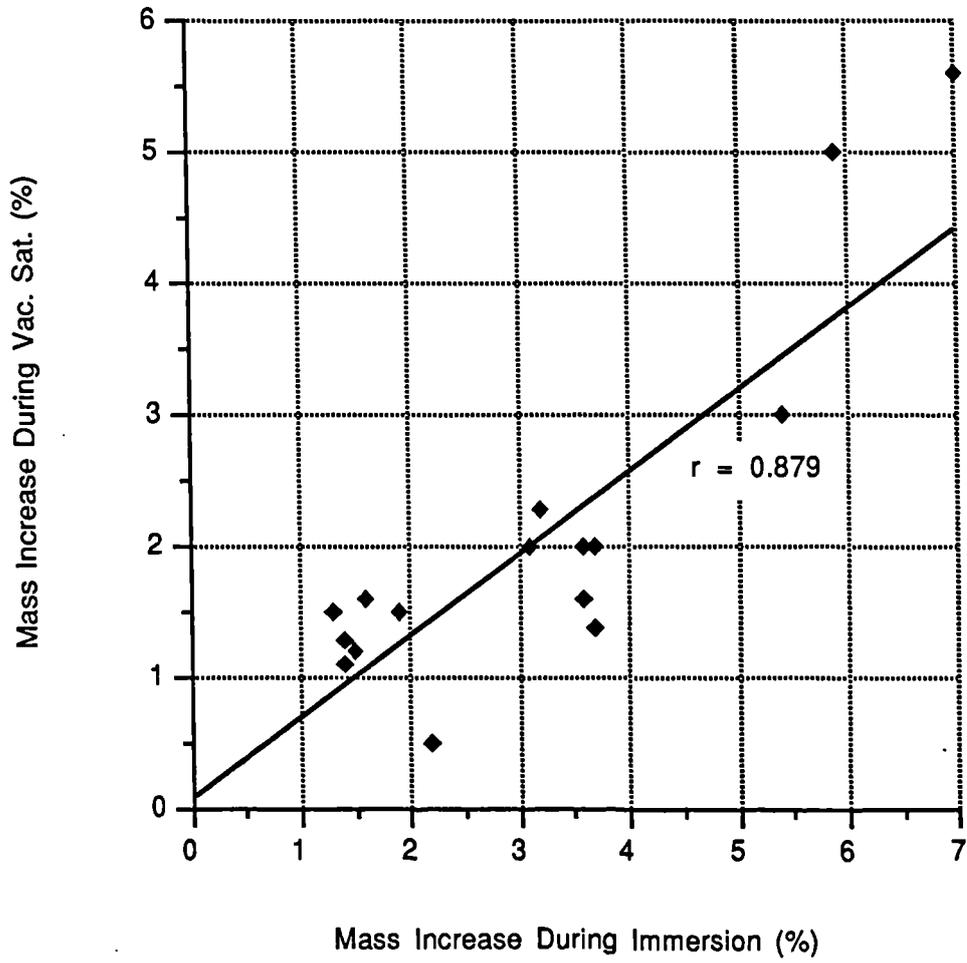
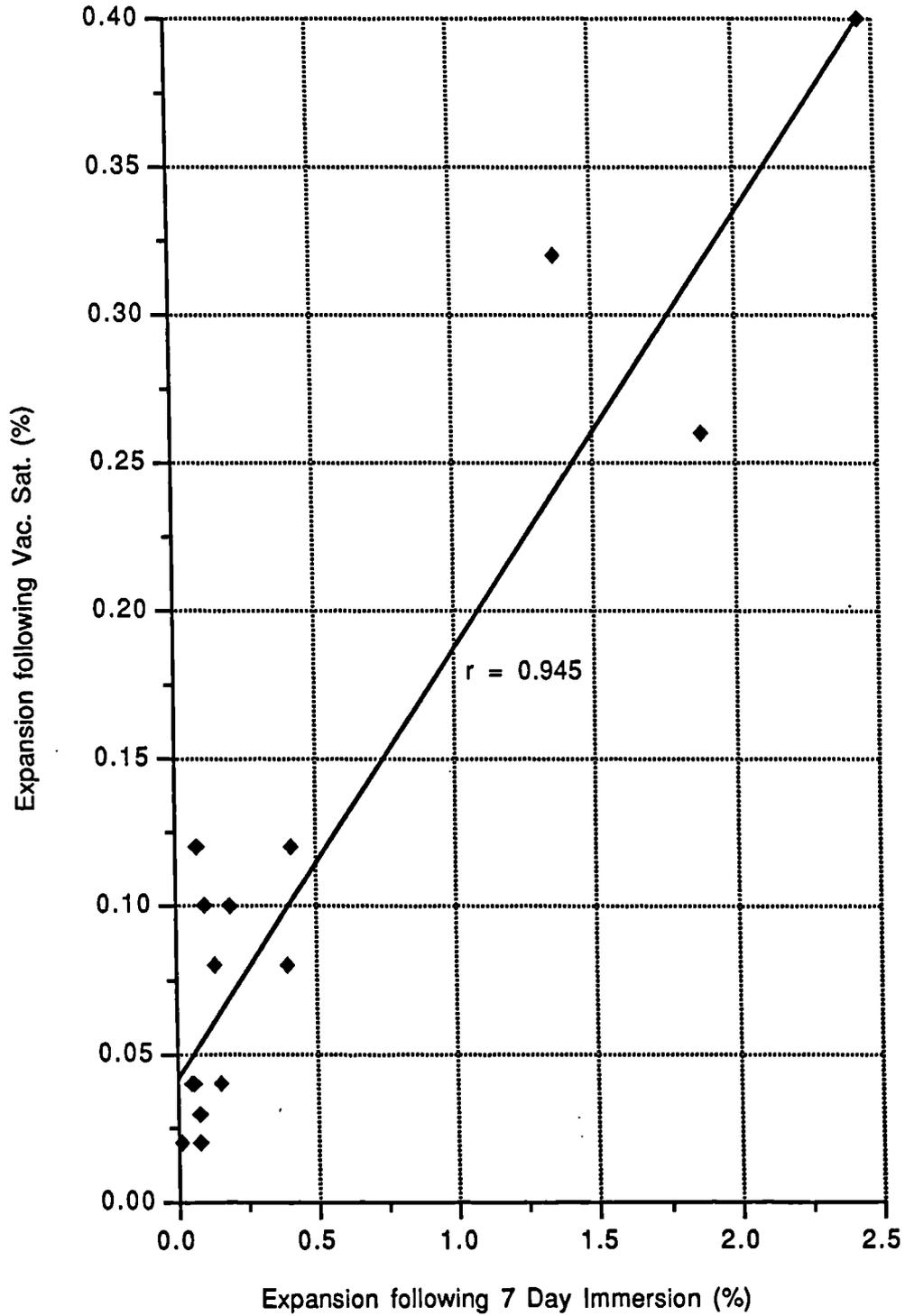


Figure 7.16 Relationship between Expansion in Vacuum Saturation and Immersion Tests for CSM.



proportion of interparticle swelling, consequently a reduction in the degree of saturation would be expected to result in a greater reduction of the associated swelling. In spite of the reduced level of saturation reached, the specimens subjected to the vacuum saturation test did expand and this expansion has been correlated with the expansion of specimens in the 7 day immersion test, as shown in Figure 7.16.

The Vacuum Saturation Ratio (VSR) is a measure of the strength change due to the saturation of CSM specimens *in vacuo*. The VSR ranges from a mere 30% for CSM 31 to 110% for CSM 72. Where strength loss occurred it did so as a result of the swelling of the matrix and individual minestone particles causing disruption to the cement bonds and fracture of minestone particles respectively. Consequently , a strong relationship exists between VSR and specimen expansion and this is shown in Figure 7.17. A small strength gain was recorded for some specimens following vacuum saturation and this occurs as a result of experimental scatter.

7.7 Prediction of the Immersion Ratio from the Vacuum Saturation Test

A comparison of the unconfined compressive strengths of CSM subjected to the Immersion Test and to the Vacuum Saturation Test is given in Figure 7.18 and shows a strong linear relationship. A simple linear regression performed on the data virtually passes through the origin and has a gradient close to unity. The equation of the relationship may be written as:-

$$f_{imm} = 0.061 + 0.912f_{vac} \quad 94.8\% \text{ fit}$$

where f_{imm} = compressive strength after 7 day immersion test

f_{vac} = compressive strength after vacuum saturation test

Figure 7.17 Relationship between Strength Loss and Expansion following Vacuum Saturation of CSM.

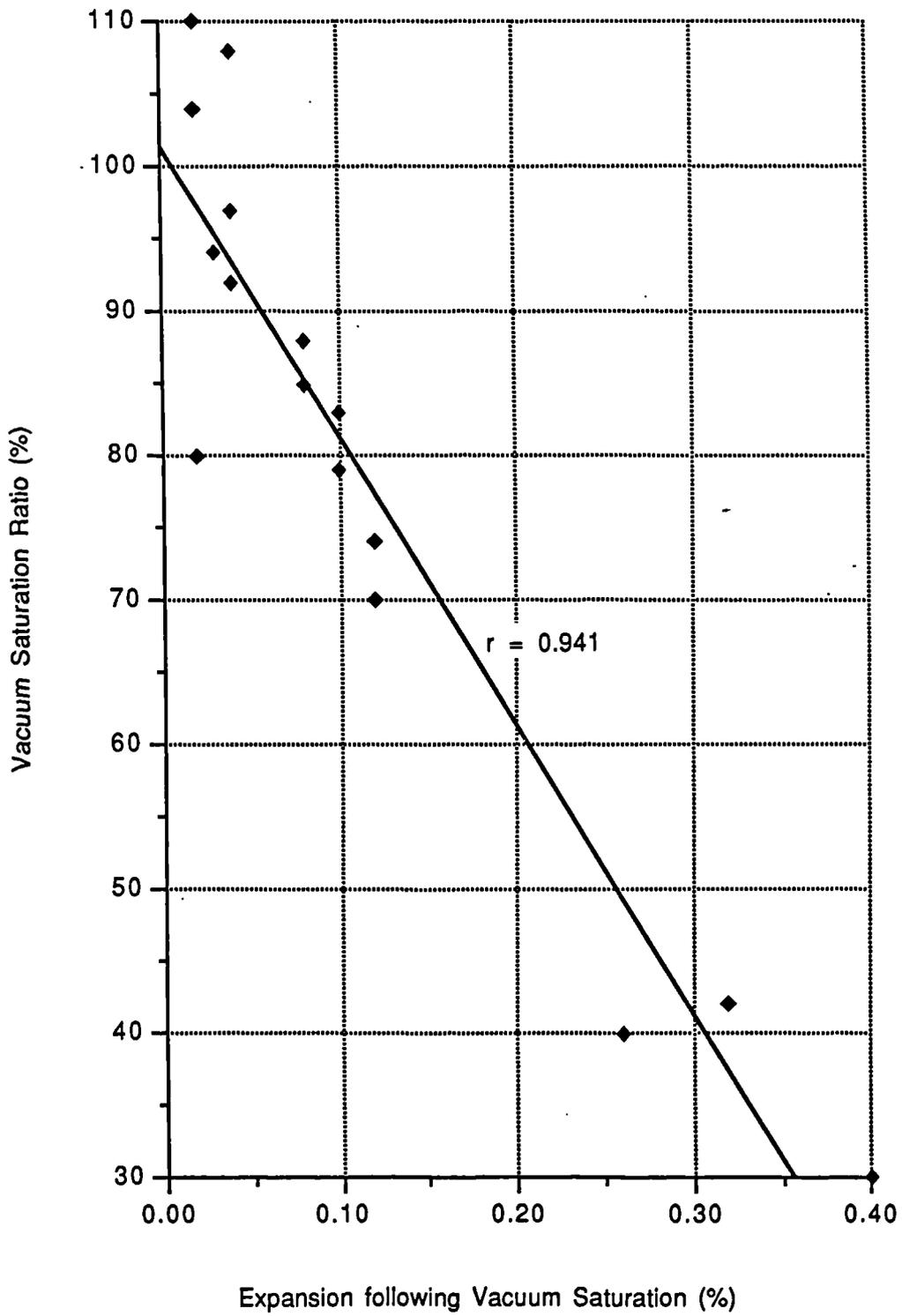
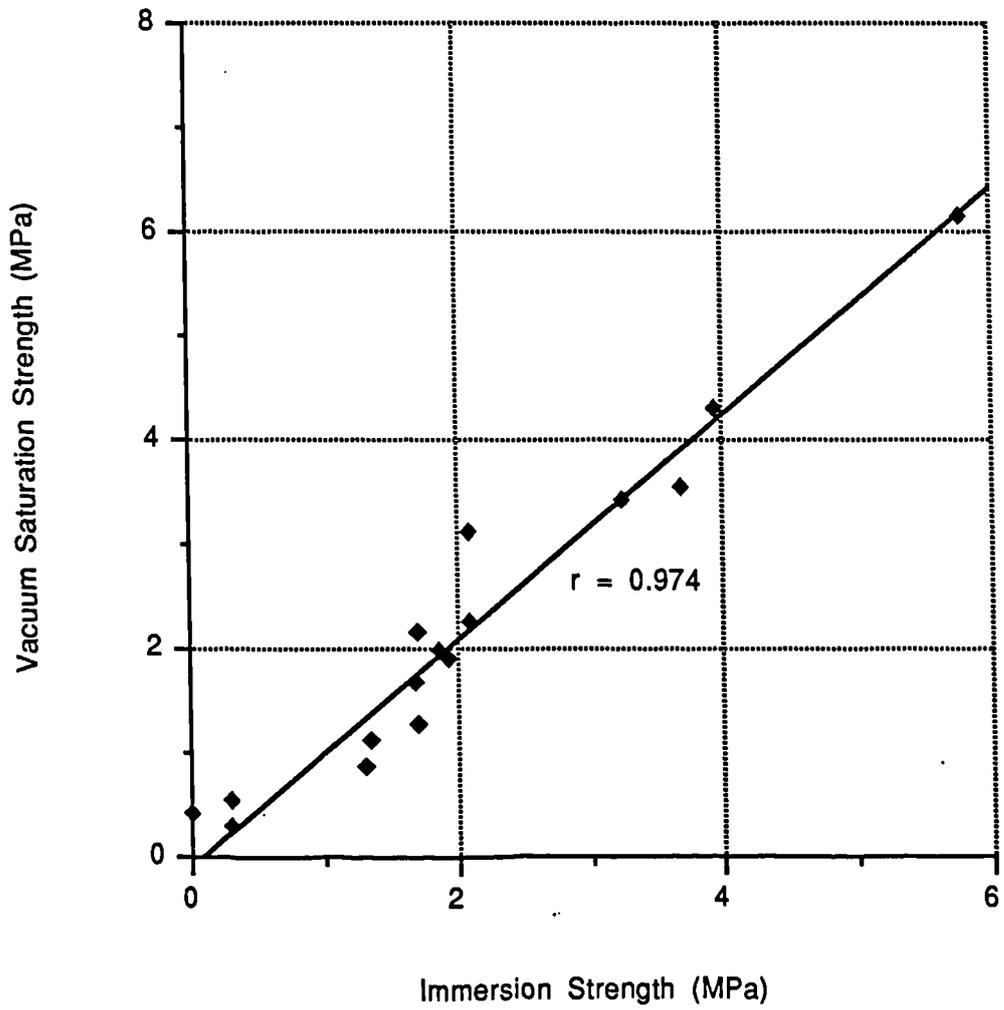


Figure 7.18 Relationship between Immersion and Vacuum Saturation Strengths for CSM.



Approximately, the strength following vacuum saturation is equal to the strength following 7 day immersion. This behaviour could not be predicted since the magnitude of expansion after the Vacuum Saturation Test test is a factor of one fifth that following immersion and hence a smaller strength loss was anticipated. The additional 7 days curing time of the Immersion Test specimens may account for some of the equality in strength as a result of further cement hydration.

The relationship between IR and VSR for the stabilised minestones is shown in Figure 7.19. The correlation between these ratios is 0.956 and the equation of the relationship is:-

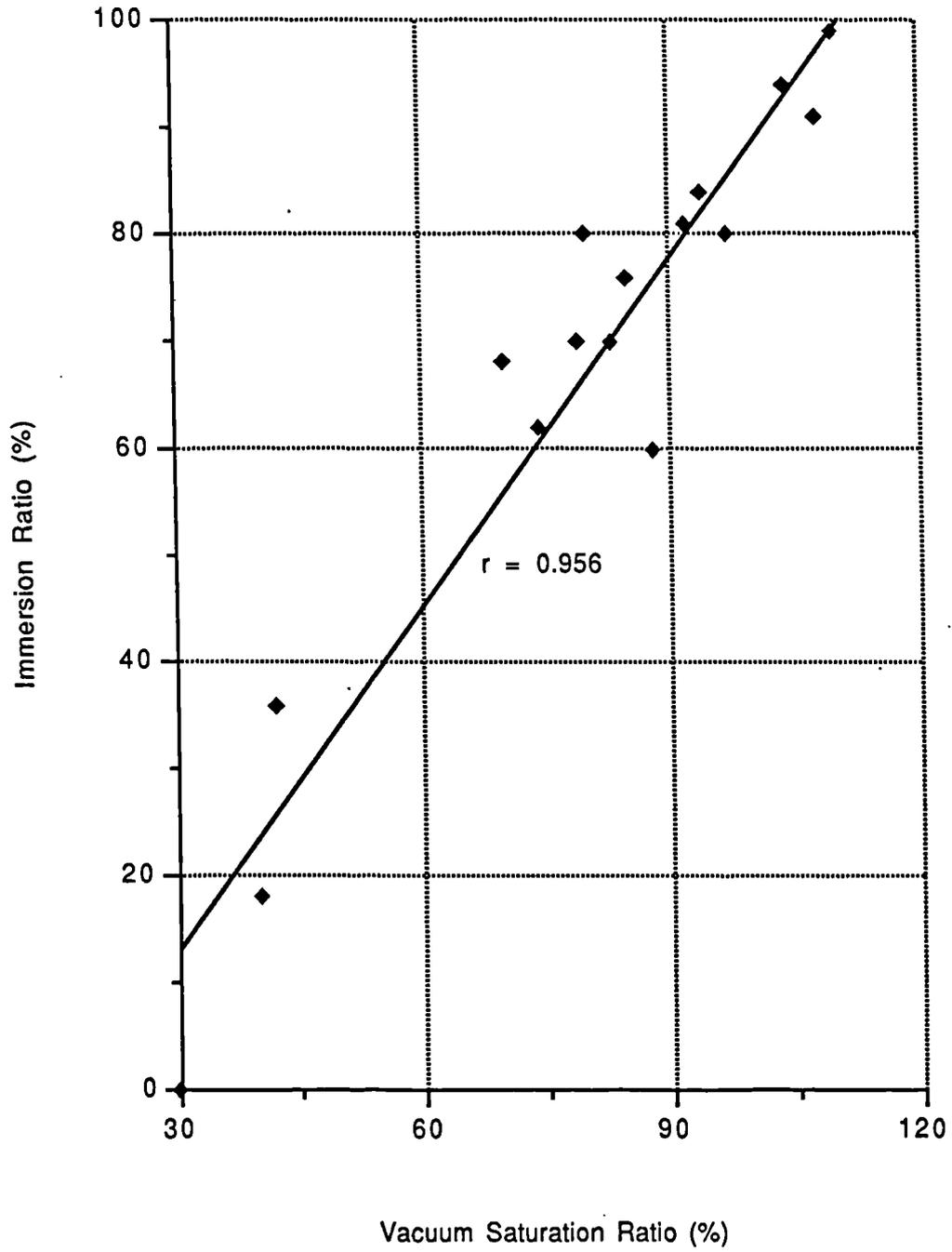
$$IR = 1.09VSR - 19.8 \qquad 91.4\% \text{ fit}$$

A multiple regression analysis using VSR as the first independent variable was performed on the data available. The parameter that increased the percentage fit by the largest increment was the water soluble sulphate content, the equation being:-

$$IR = 0.971VSR - 33.7WS - 4.75 \qquad 95.1\% \text{ fit}$$

The null hypothesis, that IR is independent of the water soluble content, can be rejected at the 1% level of significance. This model is the "best" prediction of the Immersion Ratio on statistical grounds. The Vacuum Saturation Ratio provides an assessment of the effect of physical swelling mechanisms when specimens are subject to immersion. However, the duration of inundation is not sufficient to detect the action of deleterious sulphates and the inclusion of the water soluble sulphate parameter is required to account for the chemical mechanisms operating in the longer 7 day immersion period.

Figure 7.19 Relationship between Immersion Ratio and Vacuum Saturation Ratio for CSM.



The strong correlation of this relationship suggests that the mechanism of air breakage has little effect on the swelling of CSM. Particles evacuated prior to inundation will not be susceptible to capillary tension forces as they will not contain sufficient gas to generate significant internal pressure. Interparticle swelling due to ion adsorption and ionic dispersion together with intraparticle swelling due to the absorption of water between expandable clay mineral lattices are not inhibited by evacuation prior to the inundation of specimens. On the contrary, these effects may be accelerated due to the increased accessibility of the smaller voids. Thus the results of the regression analysis would suggest that a combination of some or all of these last three mechanisms together with sulphate attack (particularly that involving the more soluble sulphate minerals) are responsible for the swelling of CSM specimens in the Immersion Test.

7.8 Summary

The short-term durability of cement stabilised minestone is controlled largely by the properties of the raw minestone such as grading, plasticity, slaking resistance and sulphate content. Predictions of both expansion and strength loss due to immersion can be made from these parameters and the Vacuum Saturation Test. However, the effect of sulphates on the CSM, although noticeable, can not be accurately assessed during short periods of immersion (even 7 days). A study of the performance of CSM subjected to long-term moisture exposure together with the geochemical stability of the stabilised material is required if the behaviour of the material through "realistic" life times is to be understood.

8. ANALYSIS AND DISCUSSION OF RESULTS FROM THE LONG-TERM DURABILITY INVESTIGATION

8.1 Introduction

This chapter is concerned with the performance of CSM when exposed to three different environments for periods of up to 410 days. Engineering performance is quantified in terms of the dimensional stability and strength development of the CSM specimens. The specimens used for the long-term study were prepared as in the short-term study (Chapter 7) and the method of preparation has been detailed in an earlier section (Section 6.4).

The sulphur bearing mineralogy was monitored throughout the exposure of the First Phase CSMs by chemical analysis. The engineering behaviour and geochemical alterations are correlated and efforts have been made to suggest tolerable limits for the sulphur bearing minerals if excessive long-term expansion and strength losses are to be avoided. XRD and SEM studies have been made on the material at the locations of disruption and cracking. Attempts have also been made to determine the role of bacteria in the geochemical processes.

8.2 Dimensional Stability and Associated Mass Changes

The behaviour of polythene wrapped specimens varied between a shrinkage of the order of 25 microns (CSM 51) and a maximum expansion of 255 microns (CSM 31) across the 50 mm specimen diameter. Any dimensional changes experienced by the polythene wrapped specimens had ceased within 50 days of demoulding and no further changes were noticed. There were no mass changes associated with any of

these specimens. The small amount of shrinkage that was detected in some CSMs may be attributed to shrinkage of the cement paste itself, a common phenomenon in concrete (Neville, 1981). The swelling occurred in the stabilised specimens formed from the more plastic minestones, with higher fines contents, and this may result as a consequence of the mudrocks absorbing some of the water added during mixing.

The changes in linear dimension with time for CSMs exposed to Environments 2 and 3 are tabulated in Appendix D1 and presented graphically in Figures 8.1 to 8.4. Following 410 days immersion the magnitude of swelling, for specimens exposed to Environment 2, varied between 116 microns (CSM 61) and 2064 microns (CSM 41) and for those in Environment 3 the range was 105 to 1694 microns (for the same CSMs). CSMs 31, 41, and 92 expanded at a far greater rate than the other materials and this might have been predicted from their excessive swelling in the standard 7 day immersion test (Chapter 7). All three of these CSMs produced a linear expansion in excess of 2% (1mm) with CSM 41 displaying swelling in excess of 4% in Environment 2. Generally, the remaining CSMs, produced from the coarse-grained, less plastic minestones, did not exhibit linear expansion in excess of 1% (500 microns). The only exception was CSM 71 which suffered an increase in diameter of over 1.3% due to the effects of immersion. On average, the 410 day expansion is a factor of 3 times greater than the 7 day expansion. This factor varies between 1.5 (CSM 31) and 5.4 (CSM 52). The final dimensions of eleven of the sixteen CSMs exposed to Environment 3 exceeded those of the same CSMs in Environment 2.

Although the rate of expansion decreases with time none of the CSMs had reached volume stability at the termination of this study. This fact may be better illustrated by plotting the expansion against the logarithm of the exposure period and examples of these relationships are shown in Figures 8.5 and 8.6 for Environments 2 and 3

Figure 8.1 Expansion of First Phase CSMs in Environment 2

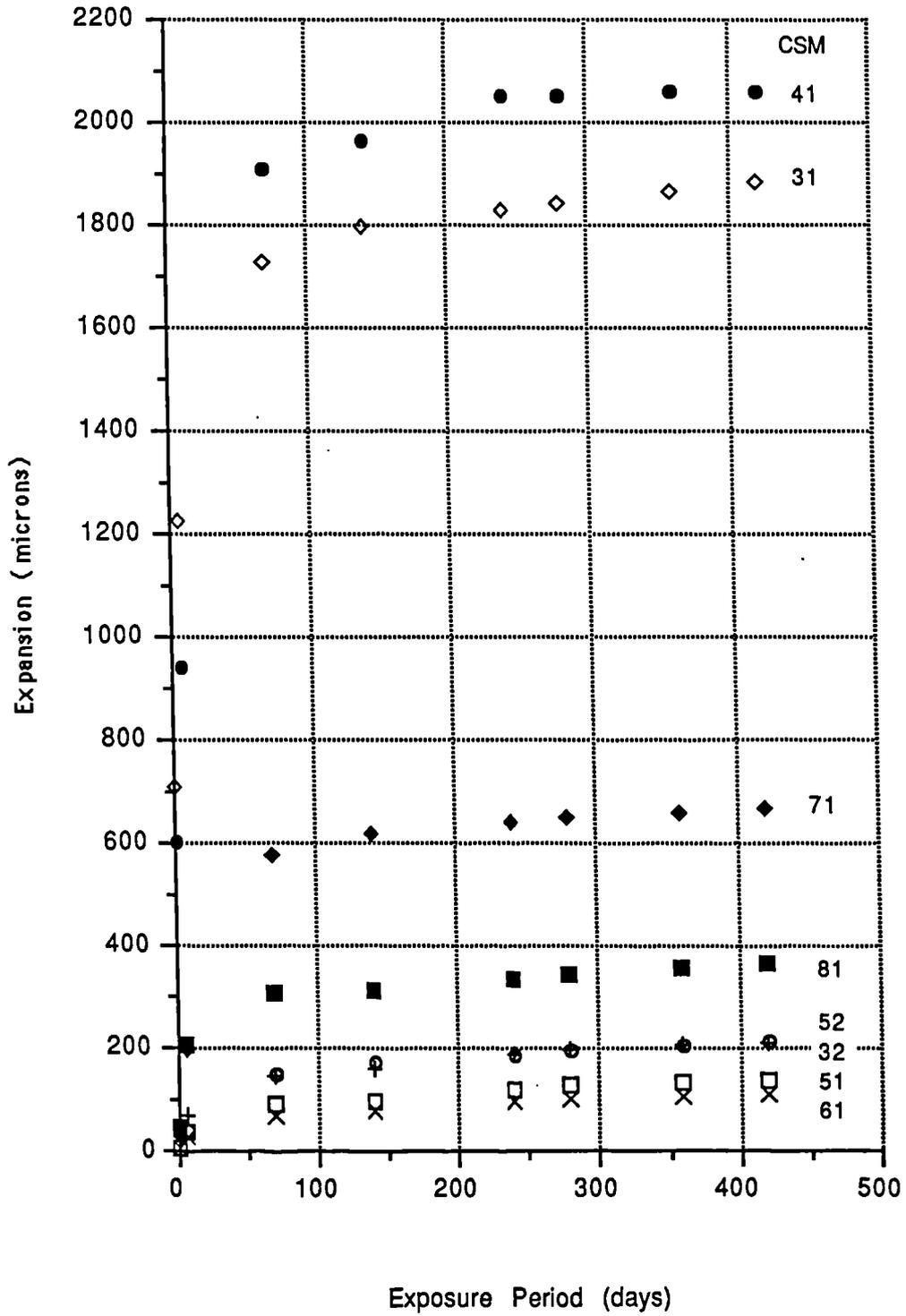


Figure 8.2 Expansion of First Phase CSM s in Environment 3.

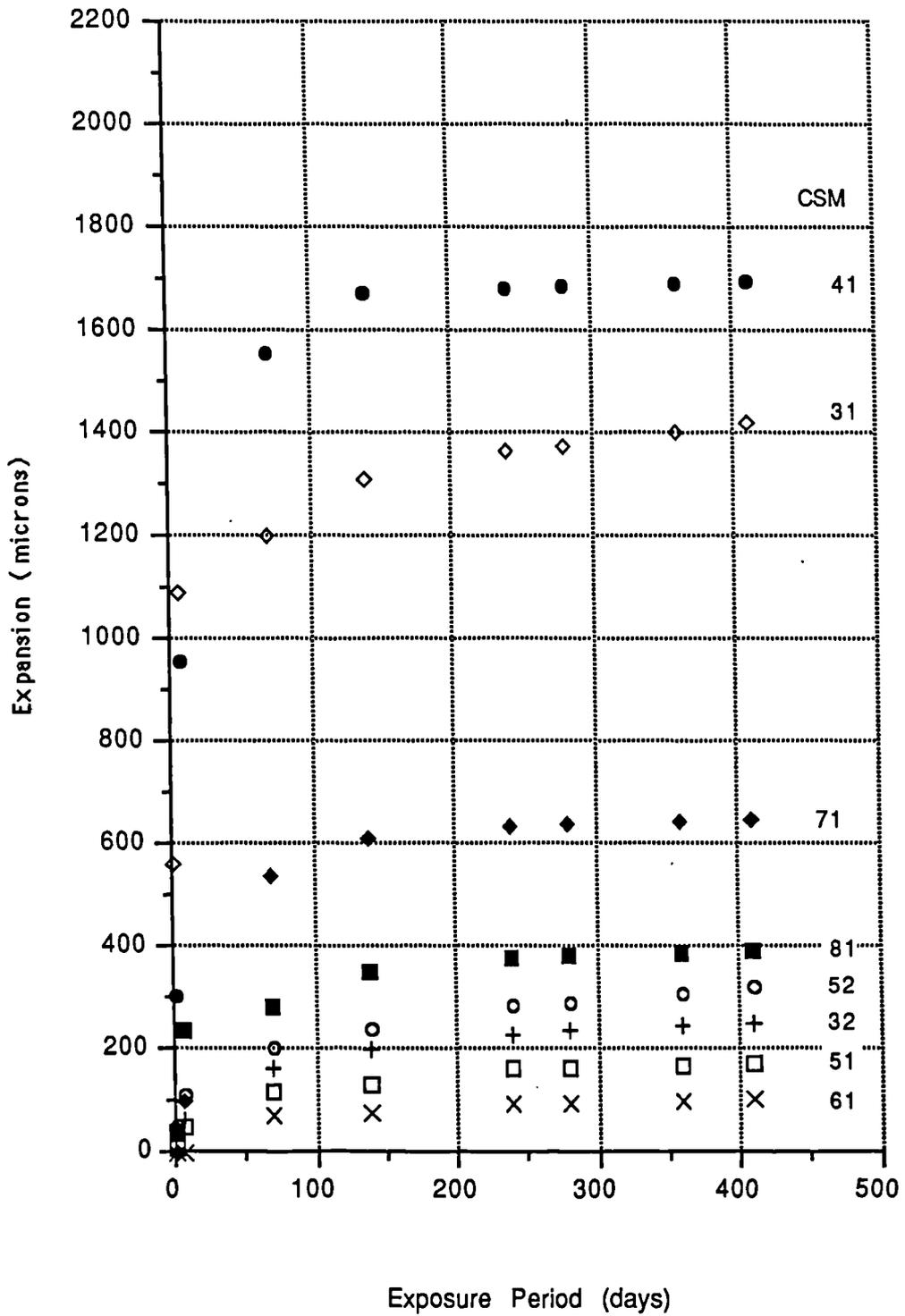


Figure 8.3 Expansion of Second Phase CSMs in Environment 2.

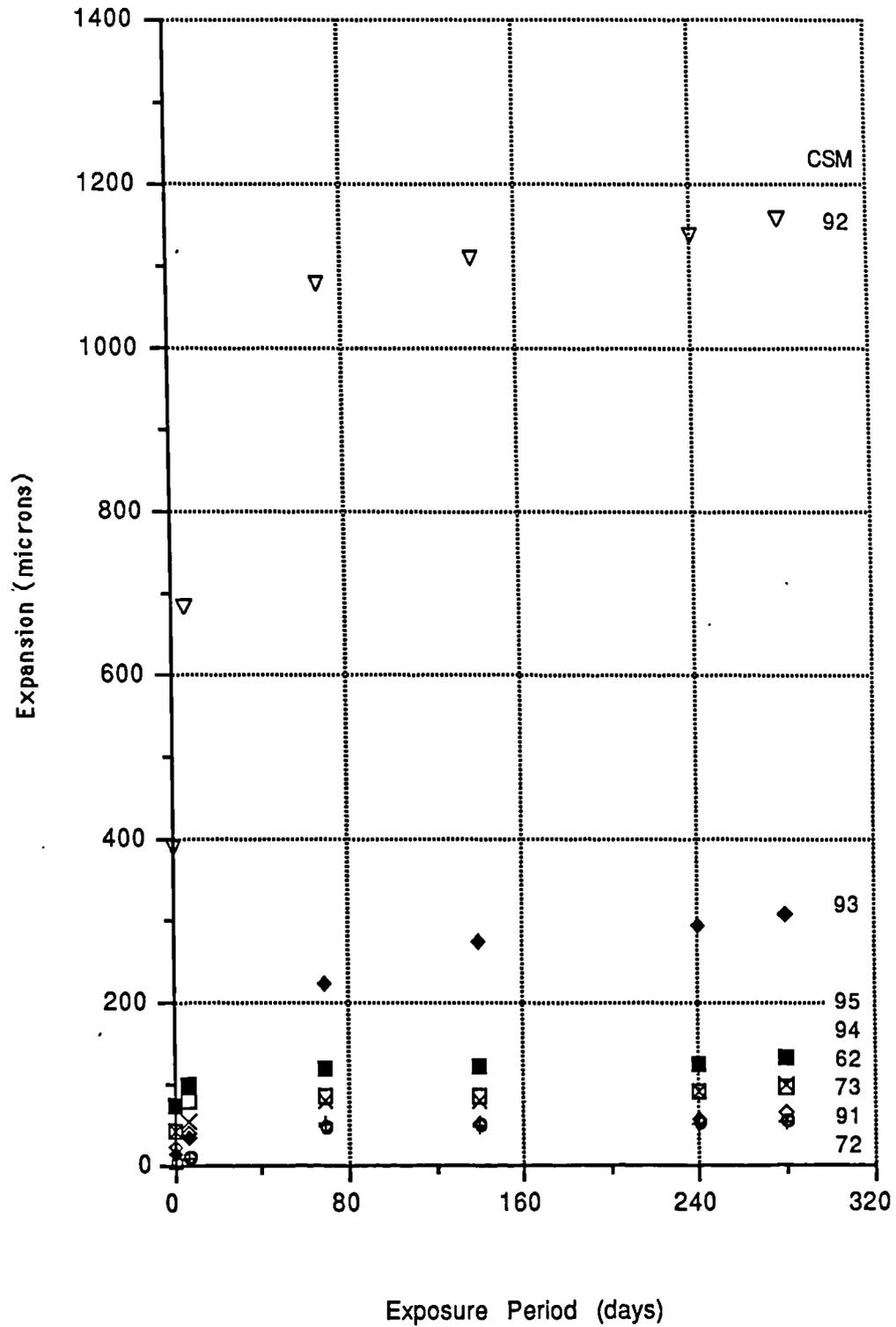


Figure 8.4 Expansion of Second Phase CSMs in Environment 3.

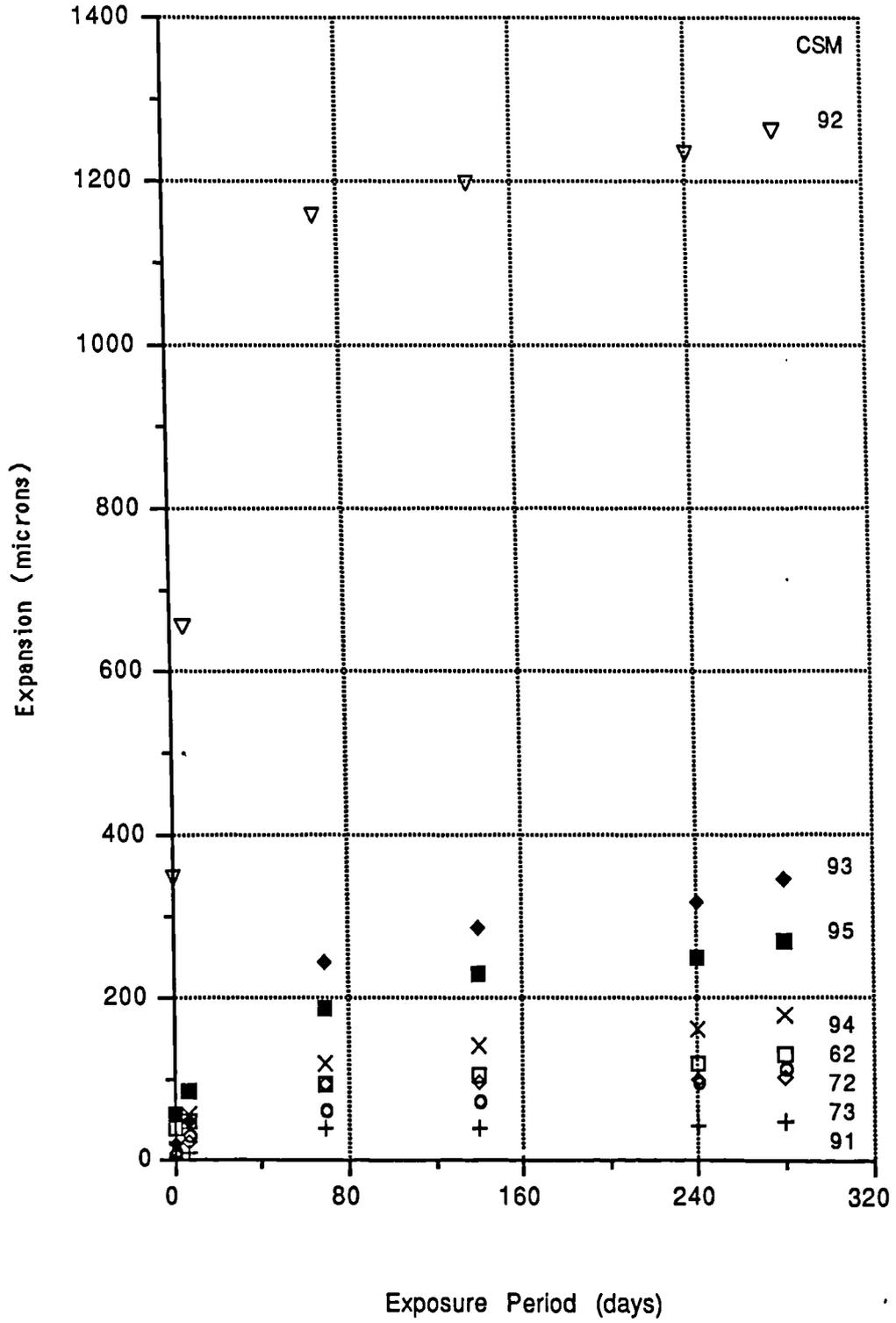


Figure 8.5 Relationship between Expansion of CSM in Environment 2 and Log Exposure Period.

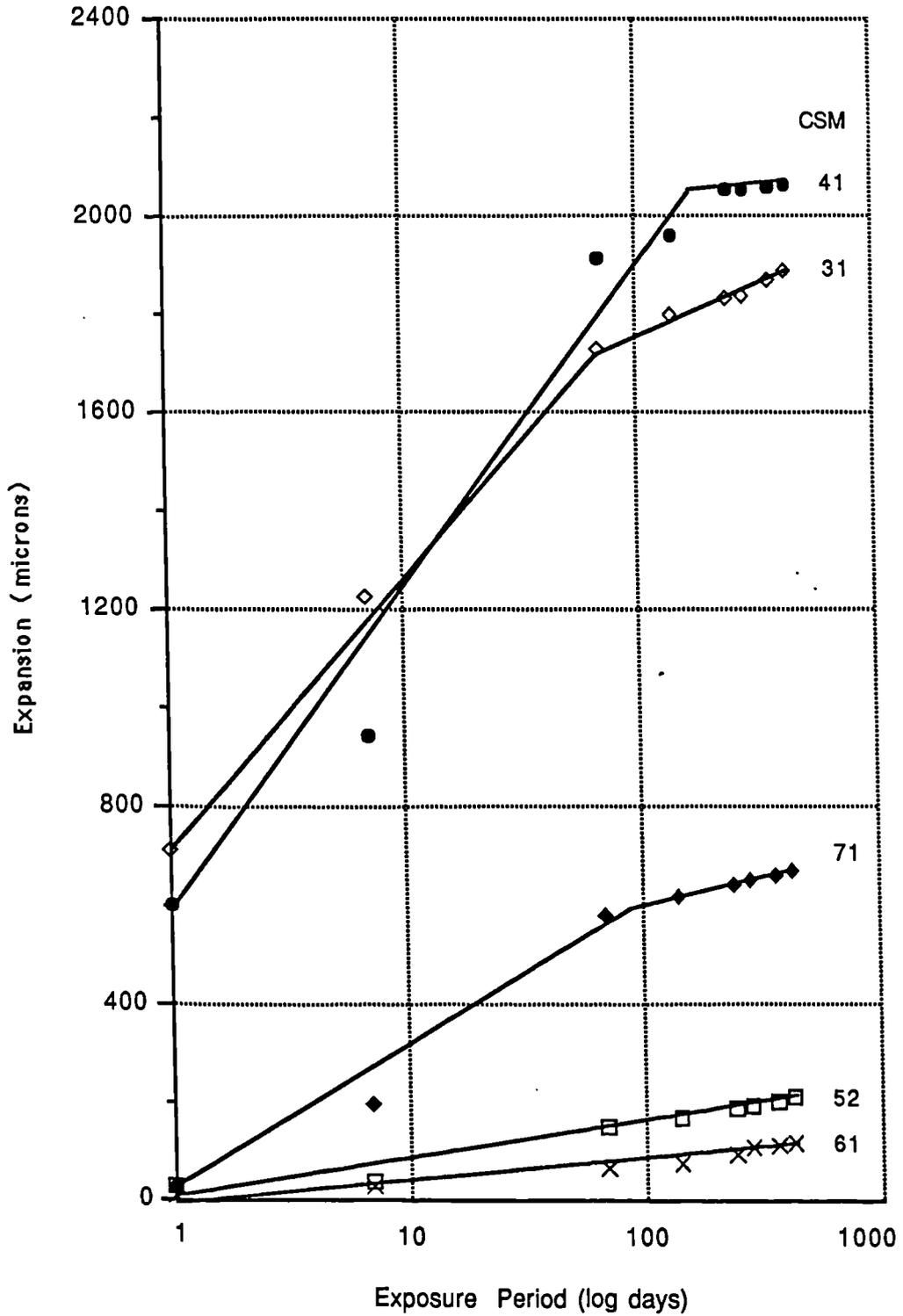
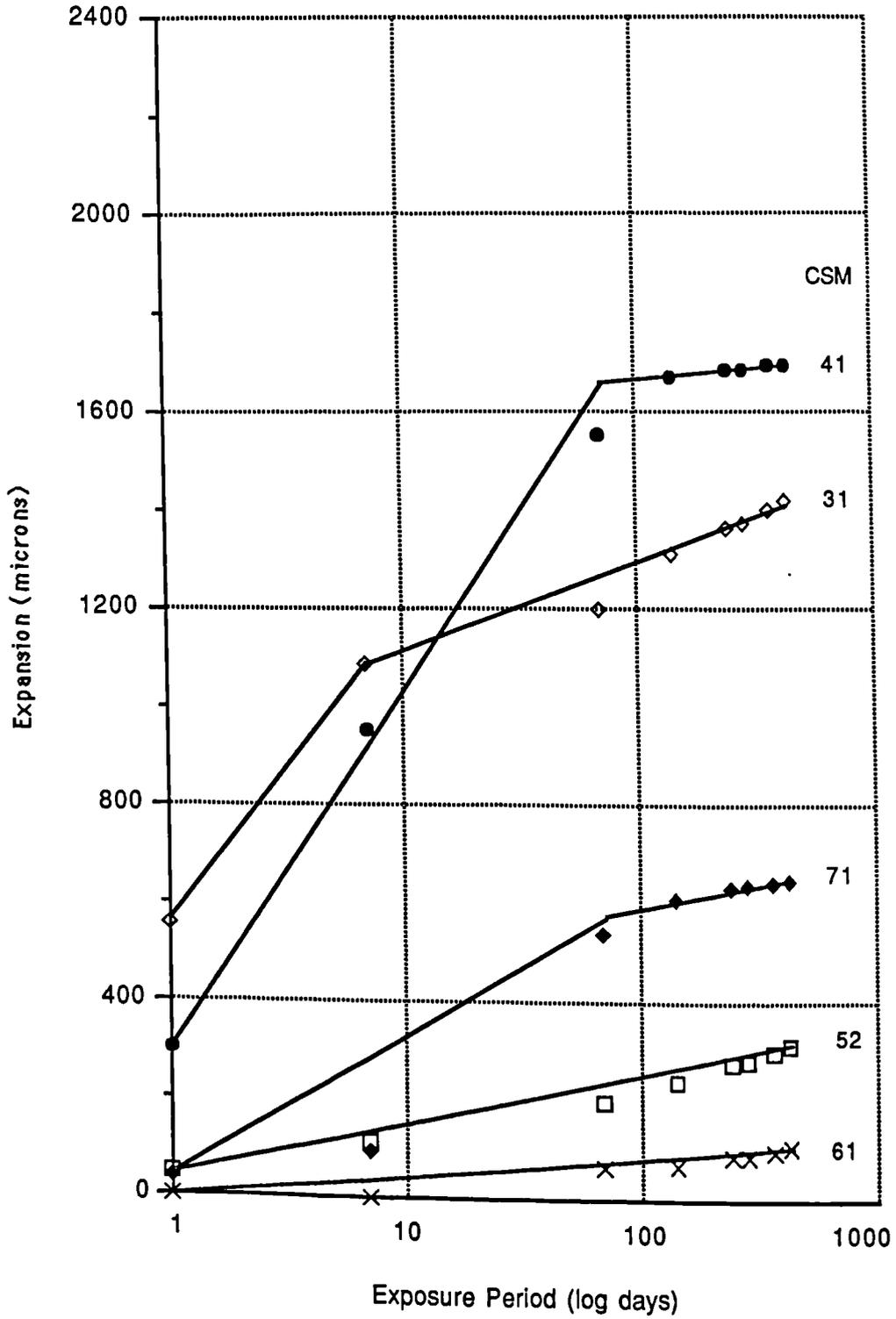


Figure 8.6 Relationship between Expansion of CSM in Environment 3 and Log Exposure Period.



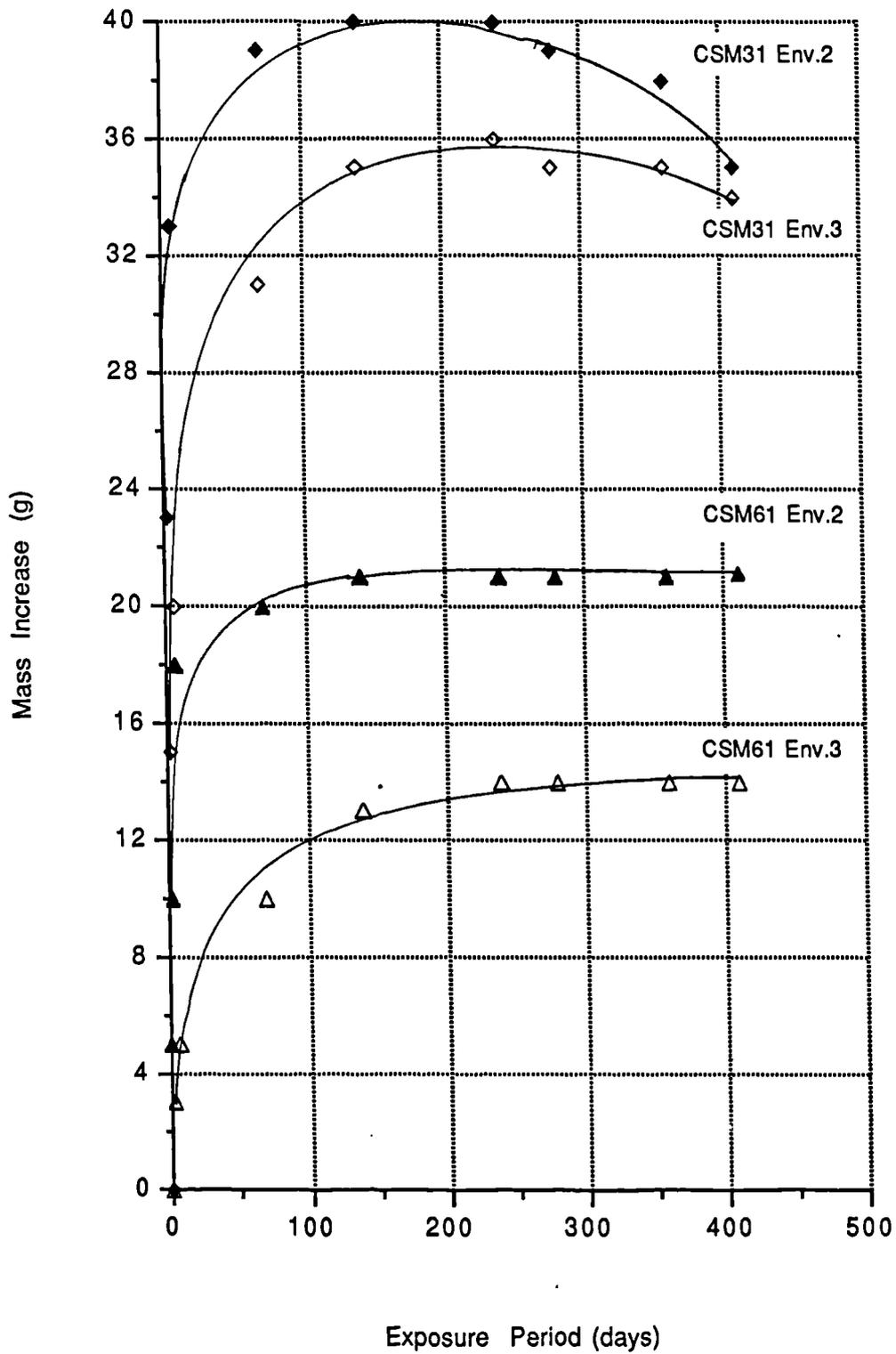
respectively. From these relationships, two swelling phases may be discerned :-

- a) an initial swelling which ceases anywhere between 10 and 200 days
- b) a secondary swelling which appears to continue beyond the 410 day duration of the study.

The gradient changes between these two phases are not so well defined for CSMs 52 and 61 and the other coarse-grained minestones behave similarly with the exception of CSM 71, and to a lesser degree 81, which have more pronounced expansion rates during the initial 200 day exposure period. CSM 31 despite showing a similar rate of initial swelling as CSM 41, continued to expand at a far greater rate beyond completion of the initial phase (i.e. 200 to 410 days).

The scope of the observed range of the rate of mass increase is shown in Figure 8.7, for both Environments 2 and 3, and it is clear that all the CSM specimens continued to exhibit mass increase for between 150 (CSM 31) and 200 (CSM 61) days. This is attributed to moisture uptake and was apparent by visual examination and subsequent oven drying, similar observations also having been reported by McNulty (1985) albeit for shorter exposures. In the longer term (150 to 410 days) some specimens (CSM 61 and 62) maintained a constant weight while others, such as CSM 31, appeared to lose weight. Specimens in this second group began to exhibit spalling unlike those in the first group which largely remained intact. The change from mass increase to mass decrease occurred as a result of the effects of spalling exceeding those of water uptake. Consequently, it is argued that CSM 31 may have continued to absorb water beyond the point of zero gradient of the mass increase curve. CSM 61 was the only material that did not display a loss in mass throughout the study. This CSM was, therefore, used to establish the relationship between

Figure 8.7 Mass Increase of CSM during Exposure to Environments 2 & 3.

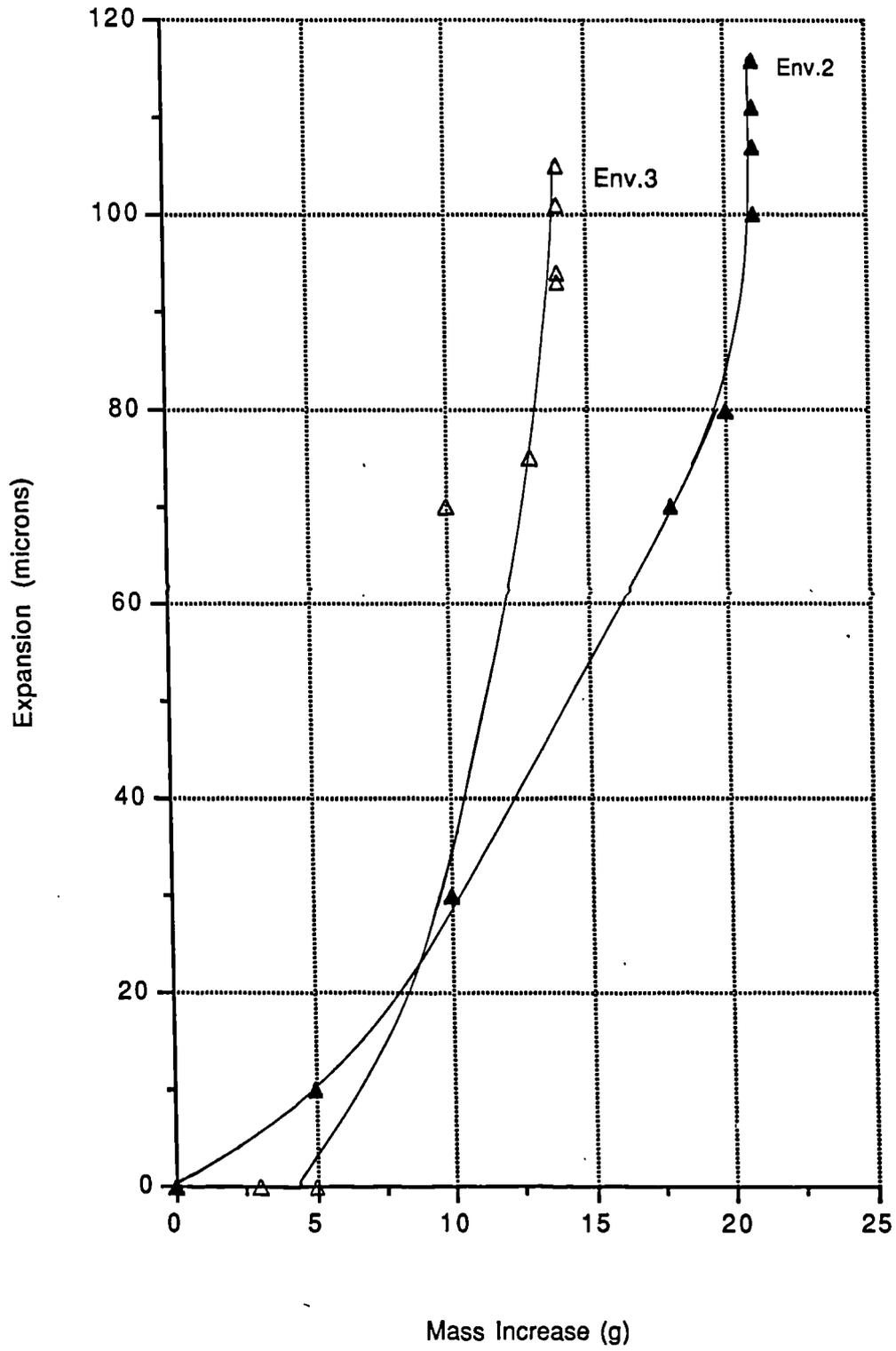


water uptake and swelling shown in Figure 8.8. The swelling of this CSM continued beyond the attainment of steady mass by the individual specimens and it is clear that swelling continues without associated mass increase.

It is suggested that the rate of water uptake decreases as the specimens approach a condition of moisture equilibrium. In the case of fully immersed specimens this will imply a state of complete saturation whereas the stable moisture content of a specimen in Environment 3 will be related to its individual moisture content/suction relationship. This stable moisture content, though being lower than the saturation moisture content does not necessarily lead to a reduced expansion of specimens in Environment 3. Although many of the mechanisms involved in the expansion of CSM due to increased moisture content (discussed in Chapter 7) do not necessarily rely on a complete saturation, other studies on soil cement (George, 1968) have suggested that much of the swelling due to physical mechanisms occurs once the larger voids are saturated and the water begins to enter the less accessible voids. Within these microvoids there is an increased surface area and the number of grain to grain contacts is larger. Consequently, swelling due to surface effects, i.e. interparticle swelling, will also increase. However, the expansion of CSM continues apparently without associated water uptake throughout the last 200 days of the study (for the First Phase CSMs) and this suggests that a second mechanism contributes to the expansion of the minestone specimens.

As the water uptake ceased with most samples around 150 days, indicating that the physical processes were complete, it is considered that this secondary swelling is probably due to chemical rather than physical actions. If this is the case then, presumably, such chemical action may have contributed to the expansion of the CSMs throughout their exposure but, until moisture uptake has ceased, the process is masked by the physical swelling. This is more obvious for those CSMs produced

Figure 8.8 Relationship between Mass Increase and Expansion for CSM 61 in Environments 2 and 3.



from minestones of medium to high plasticity and with high fines content (31, 41 and 92) where the effects of the secondary mechanisms can be more readily diagnosed following completion of the initial swelling. The rate of expansion of CSM 31 was markedly greater than CSM 41 during this later period despite similar physical characteristics of the raw materials (Table 7.2) and similar swelling in the initial period. The major differences in the two raw minestones are the levels of sulphate and pyritic sulphur (see Table 7.3). In cement stabilisation, the presence of sulphates is considered to be the most harmful of the common minerals (Section 2.4.3) and the most reasonable explanation of the different behaviours observed for CSMs 31 and 41 is that the sulphate content of the minestones controls long-term expansion following the attainment of moisture equilibrium.

It was suggested in the previous chapter that the swelling of cement stabilised coarse-grained minestones during immersion is, to some extent, controlled by their sulphate content (Figures 7.11 and 7.12). The relationships between expansion and the logarithm of time for most of these CSMs do not display dramatic gradient changes due to the decreased influence of physical mechanisms. However, CSM 71, and to a lesser extent CSM 81, expanded more rapidly than the other coarse-grained minestones during the first 100 days in Environments 2 and 3. Both of these minestones have significantly higher water soluble sulphate contents than the other coarse-grained minestones and these minerals are more likely to produce sulphate attack during early periods of exposure than the comparatively insoluble sulphate minerals (e.g. gypsum).

8.3 Long-term Strength Development

The strength developments exhibited for both First and Second Phase CSMs, in all three environments, are tabulated in Appendix D2. Figures 8.9 to 8.24 show the

Figure 8.9 Strength Development for CSM 31

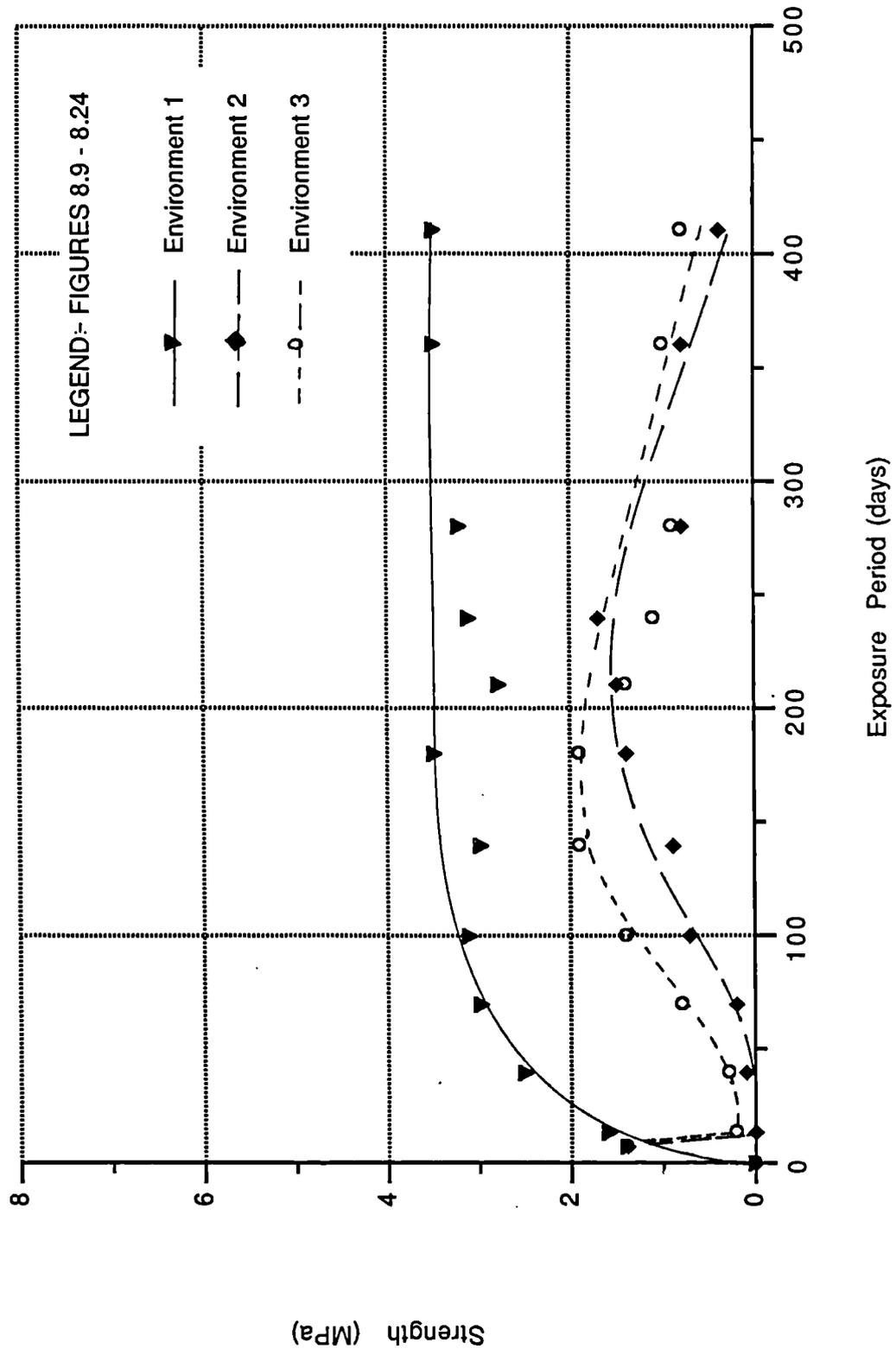


Figure 8.10 Strength Development of CSM 32.

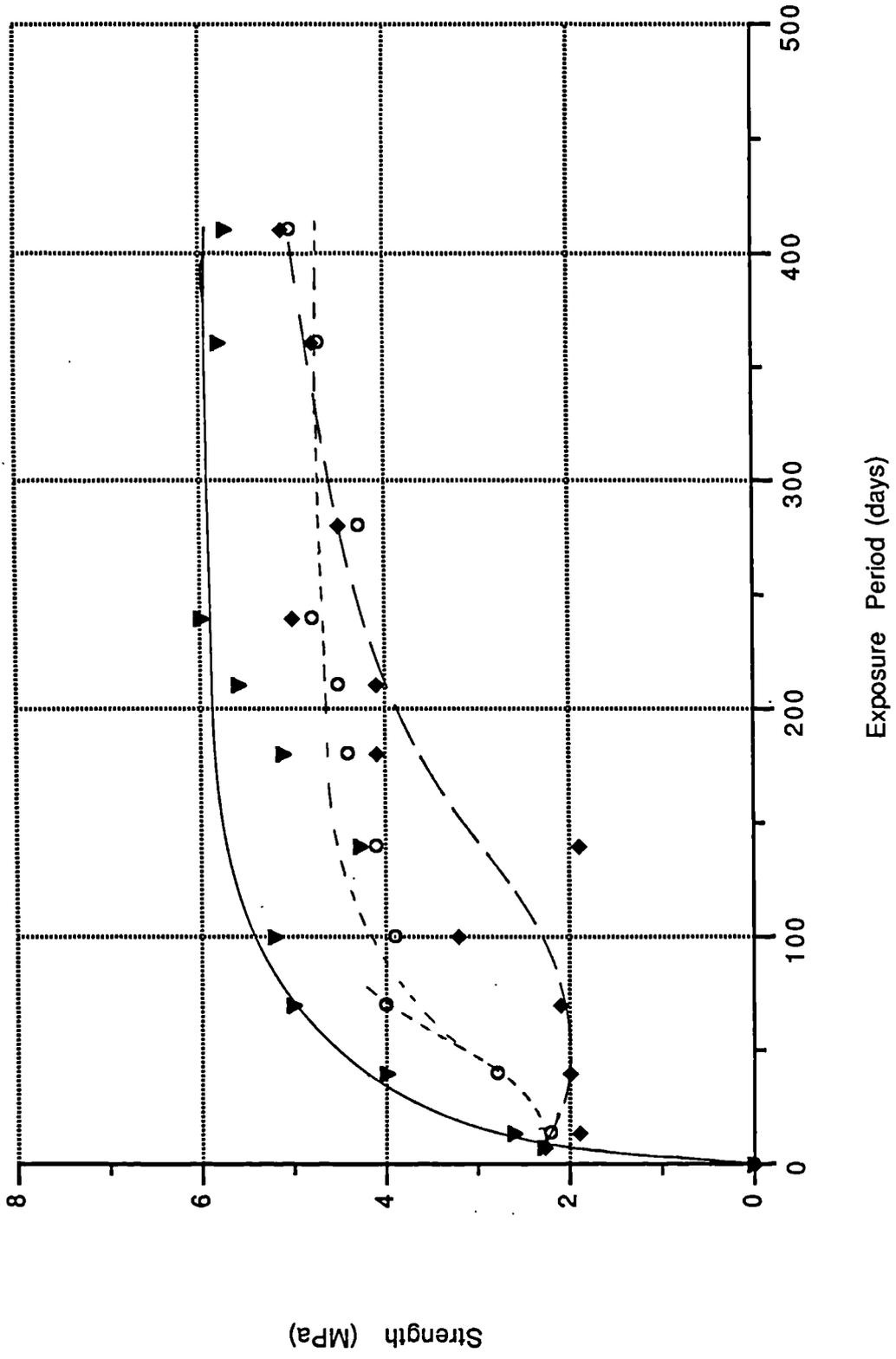


Figure 8.11 Strength Development of CSM 41.

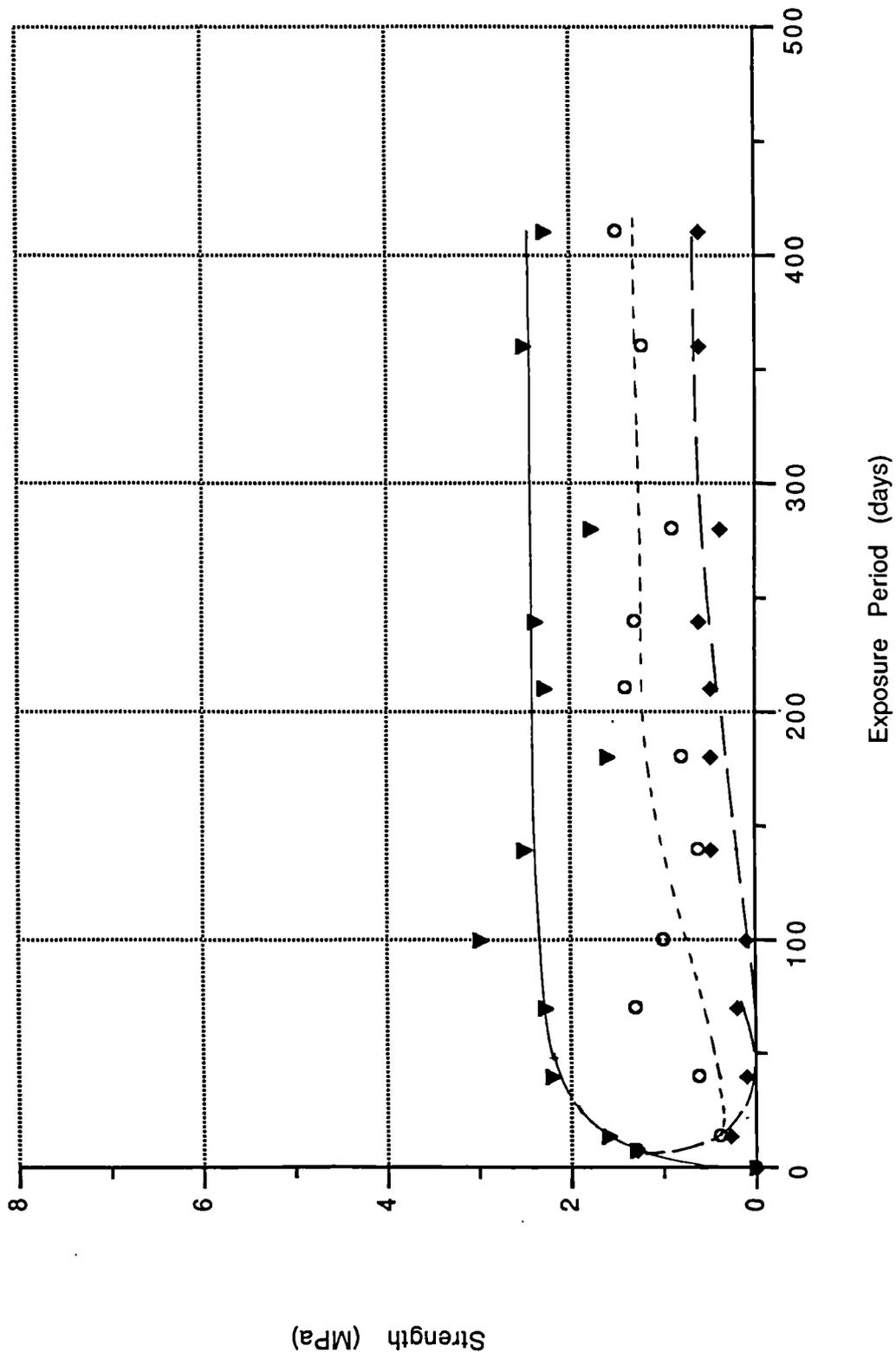


Figure 8.12 Strength Development of CSM 51.

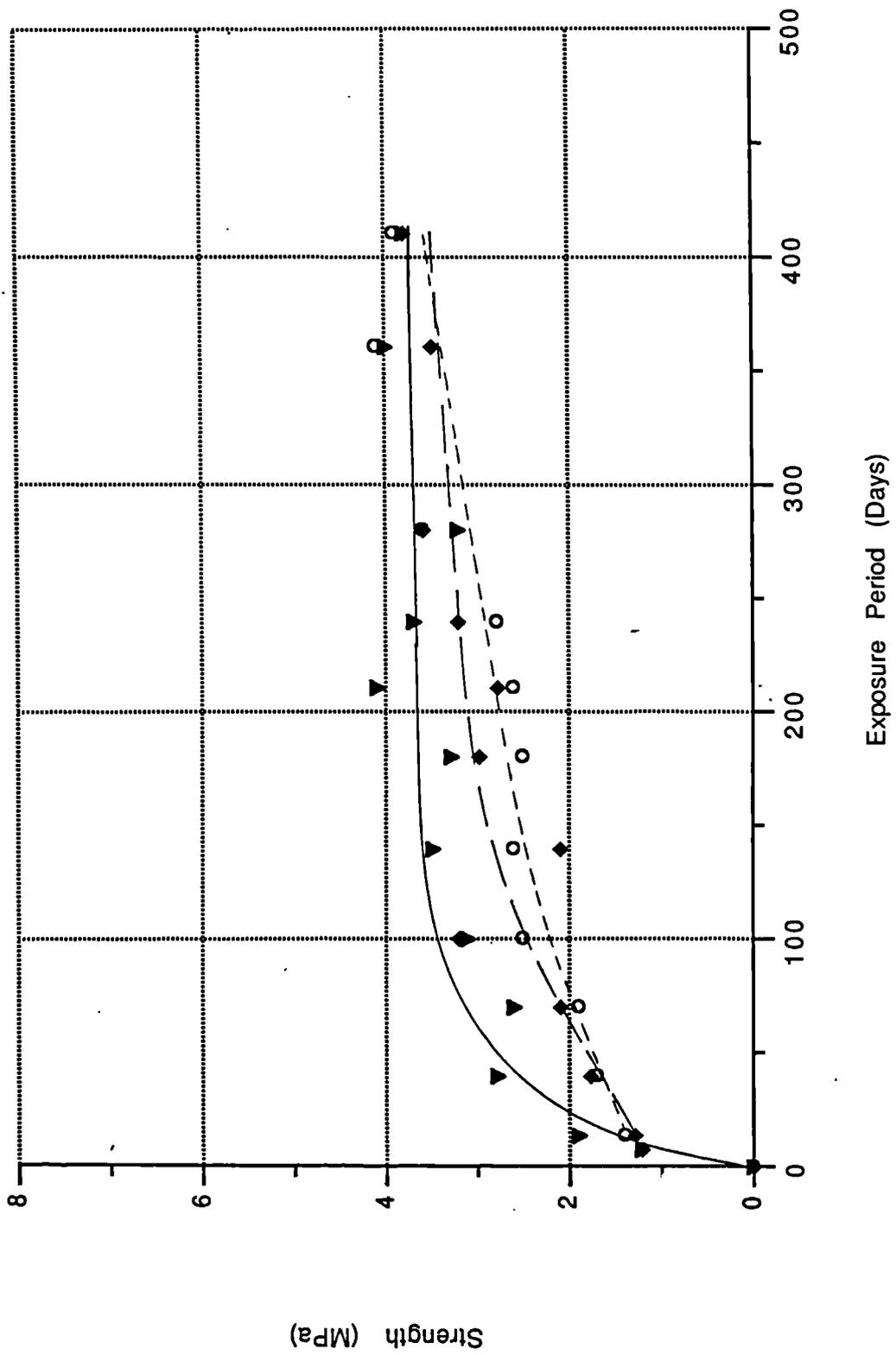


Figure 8.13 Strength Development of CSM 52

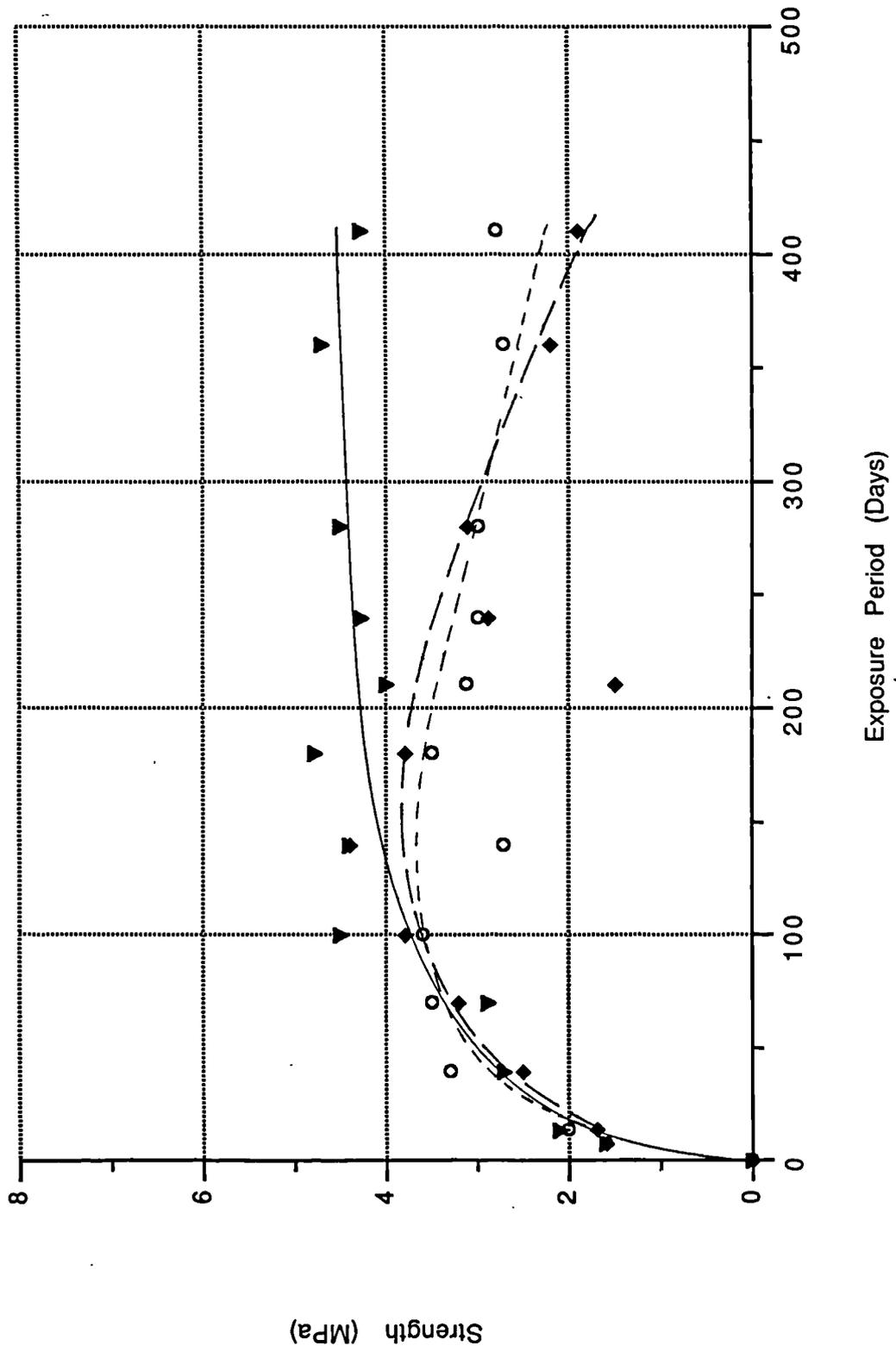


Figure 8.14 Strength Development of CSM 61.

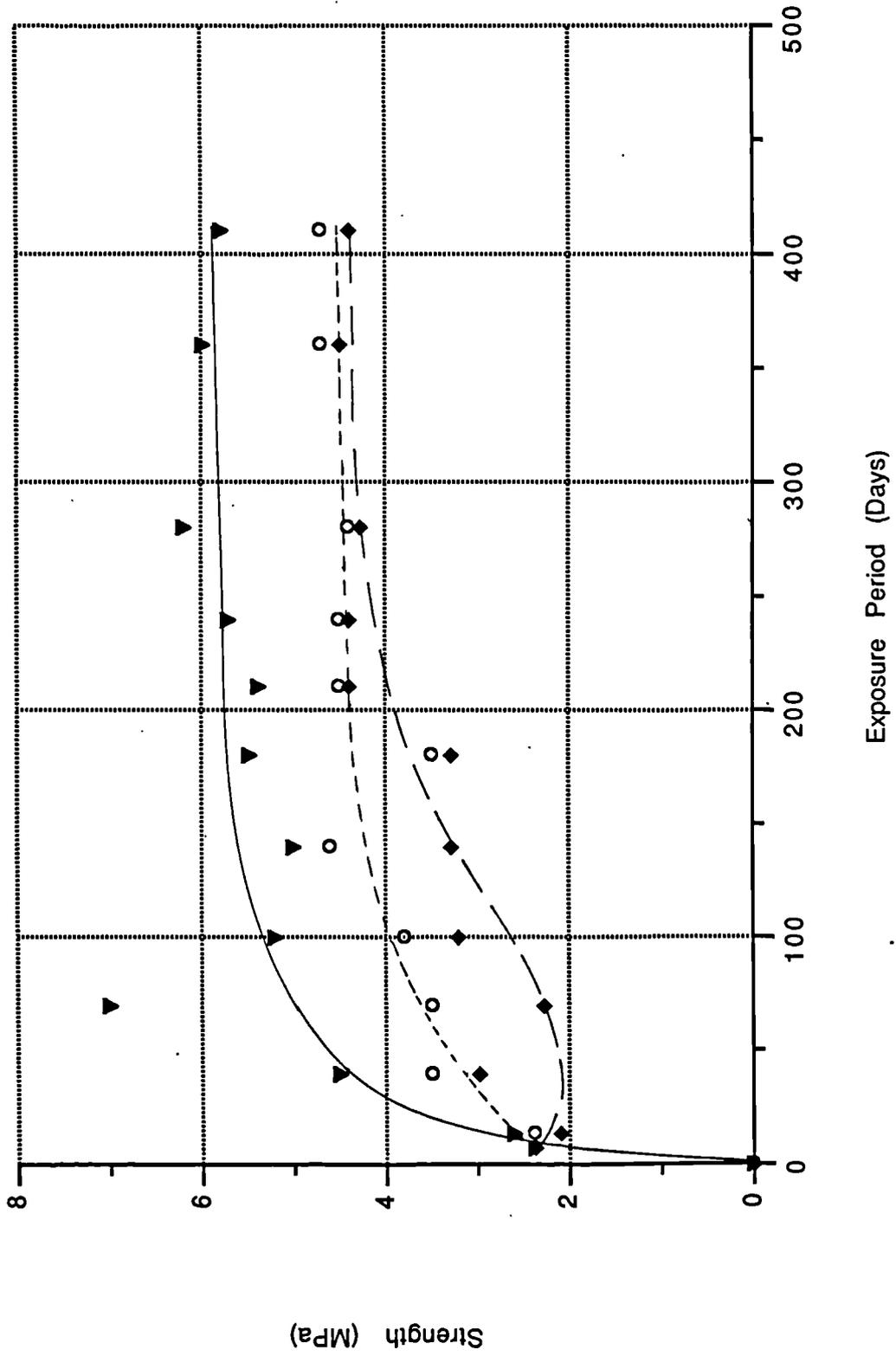


Figure 8.15 Strength Development of CSM 71

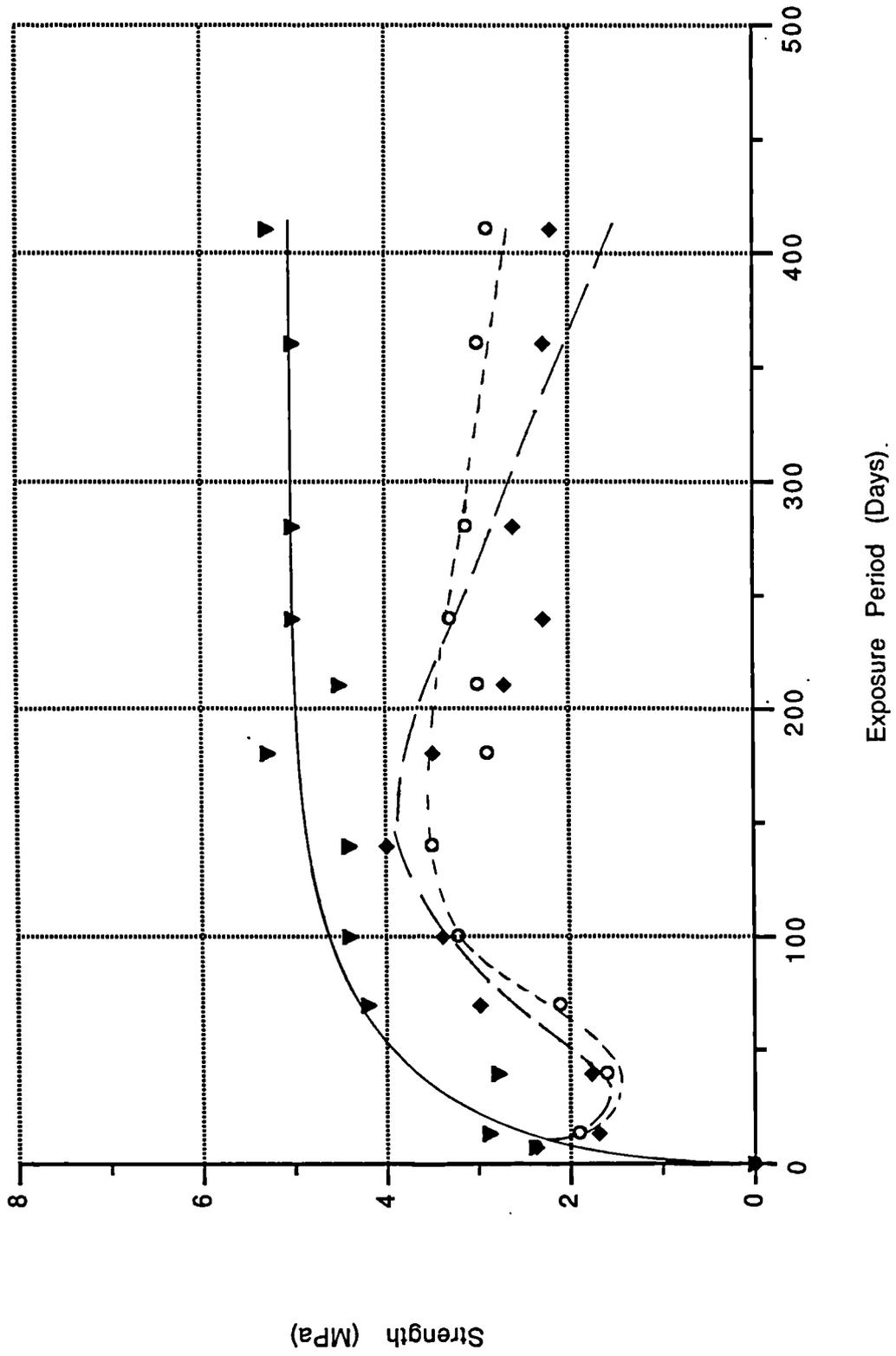


Figure 8.16 Strength Development of CSM 81

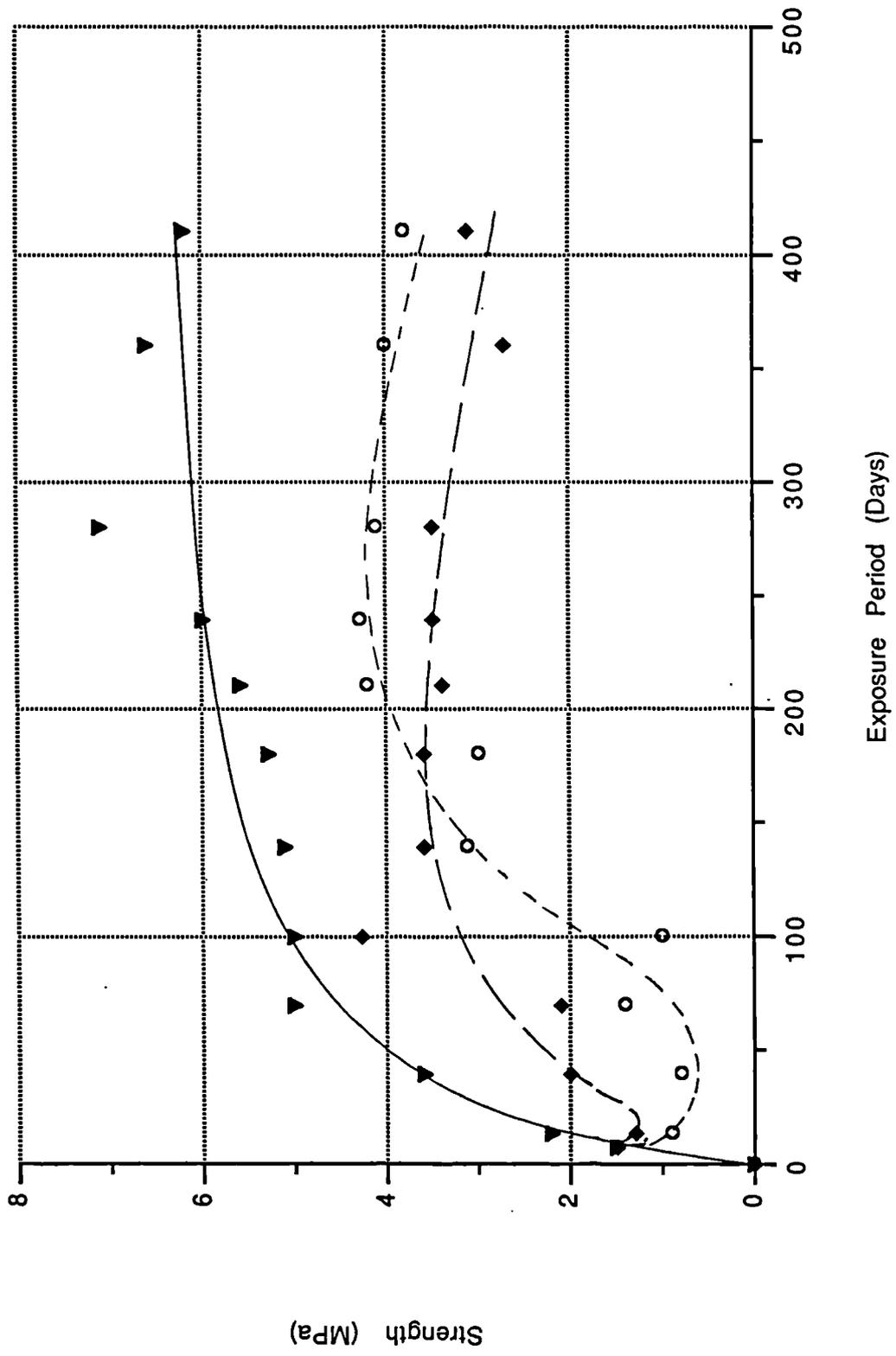


Figure 8.17 Strength Development of CSM 62.

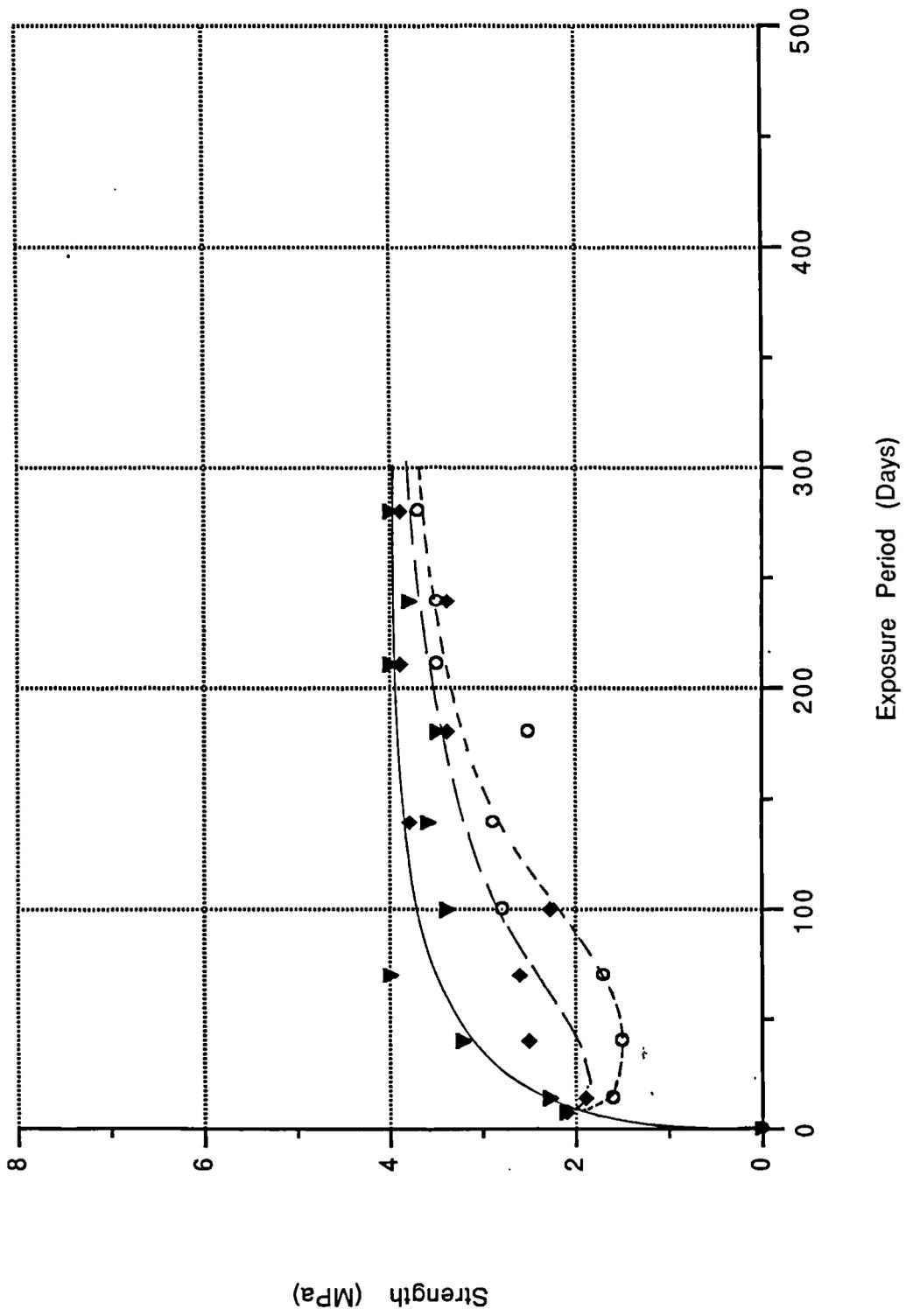


Figure 8.18 Strength Development of CSM 72

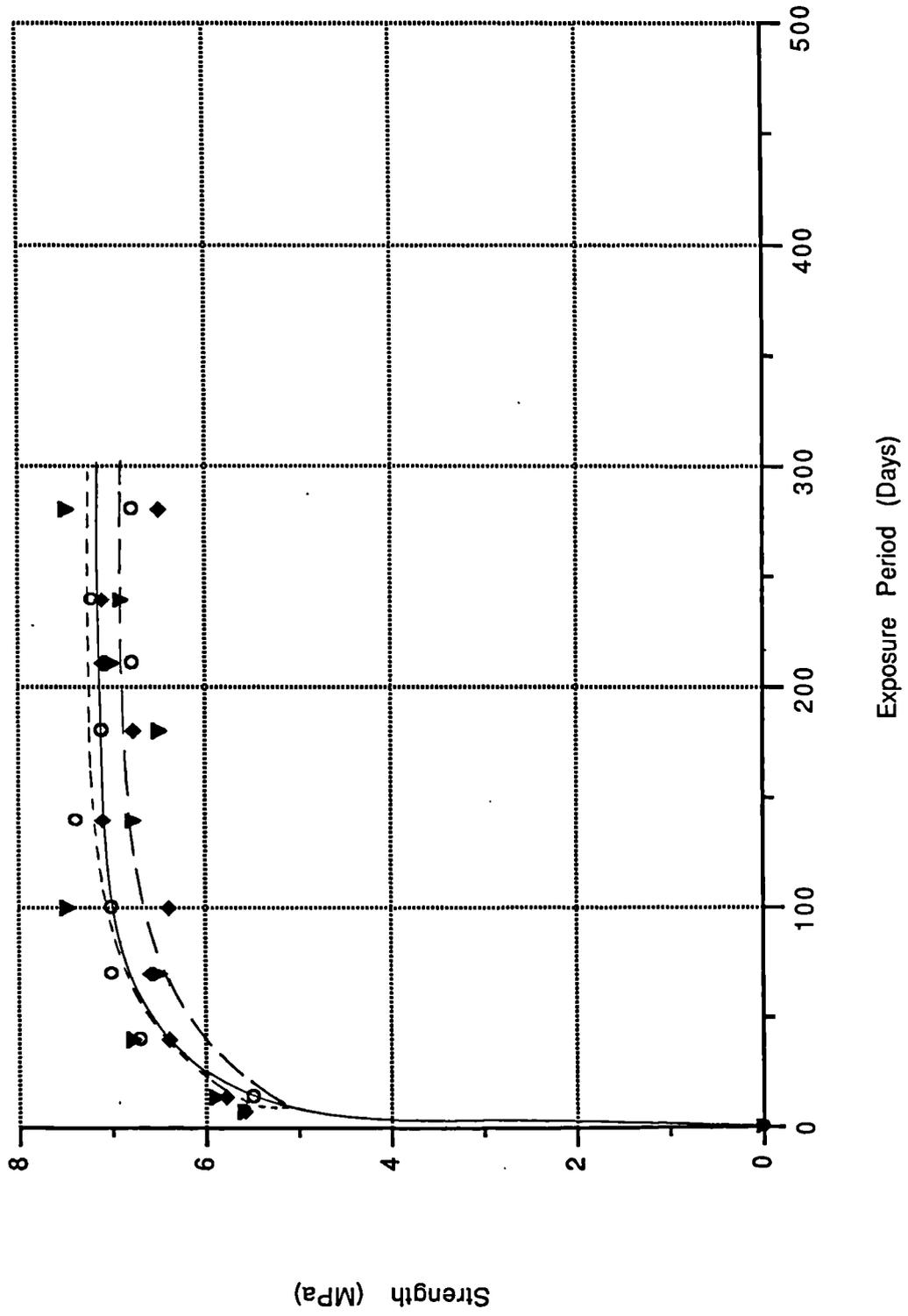


Figure 8.19 Strength Development of CSM 73.

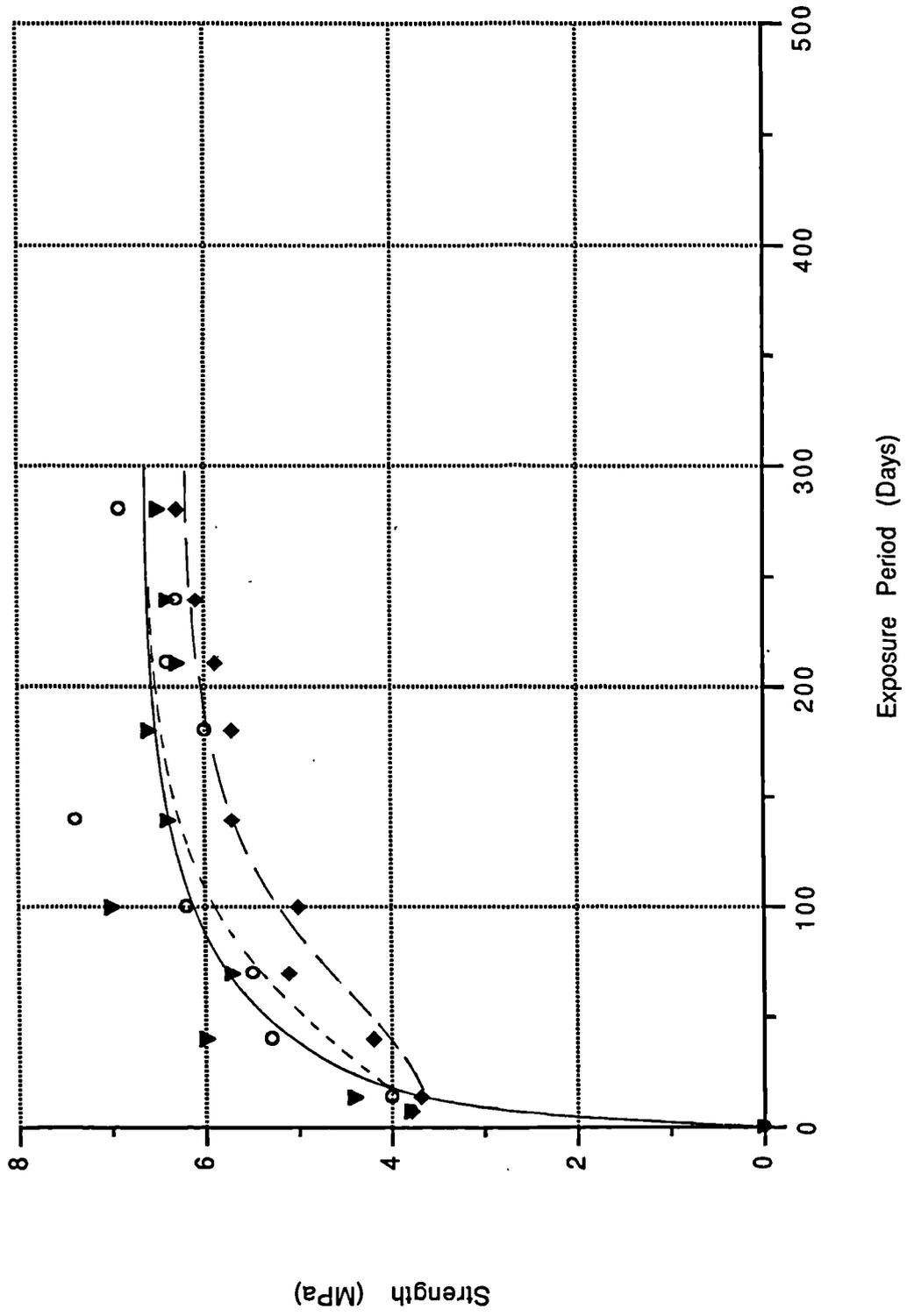


Figure 8.20 Strength Development of CSM 91.

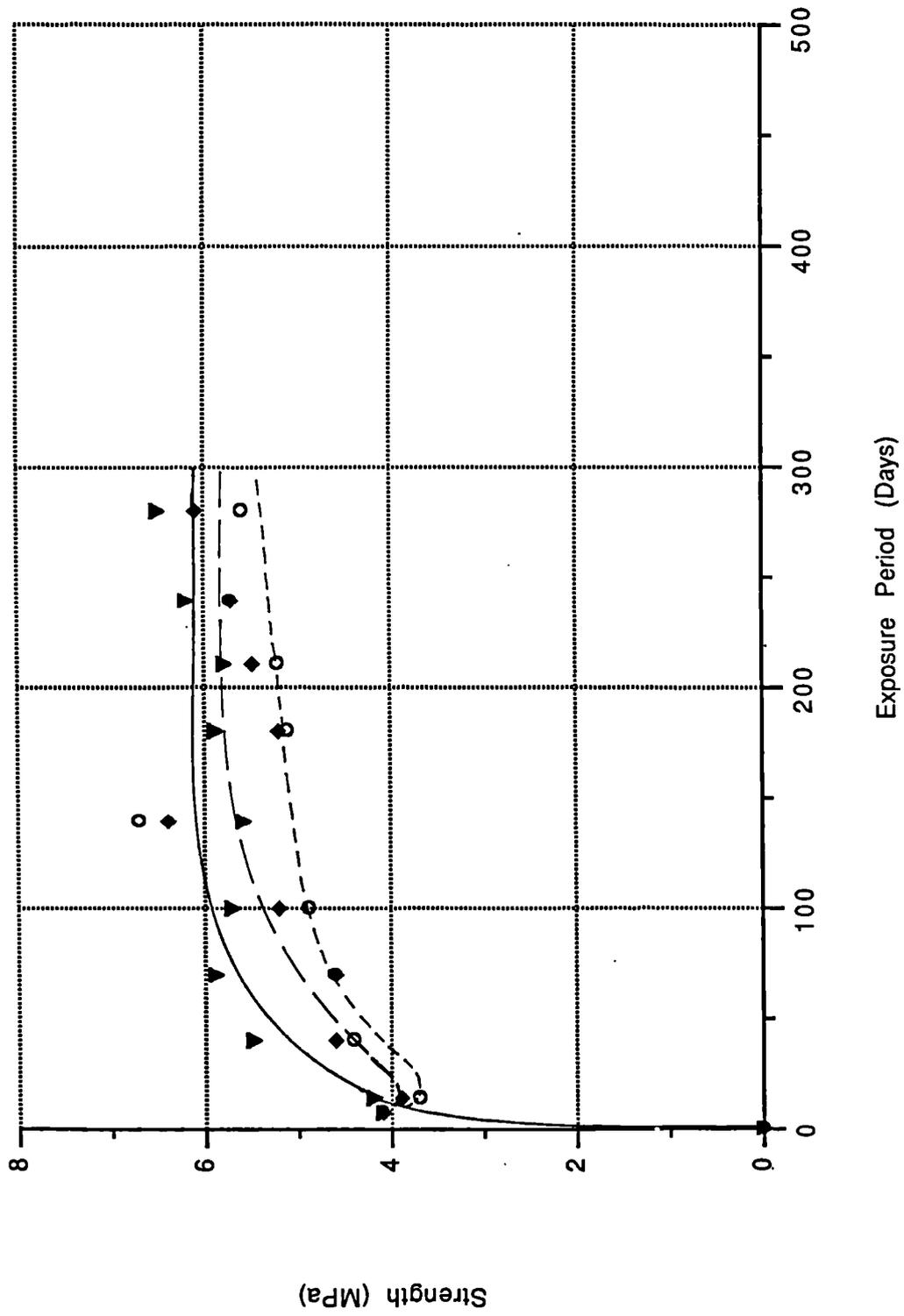


Figure 8.21 Strength Development of CSM 92.

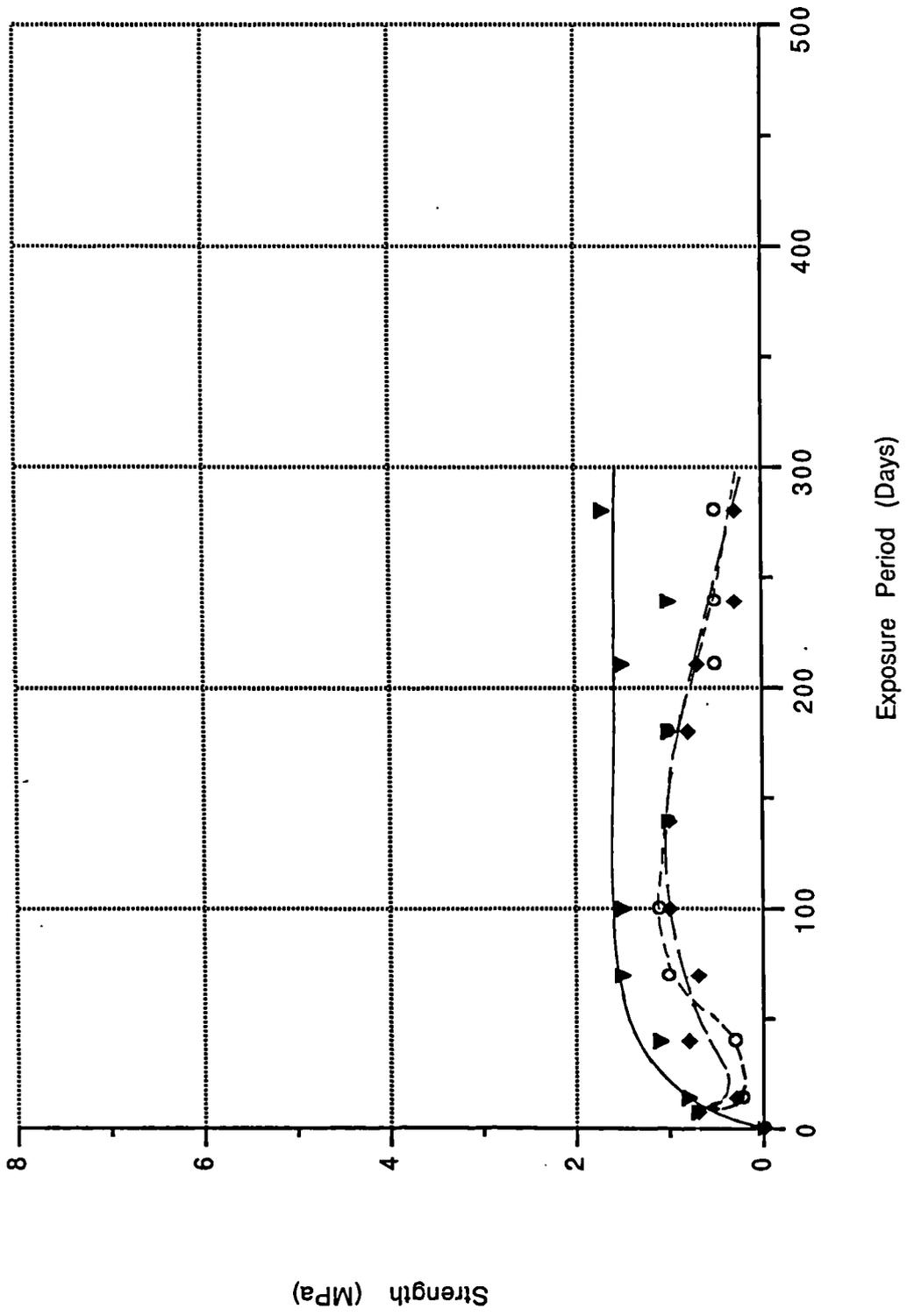


Figure 8.22 Strength Development of CSM 93.

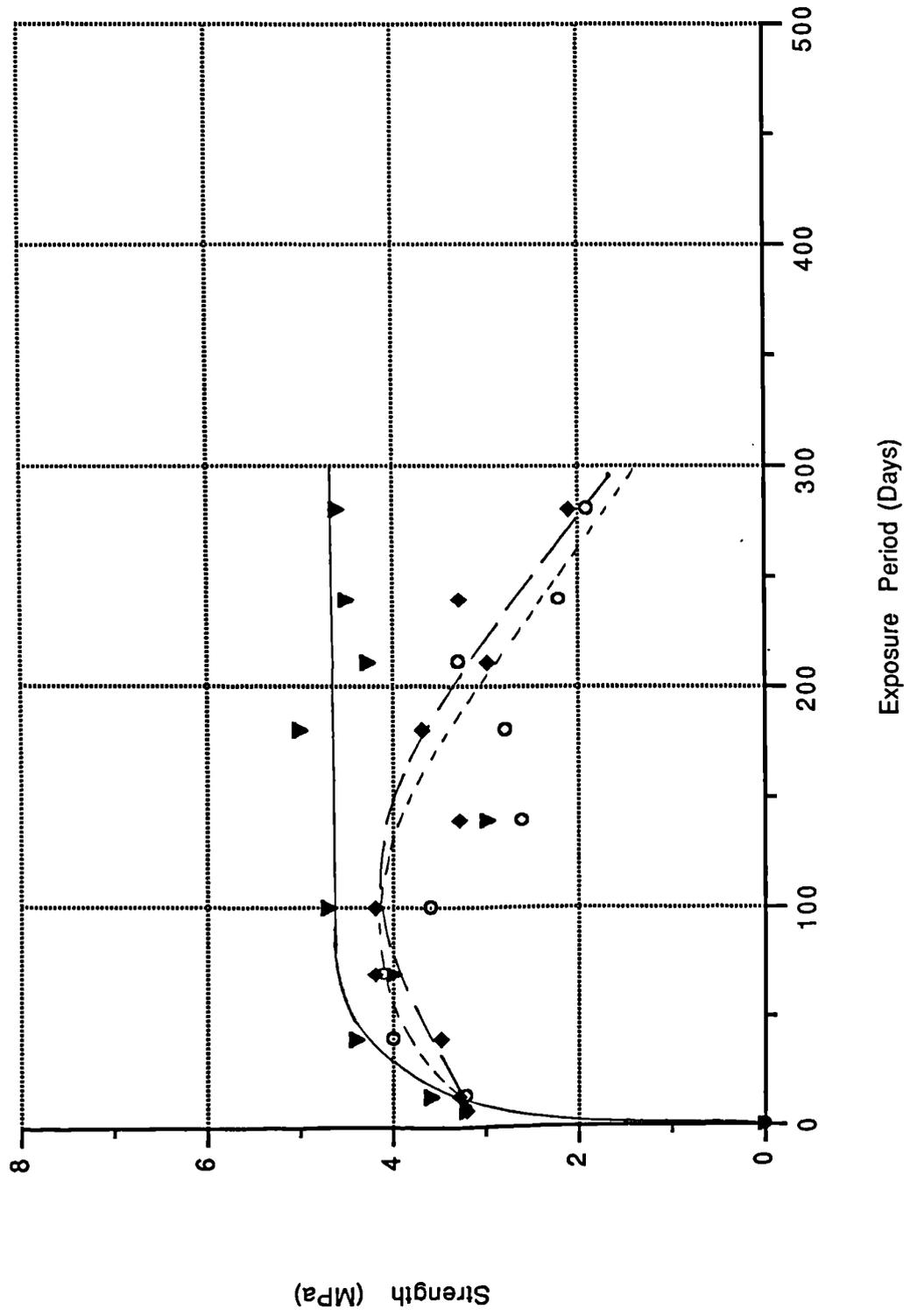


Figure 8.23 Strength Development of CSM 94.

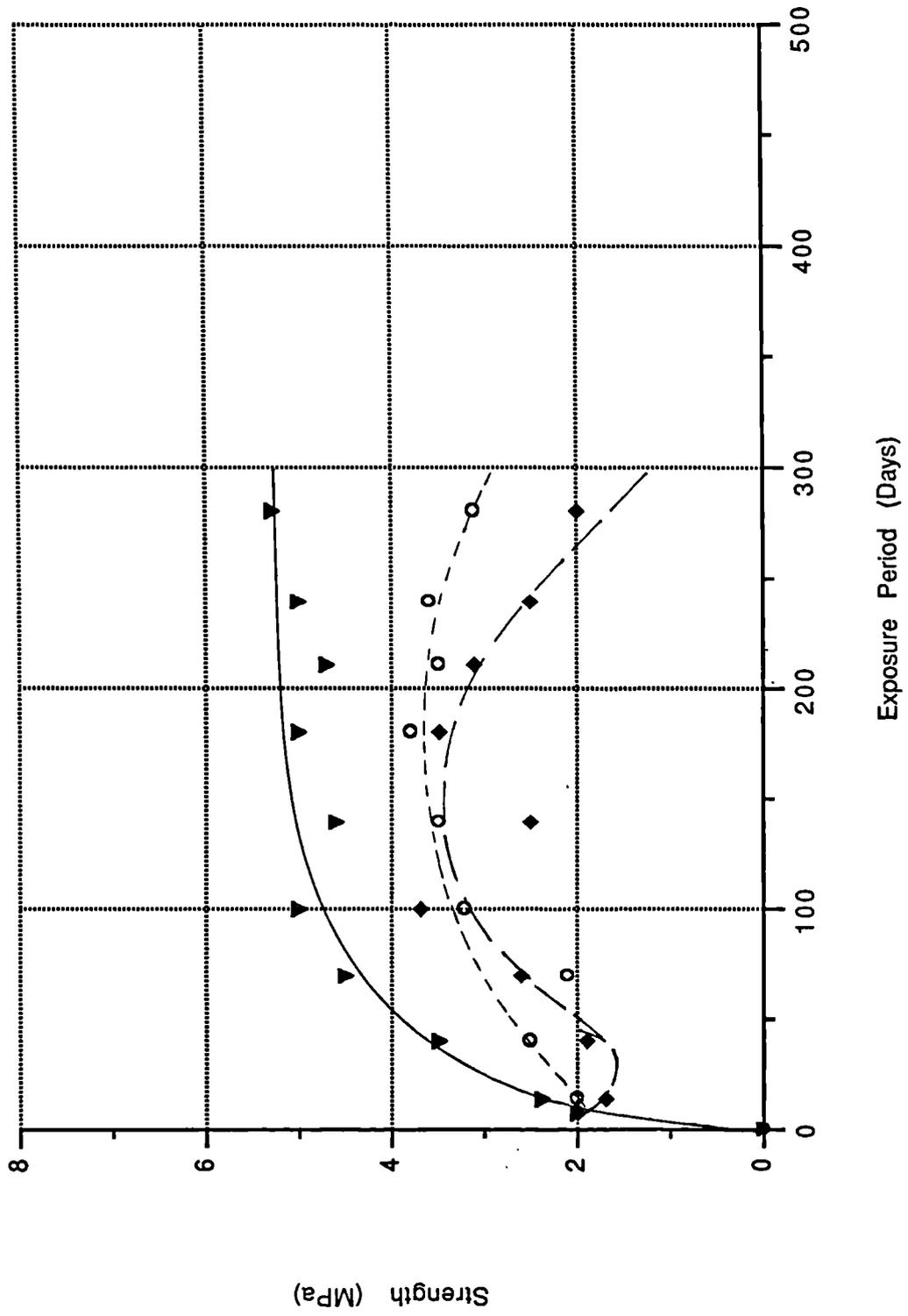
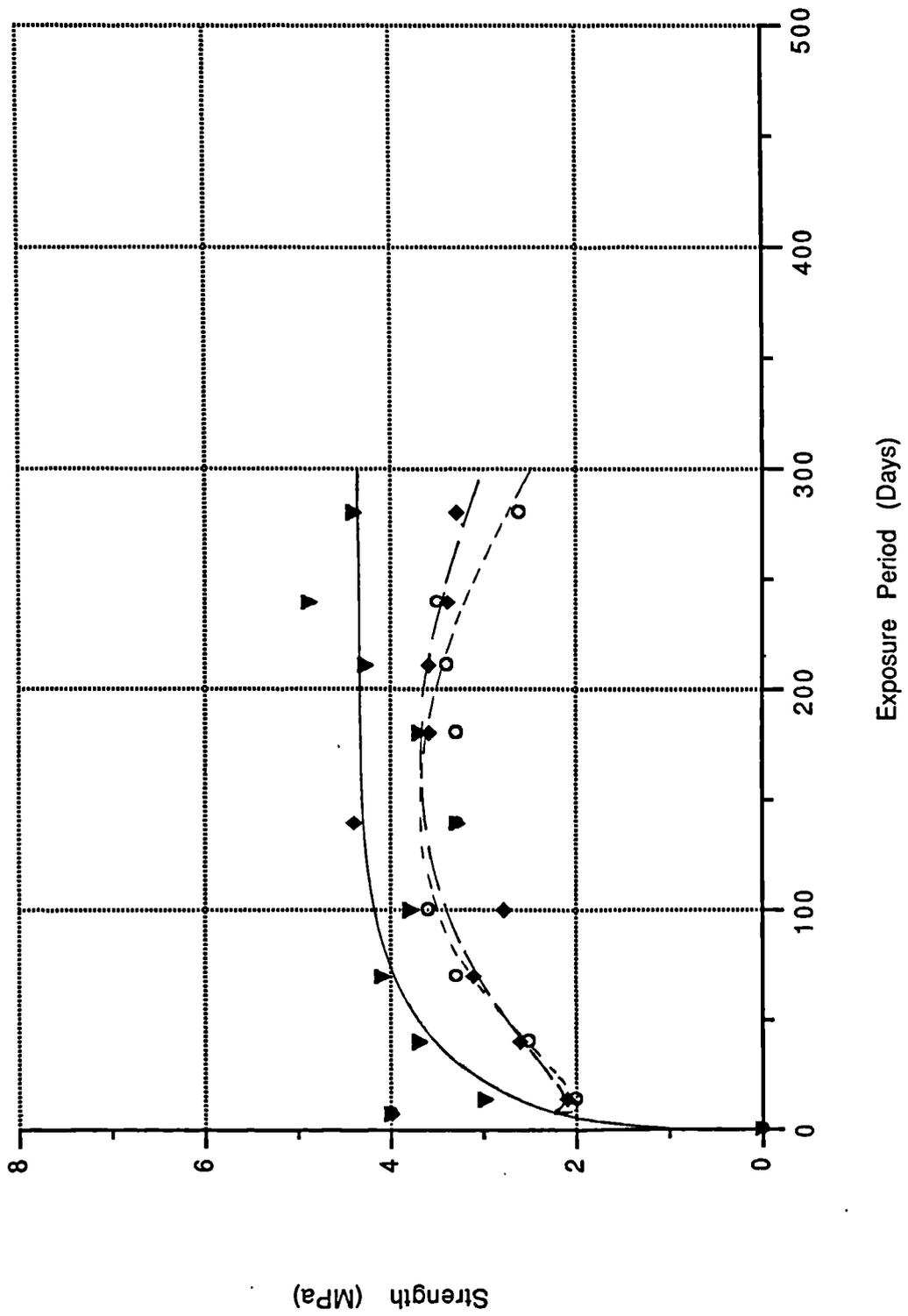


Figure 8.24 Strength Development of CSM 95.



development of compressive strength for the 16 CSMs in the different exposure conditions. The scatter of results is quite substantial, especially for the lower strength materials, and warrants comment.

The maximum particle size of the minestone was 10mm compared with the specimen diameter of 50 mm thereby reducing the chance that a single weak particle could produce premature failure. Although an individual weak particle may not substantially influence the compressive strength, a small number of such particles in close association could create a plane of weakness. The net result would be a lower compressive strength than an otherwise identical specimen with greater dispersion of such particles. Strength variation may also be caused by heterogeneity of a mix in terms of cement and moisture distribution. Thus, some specimens may have a slightly higher cement content than other specimens produced from the same mix leading to higher strength. Any variation in moisture content between specimens of the same mix, would have produced dry density differences and consequently further strength variation. It should also be noted that the simultaneous insertion of end plugs during compaction can result in density gradients in the specimens with lower dry densities at the centre (Grimer, 1958). The end plugs did not necessarily move in at equal rates and hence both the symmetry and variation of the density gradient would not have been duplicated from specimen to specimen thus providing a further source of strength variations. Although these factors did produce variation in the strength, it is possible to discern certain patterns of behaviour from the strength development curves displayed in Figures 8.9 to 8.24.

All the polythene wrapped CSMs continue to gain strength throughout the duration of the study. The rate of increase decreases with time and, in many cases (CSM 32, 52 and 61), has virtually ceased after 200 days. The strength of specimens stored for

410 days in Environment 1 is generally between 2 and 3 times the appropriate 7 day strength value. The individual factors do not correlate with fines content, plasticity or clay mineralogy and, consequently, it may be concluded that either the strength gain due to pozzolanic activity is negligible for these materials or insufficient moisture was available in this curing environment to promote further cementing reactions.

When exposed to increases in moisture content as in Environments 2 and 3, the behaviour of the CSMs shows considerable variation. However, a study of Figure 8.9 suggests that the strength development for CSM 31 can be split into three basic periods, which are :-

1. Immediate loss of strength following exposure to moisture (7 to 40 days).
2. Partial recovery of strength (40 to 200 days)
3. Long-term strength loss (beyond 200 days)

Although all the CSMs did not behave in an identical manner to that of CSM 31, it is possible to separate their performances into similar time periods in order to compare the responses to each environment.

The immediate response of CSM to immersion in water was the subject of Chapter 7. CSM 51, 52, 72 and 93 actually continued to gain strength over the first seven days of the period of immersion albeit at a reduced rate compared to the same materials stored in Environment 1. The remaining twelve CSMs suffered strength loss during this period. This loss ranged from less than 3% of the 7 day strength (CSM 73) to a complete loss in strength for CSM 31. These twelve CSMs all eventually reached a minimum strength value although the duration of this period was not constant for all

CSMs.

Following this initial period of strength loss all CSM specimens exposed to Environments 2 and 3 started to regain strength. Most of the CSMs show signs of strength recovery during the first 40 days and, with the exception of CSM 41, all had higher strengths following 70 days exposure in Environments 2 and 3 than after 7 days exposure in the same environments. Once strength recovery had commenced the subsequent rate of strength development of exposed specimens often exceeded that of their polythene cured equivalents. In some cases the specimens exposed to increased moisture achieved strengths equal to those stored in polythene (CSM 51 and 73) and specimens from CSM 72 exposed to Environments 2 and 3 actually achieved strengths in excess of those stored in Environment 1. Indeed CSM 72 exhibited similar behaviour in all three environments throughout the exposure period.

Eight of the CSMs continued to gain strength throughout the remainder of their exposure to Environments 2 and 3. These are :-

32	Littleton Fresh
41	Coppice
51	Bentinck Old
61	Wardley I
62	Wardley II
72	Tilmanstone
73	Betteshanger
91	Roseheyworth

The remaining CSMs in both environments reached a maximum compressive

strength, which was generally greater than the 7 day value, and then showed signs of suffering a second loss in strength, the time taken to reach these maxima varied between approximately 60 days for CSM 93 exposed to Environment 3 and 260 days for CSM 81 under the same exposure conditions. Generally, there is little to separate the behaviour of these CSMs in the two environments. The maximum strength and the time taken to reach it is roughly the same for a given CSM in each environment.

Once the strength development for CSMs 31, 52, 71, 81, 92, 93, 94 and 95 passes through the maxima in Environments 2 and 3, the subsequent rate of strength loss varies considerably. Specimens of CSM 31 lost more than half their strength between 180 and 410 days exposure to Environments 2 and 3. CSM 93 reached its strength maximum more rapidly than CSM 31 (at about 70 days) and loses a little over half of its strength during the next 210 days exposure to Environments 2 and 3. In some cases the deterioration did not occur until very late in the exposure periods, and at the termination of these tests these CSMs appear to be continuing to lose strength.

The initial strength loss of CSM specimens exposed to conditions of increased moisture is related to the expansion of the material and the associated disruption of cement bonds in Chapter 7. The degree of moisture uptake, expansion and strength loss of a CSM are suggested to be a function of the engineering characteristics (plasticity, fines content, slake durability) and water soluble sulphate level of the raw minestone. These mechanisms were discussed in the preceding chapter. However, it is noticeable from a study of the expansion rates (Figures 8.1 to 8.4) and the strength development curves (Figures 8.9 to 8.24) that the expansion of CSM continues beyond the initial 7 day immersion period that formed the basis of the short-term durability study, and this is associated with further reductions in

strength for periods of up to 40 days (CSM 41).

The later strength recovery of the CSMs that initially suffer strength loss is associated with decreasing expansion rates (Figures 8.1 to 8.4) and decreasing rates of water uptake (Figure 8.7). This strength recovery together with the continued increase in strength of the remaining CSMs (51, 52, 72, 93) is considered to be due to the formation of new cementitious bonds brought about by further cement hydration, the benefits of cementing action eventually exceed the disruptive effects of minestone expansion leading to a period of strength gain. In some cases the rate of this strength gain exceeds that of similar polythene cured specimens and this may be explained by the increased quantity of water made available for cement hydration. This can be explained in terms of the competition for moisture within the hydrating CSM.

Fully hydrated cement requires on average 38% (by mass of dry cement) of available water. Since the CSM specimens contain 10% (by mass) of cement then the complete hydration of this cement would require a minimum moisture content of 3.8%. However, hydrated cement gel may only form in water filled spaces (Neville, 1981) and thus for complete hydration, sufficient water must be available to fulfil the requirements of the chemistry and to maintain a suitably moist environment within the gel. In concrete this process necessitates a "free" water/cement ratio of at least 0.5 (Neville, 1981). Although this quantity of water is present in all the CSM mixes, it is not all "freely" available for cement hydration. Much of the mixing water is absorbed into the shale and mudrock pore structure or adsorbed onto their associated surfaces. Although saturated surface dry moisture contents were not measured the air dry values ranged from 2 to 10%, with those following saturation in the slaking test ranging from 7 to 24%. Thus a minimum absorption value of 6% would not be unreasonable. As the mix moisture contents, given in Table 7.4, were

mainly between 8 and 11%, it is clear that the competition for this water between the cement hydration and the minestone would be severe and so the hydration of cement is restricted in Environment 1. The conditions in Environment 2 and 3, however, increase the availability of moisture within the specimens permitting further cement hydration.

Eight of the CSMs eventually began to lose strength beyond this period of strength recovery. No increases in the rates of expansion or moisture uptake are associated with these long-term strength losses. In addition, this behaviour can not be correlated with either the physical properties of raw minestone or the earlier behaviour of the CSM specimens. Considering CSMs 41 and 93 the former, produced from a plastic minestone with high fines content, lost almost all of its strength during the initial immersion period, but once strength recovery started the CSM continued to gain in strength throughout the remainder of the study. CSM 93 (from a coarse-grained minestone of low plasticity) on the other hand is the complete antithesis. Specimens suffered no early strength loss but during the last 100 days of exposure to Environments 2 and 3 the strength loss was considerable.

8.4 Geochemical Alterations Monitored in CSM

The total sulphur, pyritic sulphur, acid soluble sulphate, water soluble sulphate and organic sulphur (obtained by difference) contents for the First Phase CSMs are tabulated (as equivalent SO_3) in Appendix D, Tables D3 to D7. These contents also include the sulphate contribution from the gypsum in the cement, which at 10% cement in the CSM is equivalent to 0.23% SO_3 in the CSM.

A statistical analysis of these contents for the CSMs stored in Environment 1 shows

that no significant change in sulphur bearing mineralogy occurs with time, with the exception of the water soluble sulphate content. At a 10% level of significance, this shows a tendency to decrease during storage. Figures 8.25 and 8.26 show the variation in total, pyritic and sulphate sulphur contents of CSM 31 during exposure to Environments 2 and 3. Changes in these contents are greater in magnitude than the remaining First Phase CSMs due to its high sulphur bearing mineral content. There is an overall decrease in the total and pyritic sulphur contents and an increase in the sulphate sulphur during exposure of CSM 31 to both Environments 2 and 3. A linear regression was performed on these together with the data for the other seven First Phase CSMs exposed to these two environments. A rate of change of sulphur contents expressed as percent SO_3 per 100 days was calculated from the gradients of the regression lines and these are presented in Table 8.1 together with an indication of the level of statistical significance. Although these are linear regression rates with respect to time (and there is some evidence that the rates increase with time from Figures 8.25 and 8.26) it is considered that they adequately quantify the changes in sulphur species.

The total sulphur content was significantly reduced over the 410 day period for CSMs 31 and 51 in both Environments 2 and 3 and CSM 61 in Environment 2 only. The reductions were far greater for CSMs 31 and 51 due to exposure to Environment 2. CSMs 32 and 52 exposed to Environment 3 gave values of increase in total sulphur content with time but neither of these relationships are statistically significant. It is suggested that these increases may be a result of material variability, experimental error, test method inaccuracy or a combination. The decrease in total sulphur content is discussed later in this section.

The pyritic sulphur content of all the CSMs in the First Phase decreases when

Figure 8.25 Variation in Sulphur Contents with Exposure to Environment 2 for CSM 31.

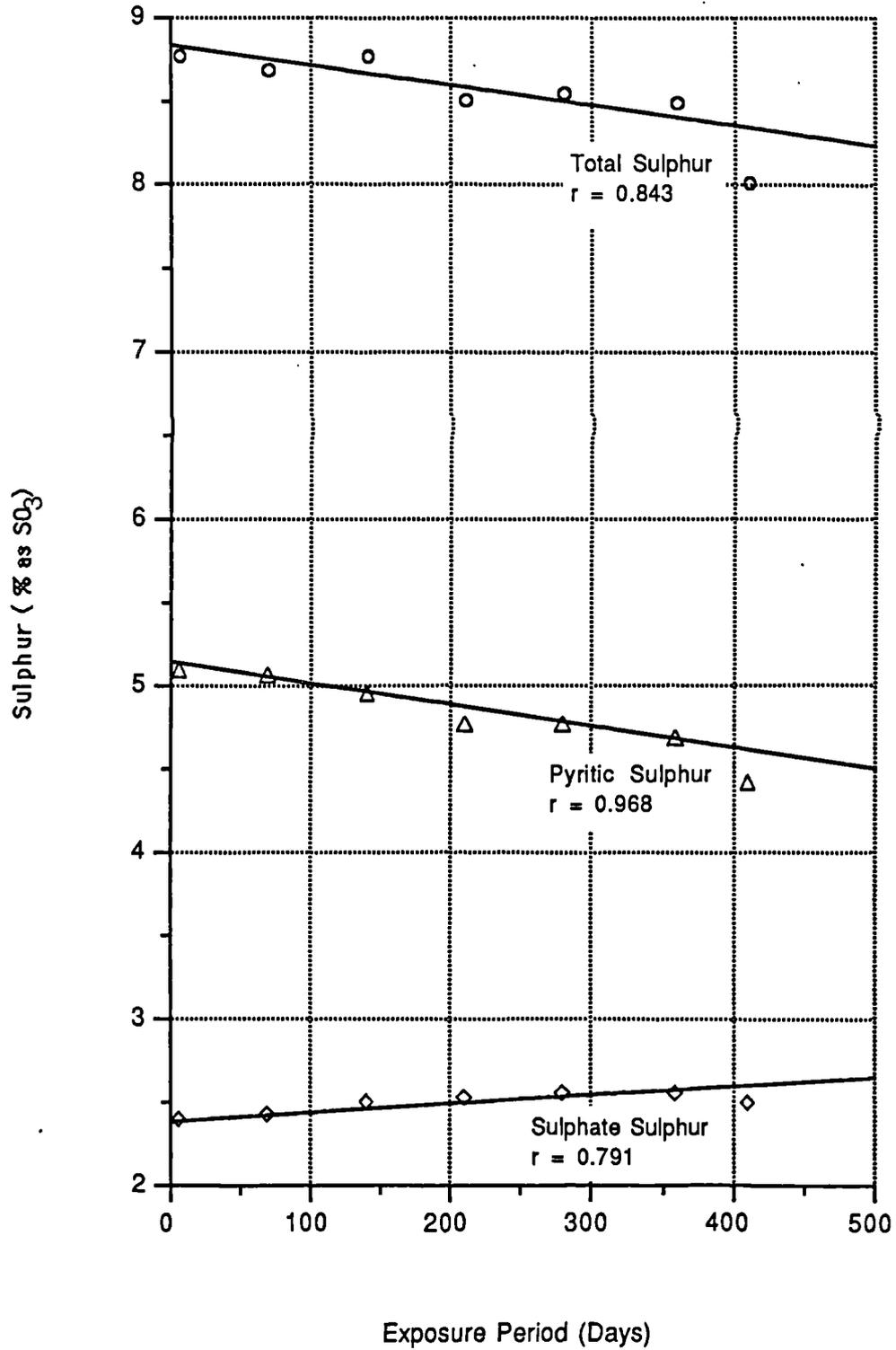
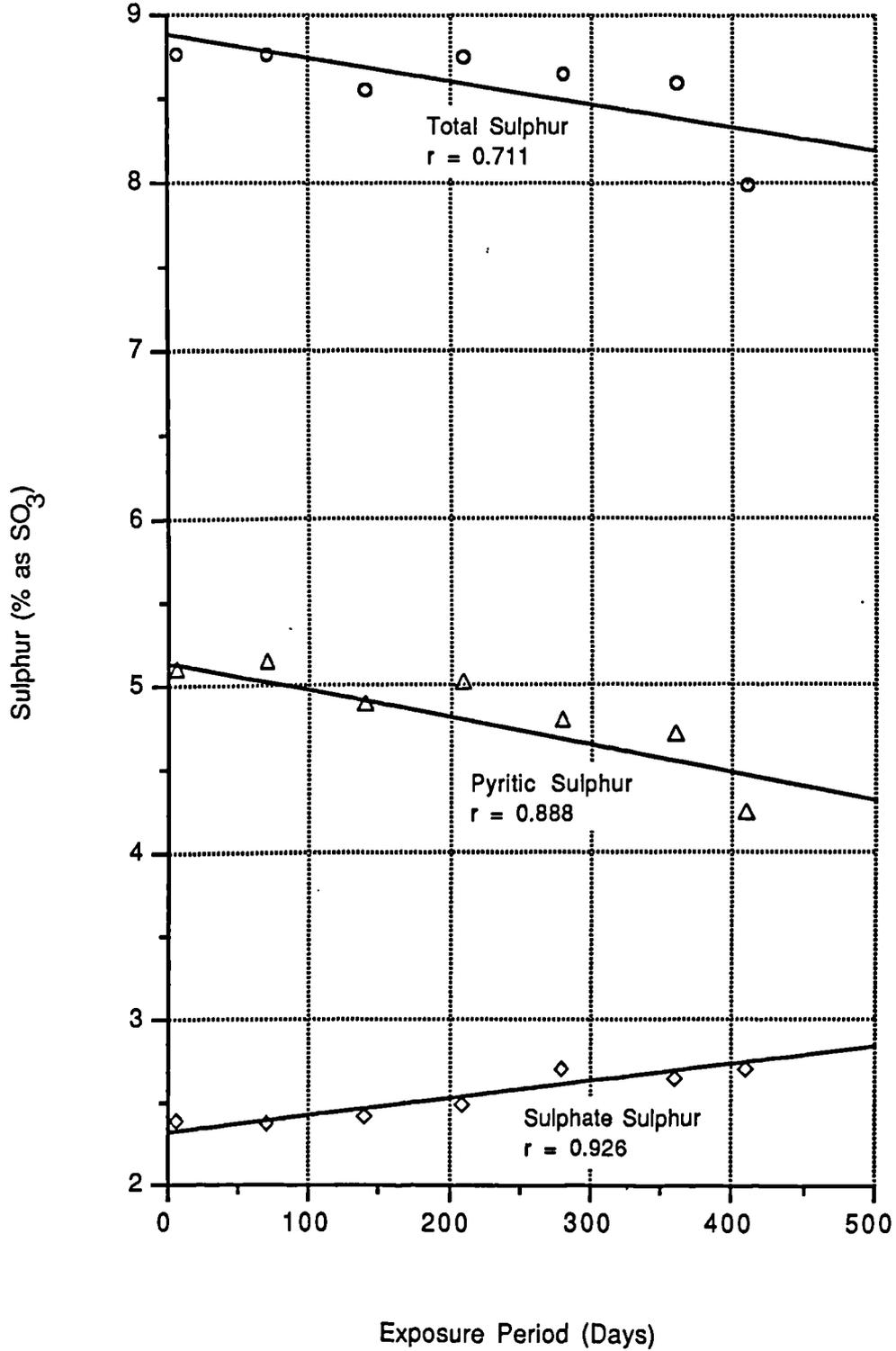


Figure 8.26 Variation in Sulphur Contents with Exposure to Environment 3 for CSM 31.



Sample	Pyrite Oxidation % SO ₃ / 100 days in Environment:-		Sulphate Production % SO ₃ / 100 days in Environment:-		Total Sulphur Loss % SO ₃ / 100 days in Environment:-	
	2	3	2	3	2	3
31	0.151	0.181	0.035	0.093	0.145	0.130
32	0.059	*0.022	0.022	0.037	*0.047	*+0.026
41	0.02	*0.016	0.015	0.024	*0.012	*0.002
51	0.062	0.061	0.022	0.033	0.053	0.028
52	0.072	0.071	0.055	0.076	*0.018	*+0.017
61	0.045	0.045	0.035	0.06	0.026	*0.016
71	*0.042	0.044	0.044	0.047	*0.011	*0.004
81	0.071	0.051	0.064	0.067	*0.029	*0.031

* Refers to changes in sulphur forms that are not statistically significant at the 10% level

+ Refers to CSM's that displayed an apparent increase in their total sulphur content

Table 8.1 Rate of Change in Sulphur Mineralogy for CSM

exposed to Environments 2 and 3 and the rate of decrease is statistically significant for thirteen of the sixteen values presented in Table 8.1. The relationships between the rate of pyrite loss in Environments 2 and 3 and the original pyrite content of the raw minestone are shown in Figure 8.27. Both these relationships are significant at the 1% level. In Environment 3 an average of 3% of the original pyrite content (as % SO₃) was oxidised in any 100 day period compared to 2.9% in Environment 2.

There is a statistically significant (at the 10% level) increase in the sulphate content of all eight First Phase CSMs in Environments 2 and 3. The relationships between the rates of sulphate production in the First Phase CSMs exposed to Environments 2 and 3 and the original pyrite content of the raw minestones are shown in Figure 8.28.

Fluctuations in water soluble sulphates were observed for some CSMs but, apart from an initial decrease, no general trend was discerned. The organic sulphur contents of the CSMs show no significant alteration with exposure to increased moisture content. Some organic sulphur contents were calculated as negative values due to the sum of the errors involved in the three determinations (total, pyritic and sulphate) employed for their calculation.

The pH determinations for water extracts from First Phase CSMs following seven days curing at 20°C and constant moisture content and following 410 days exposure to the three environments are tabulated in Table 8.2. These exhibit decreasing alkalinity in all three environments with the decrease being more marked for Environments 2 and 3.

Figure 8.27 Relationship between Rate of Pyrite Oxidation in First Phase CSM s and Pyrite Content of the Raw Minestones.

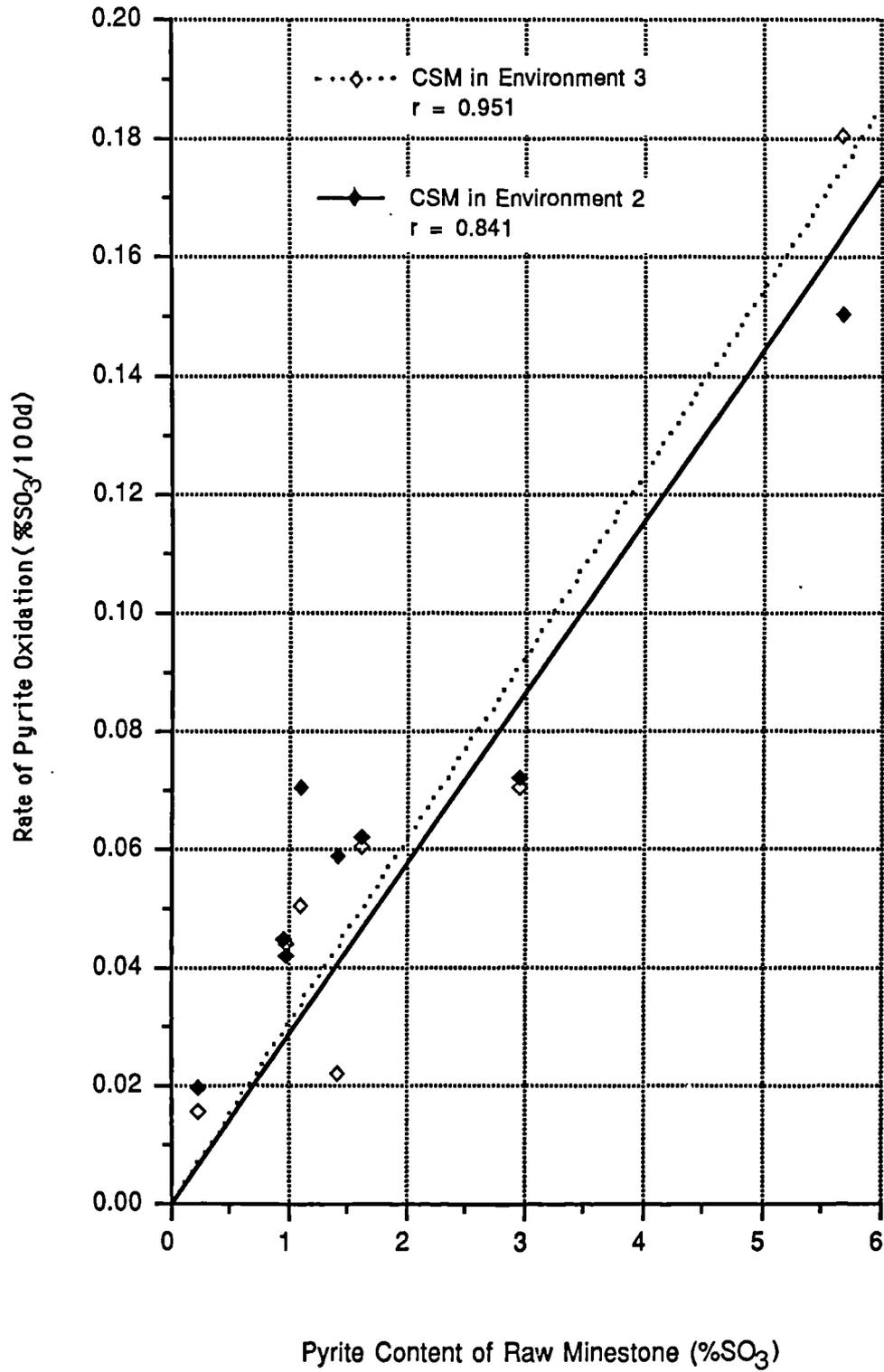


Figure 8.28 Relationship between Sulphate Production in First Phase CSMs and Pyrite Content of Raw Minestones.

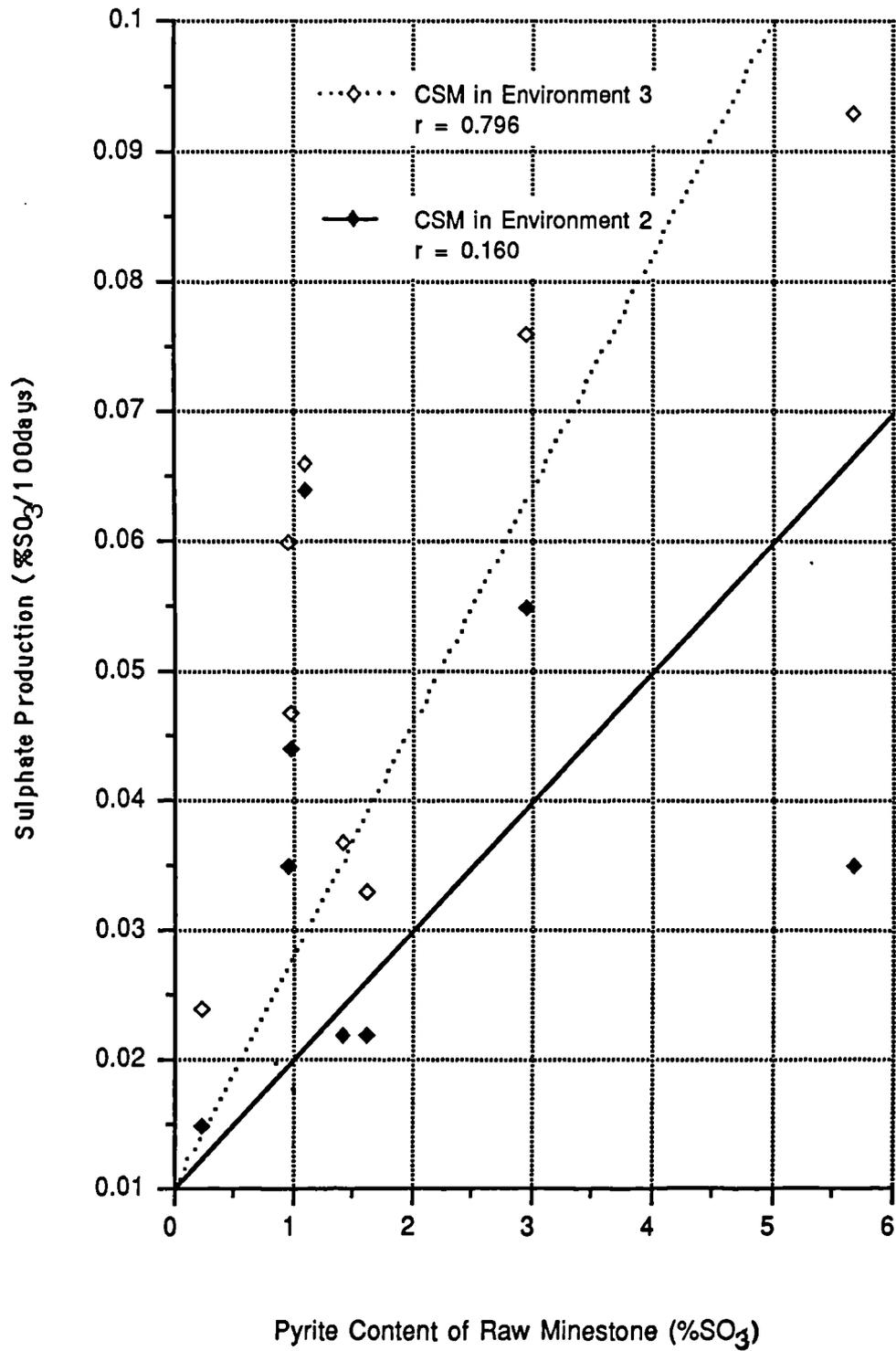


Table 8.2 Changes in the pH of CSM during Long-term Exposure.

Sample	pH values of 2:1 water/CSM extract following :-			
	7 days at Constant m/c	410 days exposure to :-		
		Env. 1	Env. 2	Env. 3
31	9.9	9.7	7.6	7.3
32	11.6	11.6	11.0	10.6
41	11.0	11.0	11.0	10.7
51	11.5	11.3	11.0	10.9
52	11.6	11.0	10.9	10.5
61	11.5	11.5	11.4	10.9
71	11.0	10.8	10.7	10.2
81	11.2	11.0	10.5	10.3

Table 8.3 Long-term Performance Parameters of CSM (see Section 8.8.1).

Sample	Long-term expansion of CSM Specimens (microns/100days)		Long-term strength development of CSM (%change/100days)	
	Env. 2	Env. 3	Env. 2	Env. 3
31	30.3	29.5	- 44.0	- 11.0
32	12.7	10.2	2.9	4.7
41	6.0	7.4	11.0	16.0
51	7.9	6.2	7.6	21.0
52	15.2	21.6	- 22.0	- 5.3
61	8.2	7.1	1.2	3.5
71	15.9	7.3	- 4.7	- 6.5
81	15.4	9.3	- 11.0	- 6.5
62	8.6	18.6	9.1	20.0
72	4.3	25.7	1.4	0.1
73	11.4	4.3	10.0	13.0
91	2.7	8.6	17.0	11.0
92	28.6	44.3	- 70.0	- 73.0
93	18.6	40.0	- 38.0	- 37.0
94	14.3	25.7	- 44.0	- 16.0
95	11.4	31.4	- 9.0	- 19.0

The observed reduction in the total sulphur content of CSM is thought to be due to the leaching of water soluble sulphates from the specimens. To test this hypothesis the sulphate level of the originally distilled, host water was determined prior to changing on three separate occasions. The average level of the host water sulphate for CSM 31 was 0.6 g/l (0.06% SO₃) in both environments. The sulphate levels of the remaining host waters lay between 0.1 and 0.2 g/l, with the exception of that of CSM 41 where only a trace of sulphate was found. The high value for the host water of CSM 31 and the absence of significant sulphate in that of CSM 41 is compatible with the sulphur bearing mineralogy of their associated raw minestones (9.45 and 0.35% respectively). However, the amount of sulphate found in the host water does not fully explain the losses in total sulphur. A further loss of sulphate may have occurred when the specimens were removed from the environments and their surfaces were dried by wiping with an absorbant cloth prior to weighing, so that surface deposits were progressively removed. Visual examination (discussed in Section 8.6) suggested that sulphate minerals may be precipitated close to the specimen surface and these minerals may be lost if surface spalling occurs resulting in further losses in the total sulphur content of the specimen.

The foregoing observations show that when specimens of CSM are exposed to Environments 2 and 3 there is a decrease in the pyritic sulphur content together with an accompanying increase in the sulphate sulphur content and a reduction in the alkalinity of the pore fluid of the specimens. Collectively these observations support the earlier hypothesis (Chapter 5) that the pyritic minerals in CSM are vulnerable to chemical oxidation if sufficient moisture is made available. The conditions in Environment 3 were thought, at the outset of the investigation, to be more favourable to oxidation as specimens are undersaturated and therefore an abundance of oxygen and water is available for chemical reaction. Complete flooding

of pyritic shales is thought to prevent pyrite alteration by the exclusion of oxygen (Hawkins and Pinches, 1984; Penner *et al*, 1971). However, the rate of pyrite loss in the immersed specimens was only marginally less than that in specimens in Environment 3. The supply of oxygen may have originated in unsaturated small pores or dissolved oxygen may have been available in sufficient quantities to promote oxidation. In addition, some oxygen would have penetrated the specimens when they were periodically removed from immersion for dimensional measurements.

The increase in sulphate sulphur is a result of the pyrite oxidation although this increase does not fully account for the quantity of pyrite oxidised. The sulphate produced can be considered to represent, on average, 70% of the pyrite lost in Environment 3 and only 50% in Environment 2. The leaching of water soluble sulphates together with the removal of surface deposits rich in sulphate (by drying of the surface or spalling) is thought to account for much of the discrepancy.

The initial decrease in water soluble sulphates results from reaction with the tri-calcium aluminate or calcium hydroxide during cement hydration to form less soluble sulphoaluminates and sulphates (ettringite and gypsum). Subsequent fluctuations in water soluble sulphate are inevitable due to the migration of some minerals into the host water and the production of others due to pyrite oxidation. These phenomena should not occur in Environment 1 and, as supporting evidence, such fluctuations were not recorded with these particular specimens.

Further evidence of pyrite oxidation can be obtained from a consideration of the changes in alkalinity given in Table 8.2. The clear decreases in the alkalinity of the water extracts from specimens placed in Envrionmens 2 and 3 are a direct result of the sulphuric acid produced during pyrite oxidation. The limited decreases in pH

from the polythene wrapped specimens suggests a reaction of the hydroxyl ions (OH^-) with carbon dioxide (e.g. $\text{Ca}(\text{OH})_2 + \text{CO}_2 \longrightarrow \text{CaCO}_3 + \text{H}_2\text{O}$; Equation 2.1).

It is now clear that the pyritic sulphur in CSM is oxidising and thus, the chemical reaction :-



must proceed in the CSMs when sufficient moisture and oxygen are made available but this reaction is prevented by ensuring CSM is not exposed to increases in moisture content. It is not possible from these results alone to ascertain whether the weathering processes outlined in Section 3.5.2 continue beyond this initial chemical reaction. However, the hydration of ferrous sulphate to form melanterite ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) is known to cause substantial volume increase (Dougherty and Barsotti, 1972) and the sulphuric acid (H_2SO_4) produced may lead to the formation of other expansive sulphate minerals. The increased sulphate content arising from this chemical reaction increases the possibility of sulphate reactions with the products of cement hydration which also lead to further expansion. Therefore, it may be concluded that the established chemical oxidation of pyrite by Equation 3.1 alone is bound to have engineering implications given sufficient pyrite and exposure to suitable environmental conditions.

8.5 Detection of Mineralogical Changes in First Phase CSMs by X-Ray Diffraction Techniques

The calcium silicate and calcium aluminate hydrates formed are considered amorphous or at least microcrystalline and, therefore, not detectable by XRD. The gypsum and sulphoaluminate contributions of the cement after 7 days are below the level of confident detection. The only discernable differences between X-Ray diffractograms of raw minestone and CSM following seven days curing are an increase to any existing calcite peak at 3.04Å and the presence of a peak at 2.63Å attributed to portlandite (calcium hydroxide resulting from the hydration of di- and tri- calcium silicates in cement). The increase in the mineral calcite results from carbonation of portlandite which is represented stoichiometrically by :-



No trace of portlandite peaks can be found on diffractograms of CSMs after 70 days in any environment. Carbonation may account for much of this disappearance (as shown by a corresponding increase in the calcite peak) although other mechanisms may be pozzolanic reactions, ion exchange and sulphate attack.

The changes in mineralogy brought about by the geochemical alteration of pyrite and its reactive products will be small in terms of the total cement stabilised material and the sensitivity of the XRD technique used is only sufficient to detect mineral transformations rather than quantifying them. In CSM 31 there is a gradual reduction of the pyrite peak height with time, when compared to the stable quartz peaks. The total erosion for a 410 day exposure to Environment 3 represents about 15% of the initial pyrite of CSM 31. Ettringite peaks at 5.60Å and 3.38Å appear on

diffractograms taken after 70 days exposure to Environment 2. Throughout the 410 days exposure to Environments 2 and 3 there is a general increase in both gypsum and ettringite peak heights (as compared with quartz peak heights). Again these changes are not observed on the diffractograms produced from samples exposed to Environment 1.

In the remaining CSMs no changes in the initial mineral peaks can be successfully detected. However, for CSMs 71 and 81 ettringite peaks can be resolved for specimens exposed to Environments 2 and 3 after 70 days. The relative height of these peaks compared to the quartz peaks increases throughout the exposure periods. No reduction in the gypsum peak is noted. Ettringite peaks are discernable for CSM 61 at a later stage during its exposure to the same environments.

These findings support the hypothesis of pyrite oxidation and sulphate attack. The oxidation process may be the direct cause of increased gypsum in CSM 31 or it may produce other sulphate salts which form gypsum by combination with portlandite or calcite. The existing sulphate minerals together with those produced by pyrite oxidation are available for reaction with cement hydration products or clay minerals to form ettringite. The oxidation process can only be diagnosed by XRD in CSM 31 where the pyritic sulphur content of the raw material is considerably greater than that of the other First Phase minestones.

8.6 Visual Examination of First Phase CSMs and Analysis of Secondary Phases.

Specimens cured in Environment 1 at constant moisture content displayed no visual signs of deterioration throughout the duration of the study. This concurs with the limited volume changes and absence of either strength loss or geochemical alteration of the same specimens.

The visual deterioration of specimens exposed to Environments 2 and 3 is largely dependent upon the source of the minestone. Cracks and fissures were noticed in some specimens after only seven days exposure with swelling of the CSM occurring at later stages. The extent and degree of cracking and spalling does not appear to be controlled by the strength of the CSM. CSM 41, having comparatively low compressive strength, suffered little visual deterioration in all three environments whereas the originally higher strength CSM 71 showed signs of surface precipitation and cracking especially in Environment 3 (see Section 8.6.3). In many cases the zones of distress were associated with crystalline deposits and, where possible, these were analysed by XRD and Scanning Electron Microscopy (SEM) techniques. Some typical examples of specimen deterioration and the subsequent analysis are presented in the following sections.

8.6.1 Deterioration of CSM 31

Plate 8.1 shows a typical specimen of CSM 31 after 140 days immersion in water at 30°C. This specimen had expanded by 3.6% over this period of immersion and displayed signs of cracking with a section of the material detached from the bulk of the specimen. At the location of this rupture plane, a black shale particle with white crystalline deposits was in evidence. A microscopic examination of this particle, Plate 8.2, revealed a laminated particle in an advanced state of disintegration with white deposits visible both on the surface of the particle and between the particle laminae.

A sample of the degraded particle was removed and prepared for electron microscope analysis. The photomicrograph, Plate 8.3, shows a cluster of rectangular and platey crystals (left) closely associated with the shale together with well ordered fibrous crystals (right). A dispersive X-Ray analysis gave calcium and sulphur as the



Plate 8.1 Specimen of CSM 31 following 140 days Immersion



Plate 8.2 Photomicrograph of Degraded Shale Particle in CSM 31 (Env. 2)

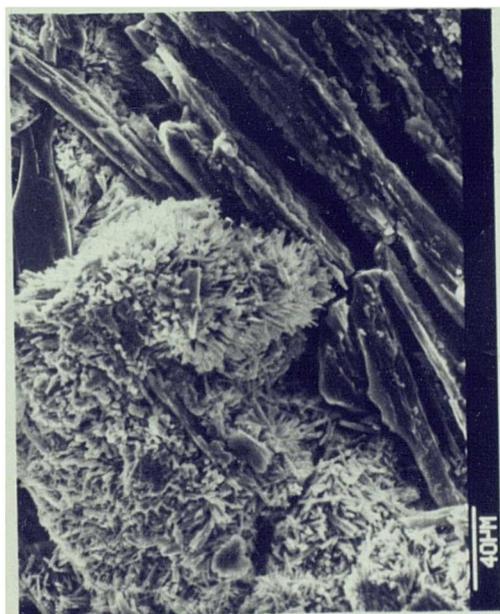


Plate 8.3 SEM Photomicrograph (x 500) of Degraded Shale Particle (Env. 2)



Plate 8.4 Specimen of CSM 31 following 410 days in Environment 3

constituent elements of the platy crystalline deposit and calcium, aluminium and sulphur for the fibrous material. This suggests that the mineral phases may be gypsum and ettringite respectively. XRD analysis of a scraping of altered material gave gypsum as the principal mineral after the quartz and clay minerals associated with the background particle. Other minerals present in order of diminishing peak heights were ettringite, pyrite, calcite and a small trace of jarosite.

The particle must have been intact at the time of mixing or it would have been dispersed through the specimen and, although some physical damage may have occurred as a result of compaction, the mineralogical alteration must have occurred during exposure of the CSM. The particle, a sulphide bearing mudrock or shale, has undergone geochemical breakdown as a result of pyrite weathering. The formation of gypsum in close association with the degraded rock may result as a reaction between the products of weathering and calcium either from the rock particle or from cement minerals. Ettringite may be formed by chemical reaction between sulphates and clay minerals or more likely by sulphate attack on the products of cement hydration. These products, gypsum and ettringite, are undoubtedly the cause of the disruption seen in Plate 8.1.

Plate 8.4 shows a specimen of CSM 31 after 410 days exposure to Environment 3 during which it suffered an expansion of 2.8% and a complete loss of strength. The specimen had an extensive pattern of cracks which led to a complete disruption of the uppermost material when the specimen was removed from this environment. The CSM was easily prised apart at the location of the crack marked X on Plate 8.4. The upper surface was examined by reflected light microscopy and Plate 8.5 shows a coating of crystalline mineral deposits. A scanning electron photomicrograph, Plate 8.6, shows needle like crystals on the surface with elements calcium, aluminium, sulphur and silicon counted by dispersive X-Ray analysis. The needles are typical of

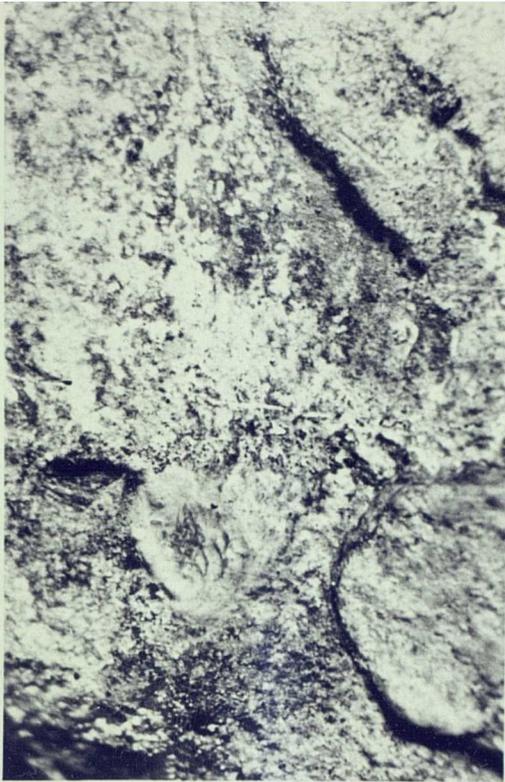


Plate 8.5 Photomicrograph of Crack Infill Material in CSM 31 (Env. 3)

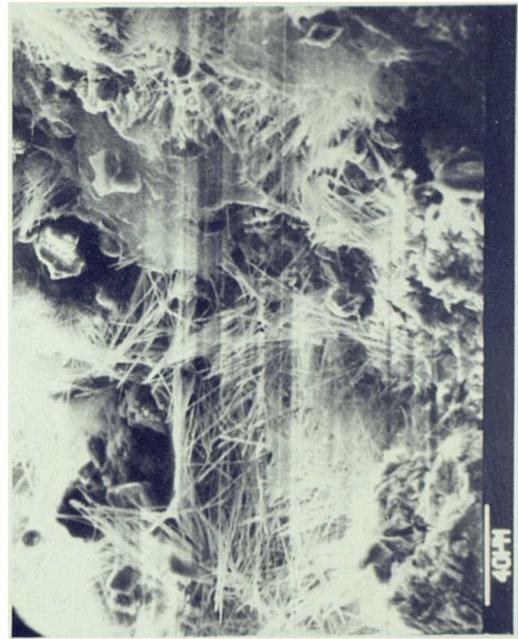


Plate 8.6 SEM Photomicrograph x 10 of Crack Infill in CSM 1 (Env. 3)



Plate 8.7 Specimen of CSM 52 following 410 days in Environment 3



Plate 8.8 SEM Photomicrograph (x 500) of Fracture Surface in CSM 52 (Env. 3)

ettringite and the associated platelets, of gypsum. XRD analysis of the white mineral confirmed the presence of ettringite with very small traces of gypsum. The silicon probably originates from the background quartz and clay minerals or cement paste minerals.

The opening of this fissure (marked X on Plate 8.4) is undoubtedly the result of ettringite formation. The gypsum may have been present at compaction and a large proportion could have reacted with cement or clay minerals to form the ettringite. Alternatively, the gypsum may be a later phase due to magnesium sulphate attack on ettringite (or calcium silicate hydrates), sulphate attack on calcium hydroxide (or its carbonated form) or pyritic sulphur oxidation.

8.6.2 Deterioration of CSM 52

Plate 8.7 shows a specimen of CSM 52 after 410 days in Environment 3. After this period of exposure CSM 52 had suffered 0.63% linear expansion and exhibited a gradual strength reduction. A visual examination of specimens gave no indication of material deterioration although white crystalline deposits were in evidence at the surface of some specimens (Plate 8.7). Following strength determination at 410 days, the surfaces of the crushed material were examined by SEM, and this showed that in general the majority of the fractured surface area was devoid of sulphate bearing phases. However, locally the minerals gypsum and ettringite had formed within the material matrix but not in intimate association (Plate 8.8 and 8.9). Minestone 52 has a total sulphate content of only 0.05% and it is unlikely that either this small quantity of sulphate bearing minerals or that contributed by the cement would form at discrete locations but would rather be dispersed throughout the specimen. The presence of gypsum and ettringite at isolated locations is probably due to the production of sulphate at these sites by the alteration of sulphide rich

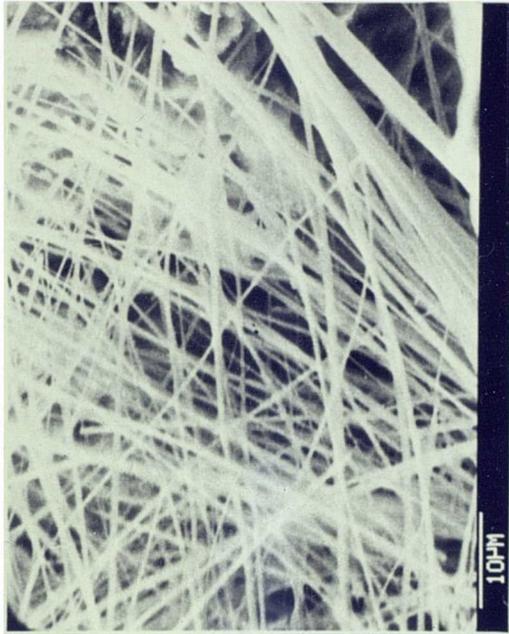


Plate 8.9 SEM Photomicrograph (x 20 0) of Fracture Surface in CSM 5 (Env. 3)

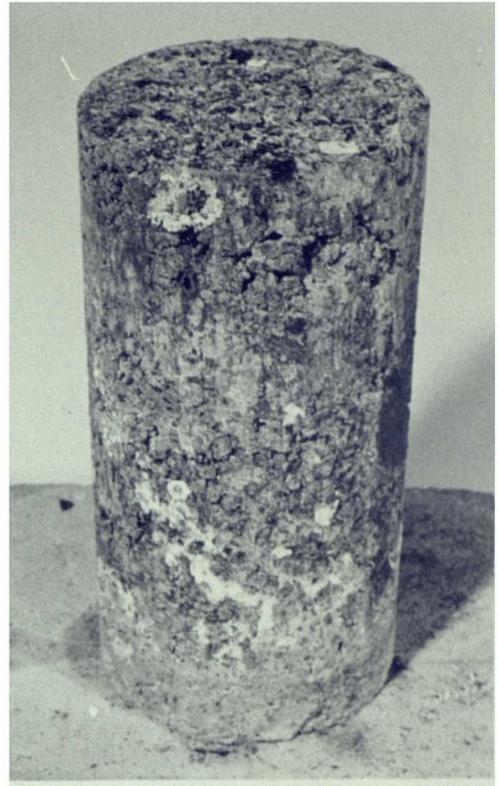


Plate 8.10 Specimen of CSM 1 following 11019 days immersion



Plate 8.11 SEM Photomicrograph of Crack Infill Material in CSM 71 (Env. 2)



Plate 8.12 Specimen of CSM 71 following 410 days in Environment 3

particles and this may explain the eventual strength loss of this CSM. Since these phases were only visible by SEM, it was not possible to physically isolate the minerals for identification by selective X-Ray diffraction.

8.6.3 Deterioration of CSM 71

Plate 8.10 shows a specimen of CSM 71 after 70 days immersion at which stage there was little deterioration in strength. White crystalline deposits had formed within some of the surface voids and XRD analysis of this material gave the chief minerals as ettringite and thenardite (sodium sulphate). Crack infill material from specimens immersed for 300 days was also examined by SEM and the photomicrograph, Plate 8.11, shows ettringite needles forming in cracks and fissures.

Plate 8.12 shows a specimen of CSM 71 that had been exposed to Environment 3 for 410 days. Cracks were in evidence on the outside of the specimen and areas coated with white mineral precipitation were clearly visible. Considerable spalling for the surface of the CSM was associated with this area of precipitation. XRD analysis gave the principal mineral deposited at the surface as thenardite (sodium sulphate). Plate 8.13 shows a photomicrograph of a piece of CSM that had ruptured from the area of spalling. Ettringite needles coat the surface of the particle, but the elemental analysis also shows traces of sodium. Thenardite is a soluble sulphate mineral and was probably deposited at the surface of the CSM specimen by pore water movements. The sulphate content at the surface, therefore, increased and consequently the potential for sulphate attack by the saturated sulphate rich pore water became greater. The result is ettringite formation within the outermost material leading to disruption of bonds and CSM spalling. A photomicrograph of the inner surfaces of these spalled fragments, Plate 8.14, shows ettringite formation

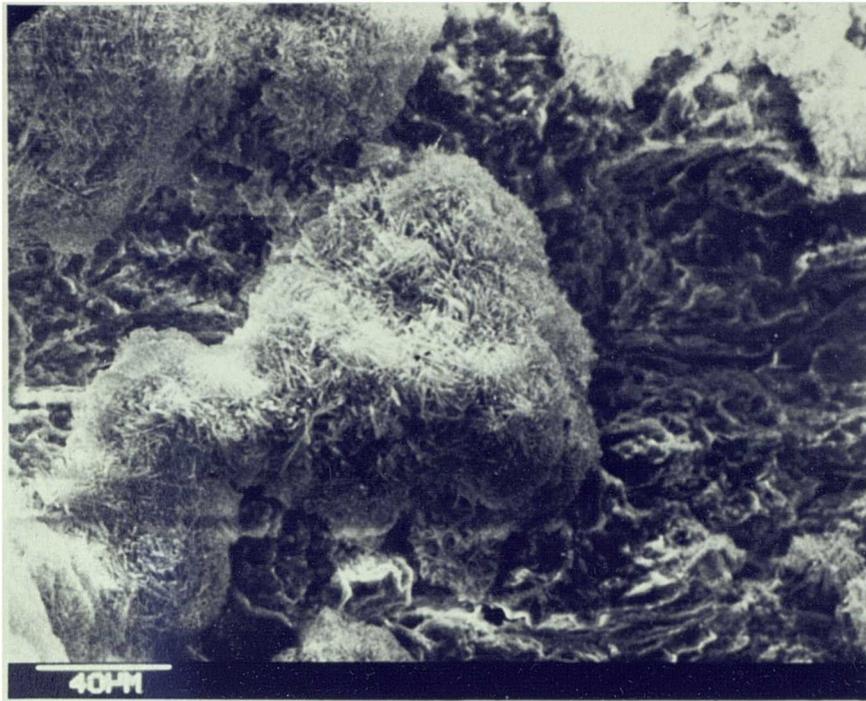


Plate 8.13 SEM Photomicrograph (x 500) of Disrupted CSM 71 (Env. 3)

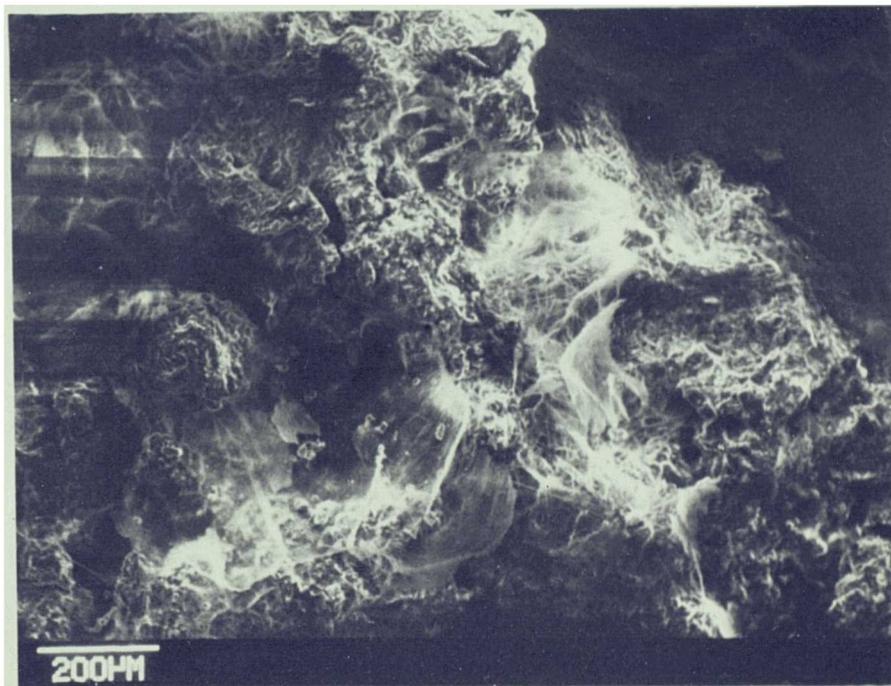


Plate 8.14 SEM Photomicrograph (x100) of Internal Crack Surfaces in CSM 71 (Env. 3)

similar to that shown in Plate 8.11 for the immersed specimen.

8.6.4 Behaviour of the Remaining First Phase CSMs

CSMs 32, 51 and 61 gave no visual indication of distress. Examination of fracture surfaces following crushing strength determinations revealed very little ettringite or other sulphate mineral formation. CSM 41, despite losing substantial strength and suffering considerable expansion in the short-term, did not display visual deterioration in the long-term and microscopic examination failed to produce evidence of secondary mineral phases. All four of these CSMs had total sulphur contents less than 2% (as SO_3) with sulphate contributions less than 0.3%

CSMs 71 and 81 behaved similarly with some degree of external precipitation and spalling. Ettringite was found, both in association with the spalled material and the internal cracks. The sulphur mineral proportions of the two raw minestones were alike, with total sulphur contents of 2.1 and 2.15% and sulphate contents of 0.96 and 0.80% (all as SO_3) for minestones 71 and 81 respectively.

8.6.5 Summary

The minestones with the highest sulphate (both total and water soluble) contents produced CSMs that were prone to disruption due to ettringite and gypsum formation. The high pyrite content of minestone 31 resulted in disruption due to the breakdown of sulphide rich particles. The pyrite in CSMs 71 and 81 may not have been identified as a direct cause of disruption but its weathering undoubtedly increases the potential for sulphate attack in an already susceptible material. CSM 52 exhibited strength deterioration and yet has less sulphate sulphur than CSMs

32, 51 and 61 which continued to gain strength in all environments. SEM examination of CSM 52 revealed ettringite and gypsum coated fracture surfaces and these are thought to result from the oxidation of the pyritic sulphur which is abundantly available in the raw minestone. CSM 41, though a poor engineering material, is considered to be stable in the long-term as a result of the extremely low pyritic and sulphate sulphur contents of the raw minestone.

The long-term durability of CSM specimens is largely dependent on the availability of sulphate and sulphide minerals in the raw minestone rather than the strength of the stabilised material. This fact is exemplified by the behaviour of CSMS 41 and 71, the latter material, despite achieving considerably higher strength in Environment 1, suffers considerably greater deterioration in the other two environments. Consequently, if sufficient deleterious sulphur compounds are present, the CSM would, inevitably, be expected to deteriorate regardless of its short-term engineering performance, the degree of breakdown depending on the environmental conditions.

8.7 Microbiological Involvement

The presence of bacteria, of either the Thiobacillus or Ferrobacillus genus, was not identified in any of the CSM samples examined. This suggests that the alkalinity of the environment is sufficient to inhibit bacterial activity even in the more weathered CSMS where the pH is somewhat less alkaline.

The first stages of pyrite weathering involve the chemical oxidation of pyrite, Equation 3.1, and the oxidation of ferrous to ferric iron, Equation 3.2. The occurrence of the first reaction has been established in CSM by this study. The second reaction may occur abiotically (without microbiological involvement)

during the early stages of pyrite alteration (Kleinmann *et al*, 1981) but it has been reported that the reaction can not occur chemically in an acid environment (Penner *et al*, 1970). The reaction path for the oxidation of pyrite in cement stabilised materials is, therefore, unlikely to be bacterial. However, the oxidation of pyrite, Equation 3.1, the oxidation of ferrous to ferric iron, Equation 3.2 and the resulting oxidation of pyrite by the ferrous iron, Equation 3.3, is an established chemical path for the aqueous oxidation of pyrite (Lowson, 1982). Therefore, with the maintenance of alkaline conditions in CSM there is a possibility that the complete chain of reactions, Equation 3.1-3.3, can take effect without bacterial interaction.

8.8 Engineering Implications of Geochemical Alterations

8.8.1 Measurement of Engineering Performance

The rates of sulphide oxidation and sulphate production discussed in Section 8.6 were defined as percentage change (in SO_3) per 100 days. In order to assess the implications of original sulphate levels and subsequent geochemical alteration it was necessary to establish similar parameters capable of characterising the long-term engineering performance of CSM. The long-term strength of CSM appears to be independent of the physical characteristics and, as with the long-term expansion, alternative explanations must be sought using the chemical evidence revealed in the previous sections. It was considered that by quantifying the strength and expansion behaviour of CSM during the final phase of exposure (beyond 240 days), it may be possible to correlate these parameters and link them to the chemical factors outlined earlier.

Expansion:-

The long-term expansion rate is defined as the magnitude of swelling per 100 day exposure period following 240 days. For the First Phase CSMs this quantity could be determined by linear regression of the data between 240 and 410 days. For the second phase CSMs it was necessary to multiply the expansion that occurred between 240 and 280 days by a factor of 2.5 to provide an approximation of the amount of expansion that would have occurred between 240 and 340 days.

Strength Development:-

For the First Phase CSMs it was possible to use the strengths determined between 240 and 410 days in a linear regression analysis. From this analysis the strength change per 100 day exposure period expressed as a percentage of the 240 day strength of specimens in the same environment could be computed. Again there were not sufficient data available to use the same procedure for the Second Phase CSMs. Due to the degree of scatter encountered in the strength determinations between 240 and 280 days these data were not considered to be sufficient to provide a rate of strength development. Therefore a linear regression of strengths between 180 and 280 days was used to compute the strength change of CSM during this period expressed as a percentage of the 240 day strength. Positive values indicate strength gain and negative values were obtained for CSMs that suffered long-term strength loss.

These parameters are displayed in Table 8.3.

8.8.2 The Effect of Sulphur Forms on the Volume Stability of CSM

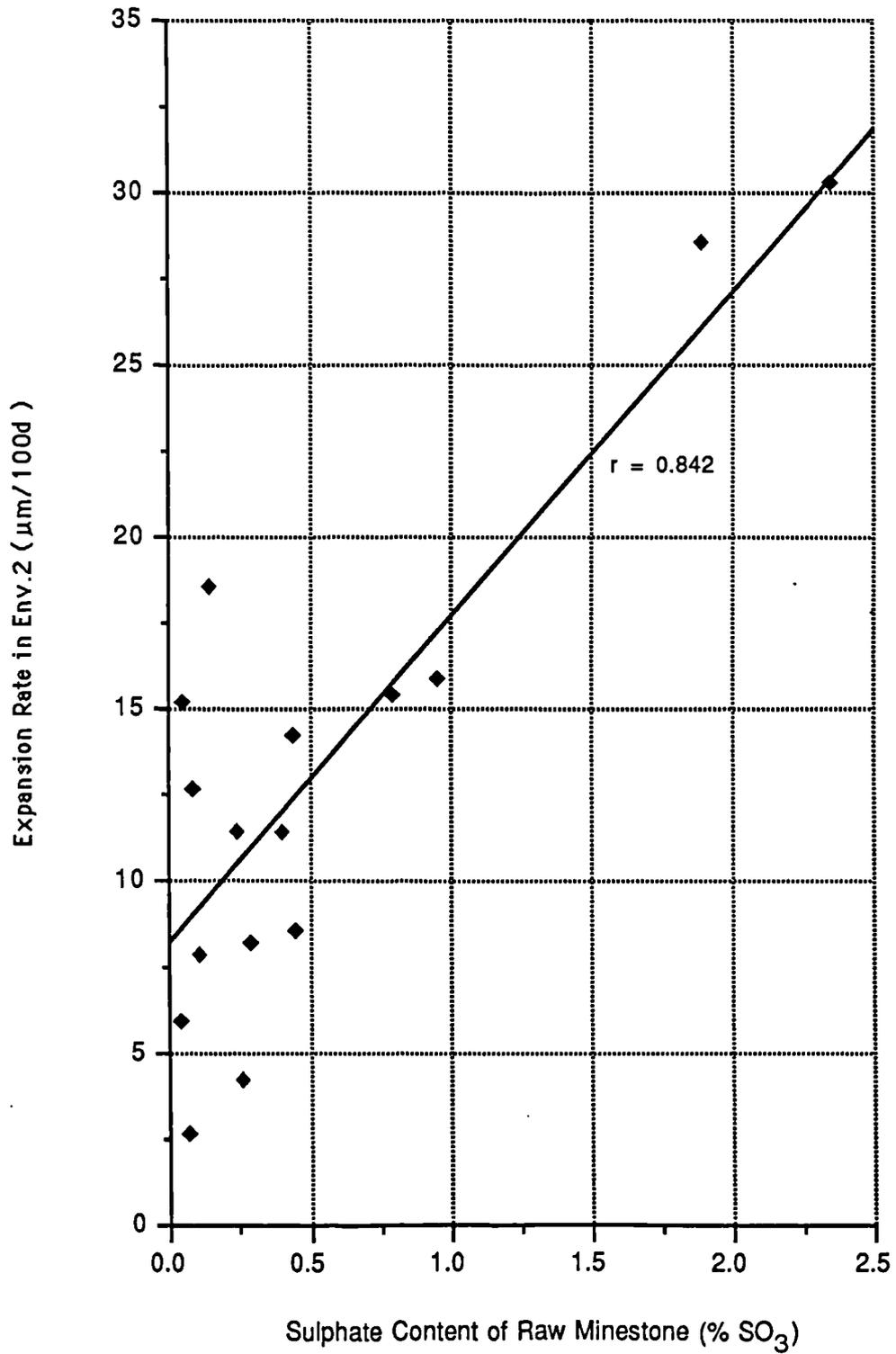
The effect of pyrite on CSM depends entirely on its oxidation. If the mineral does not oxidise and produce sulphate minerals it will have no deleterious effects. However, it has been established that the rates of pyrite oxidation and sulphate production are governed by the quantity of pyrite initially available, Figures 8.27 and 8.28. Thus the original pyrite content of the raw minestone was used in the subsequent analyses as these data were available for all sixteen minestones.

The relationship between the long-term expansion rate of immersed CSM specimens and the total sulphate content of the raw material is shown in Figure 8.29. The relationship shows that as the acid soluble sulphate content of the raw material increases then the expansion also increases. The mineral form of the sulphates is obviously a factor in determining the rate and degree of sulphate attack and this is not reflected in the relationship in Figure 8.29 which exhibits considerable scatter at low sulphate contents. Most sulphate minerals will ultimately react with tri-calcium aluminate to produce ettringite, but, the rate of this reaction is controlled by the stability of the sulphate mineral. Some sulphates react with calcium hydroxide to form gypsum. Magnesium sulphate may also react with both calcium silicate hydrates and ettringite to form further gypsum. The reactions were discussed in Section 2.4.3.

The oxidation of pyrite within immersed CSM specimens has been established from the results of this study (Section 8.4), and this has been linked, by a multiple regression analysis of the data, to give the following estimate of the expansion (in microns/100 days).

$$\text{Expansion} = 5.3 + 7.2 \text{ AS} + 1.6 \text{ PS} \quad \% \text{ fit} = 84\% \quad \text{Equation 8.1}$$

Figure 8.29 Relationship between Long-term Expansion Rate of CSM in Environment 2 and Sulphate Content of Raw Minestone



Where; AS = acid soluble sulphur of the raw minestone
PS = pyritic sulphur of the raw minestone

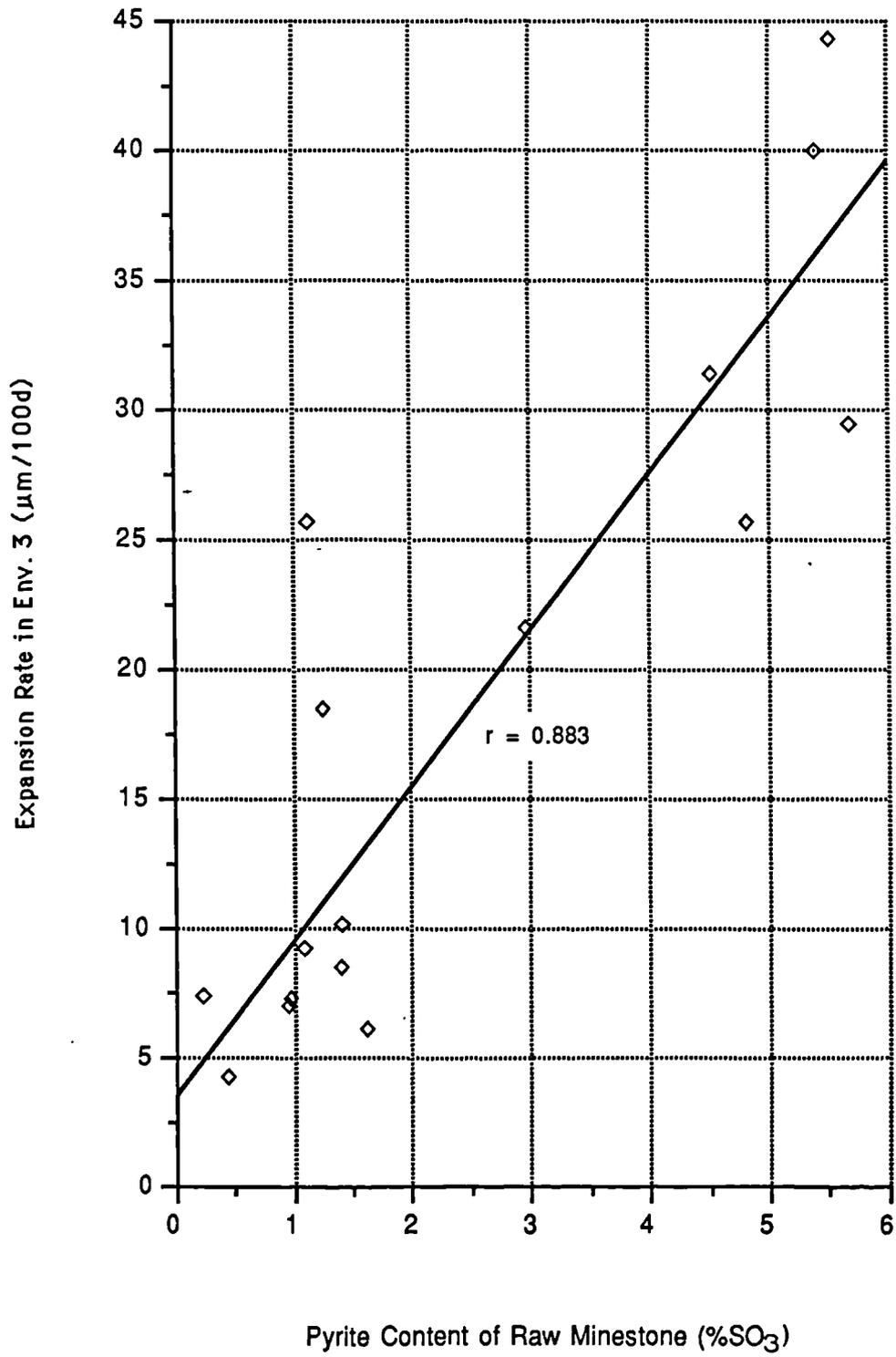
The null hypothesis, that the expansion is independent of the pyritic sulphur content, can be rejected at the 1% level of significance. This expansion contribution is undoubtedly the result of the oxidation of pyrite, the rate of which was shown to be linearly proportional to the original pyritic sulphur content (Figure 8.27).

The expansion of specimens in Environment 3 is largely controlled by the pyritic content of the raw minestone, as shown in Figure 8.30. Again this can be attributed to the oxidation of the pyrite. The equation for this relationship is :-

$$\text{Expansion} = 4.4 + 5.7\text{PS} \quad r = 0.883 \quad \text{Equation 8.2}$$

The expansion of the specimens in this environment does not appear to be affected by the sulphate content of the raw minestone, with a correlation coefficient of only 0.42 being calculated for these two variables. In addition, using either total or water soluble sulphate as a second independent variable in a multiple regression does not significantly increase the degree of correlation of Equation 8.2. A greater degree of correlation was expected as the conditions were thought to be conducive to sulphate attack and ettringite formation. One explanation, for the reduced effect of sulphate attack might be the increased pore water movement in specimens exposed to Environment 3. The more soluble sulphates are readily transported by pore fluid and were often found precipitated at the surface of the specimens. However, the quantity of sulphate removed by this process is small and the pore fluid will contain sufficient sulphate ions to promote sulphate attack. The role of the sulphates available at the time of mixing in determining the performance of CSM in

Figure 8.30 Relationship between Long-term Expansion Rate of CSM in Environment 3 and Pyrite Content of Raw Minestone.



Environment 3 should not be ignored because of this lack of correlation, for these have certainly been shown to correlate with the short-term expansion (i.e. Chapter 7).

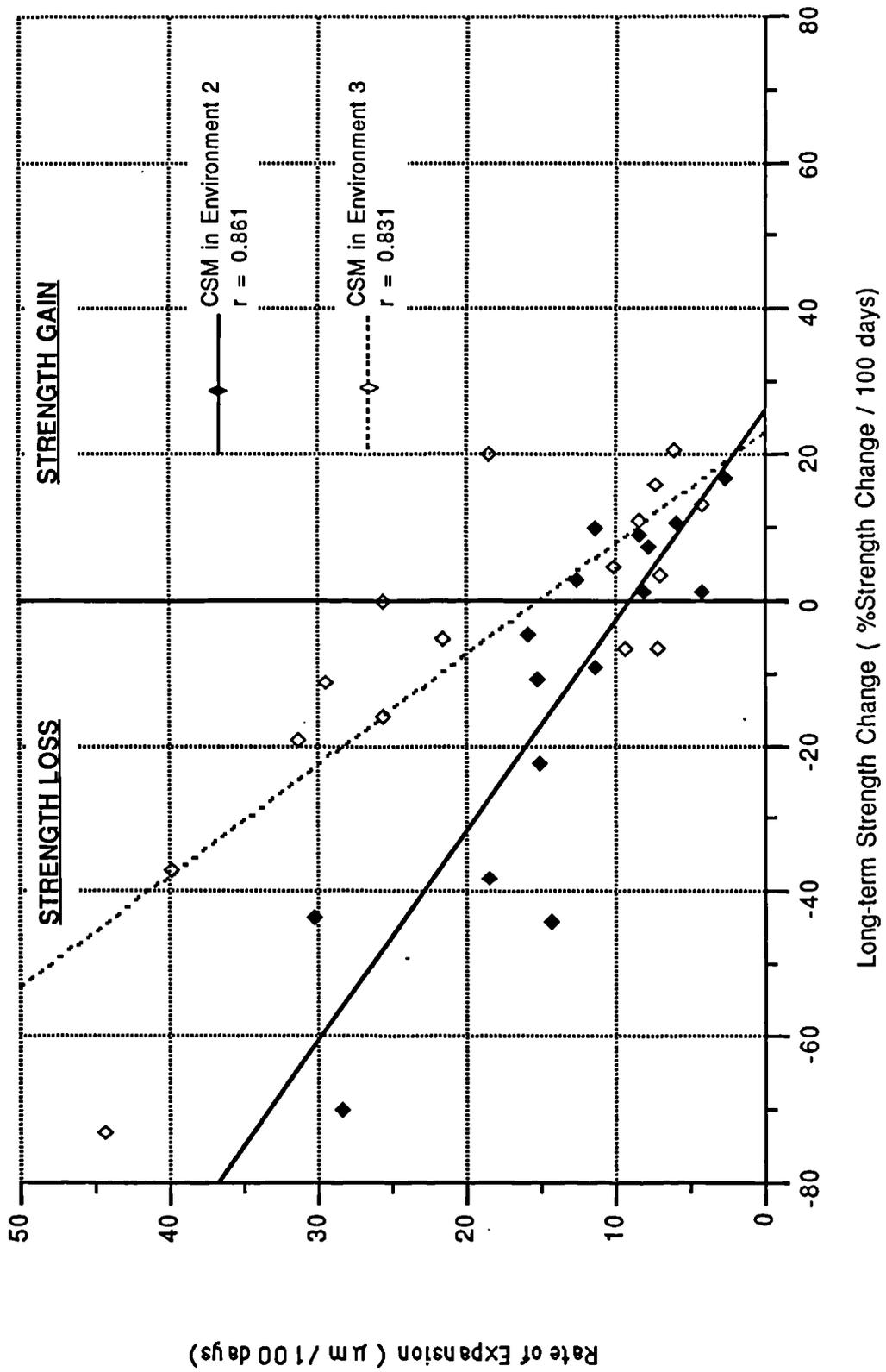
The relationship shown in Figure 8.29 contains a constant of 8.1 microns/100 days and this high value is largely attributed to the contribution of pyrite oxidation to the expansion of immersed CSM. This contribution is included in the multiple regression shown in Equation 8.1 and consequently this relationship has a reduced constant of 5.3 microns/100 days which is similar to the constant of 4.4 microns/100 days in Equation 8.2 for specimens in Environment 3. These approximations suggest that a part of the expansion is due to mechanisms other than sulphur chemistry, although a substantial portion of the intercept values may be allotted to experimental scatter.

8.8.3 The Effect of Long-term Expansion Rates on the Strength of CSM

The relationship between the long-term strength changes and expansion rates for specimens exposed to Environments 2 and 3 are shown in Figure 8.31. Both relationships have a similar intercept, these being 25.6 and 23.0 % strength gain/100 days for Environments 2 and 3 respectively. These constants are attributed to the strength development due to the continuing hydration of cement.

Higher expansion rates are required to produce strength losses in specimens in Environment 3 that are comparable to the losses suffered in Environment 2. This is possibly a corollary of the higher strengths achieved by CSMs exposed to Environment 3 and so they were more capable of resisting the effects of expansion. In addition, the deterioration of CSM 71 exposed to Environment 3 (see section 8.6.3) showed a large degree of degradation at the surface of the specimen. This

Figure 8.31 Relationship Between Long-term Strength Development and Expansion Rates for CSM.



phenomenon may produce overall linear expansion without the expected loss in strength as the interior of the specimen remains relatively intact.

8.8.4 The Effect of Sulphur Forms on the Long-term Strength Development of CSM

The long-term strength development for immersed CSM specimens does not reliably correlate with the sulphate sulphur content of the raw minestone alone but multiple regression analysis provides reasonable estimation of the strength modification when both total sulphate and pyritic sulphur are considered, the equation being :-

$$LS = 17.1 - 10.2 AS - 9.3 PS \quad \% \text{ fit } 83\% \quad \text{Equation 8.3}$$

Where; LS = long-term strength development (% change /100 days)

AS = acid soluble sulphate content of raw material (% SO₃)

PS = pyritic sulphur content of raw material (%SO₃)

The percentage strength change in 100 days after long-term immersion is thus controlled mainly by a combination of the sulphate and pyritic sulphur available in the raw material.

An examination of the regression coefficients of Equations 8.1 and 8.3 would suggest that the pyritic content has greater influence on the strength than on the expansion of immersed CSM specimens. Pyrite oxidation not only forms minerals of lower density but also results in the deterioration of sulphide rich particles which will produce areas of weakness in CSM. The latter may reduce the strength of the CSM

without necessarily resulting in overall specimen expansion.

Since the coefficients of the sulphur contents in the multiple regression are of similar magnitude it is possible to use the sum of sulphate and pyritic sulphur as a single independent variable in a regression giving:-

$$LS = 17.2 - 9.5 (AS + PS) \quad r = 0.910 \quad \text{Equation 8.4}$$

The organic sulphur represents a relatively small proportion of the total sulphur content, thus the latter may be used in place of the sum of sulphate and pyritic sulphur with a negligible decrease in reliability. The equation is:-

$$LS = 15.9 - 8.4 TS \quad r = 0.901 \quad \text{Equation 8.5}$$

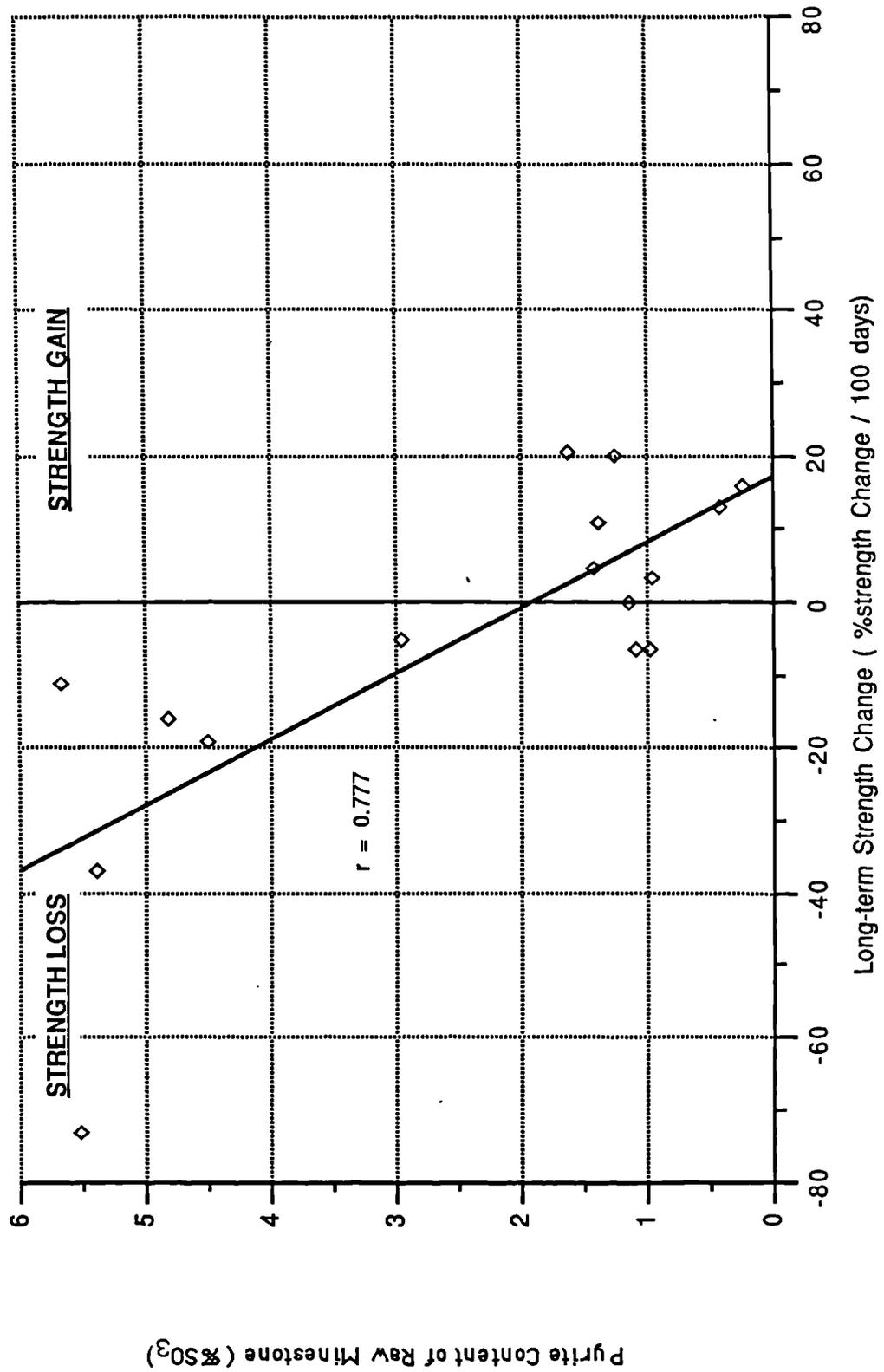
Where; TS = total sulphur content of raw minestone

For CSM exposed to Environment 3, the rate of strength change is largely dependent on the pyritic sulphur content alone. The relationship is shown in Figure 8.32 and may be represented by:-

$$LS = 17.5 - 9.3 PS \quad r = 0.777 \quad \text{Equation 8.6}$$

The intercept value of 17.5% gain/100 days for this relationship is similar to the intercept of 17.1% gain/100 days for the multiple regression analysis (Equation 8.3) for the immersed specimens. Again these constant terms can be attributed to the strength gain that could be expected in these environments for specimens without deleterious sulphur minerals.

Figure 8.32 Relationship Between Long-term Strength Development of CSM in Environment 3 and Pyrite Content of Raw Minestone.



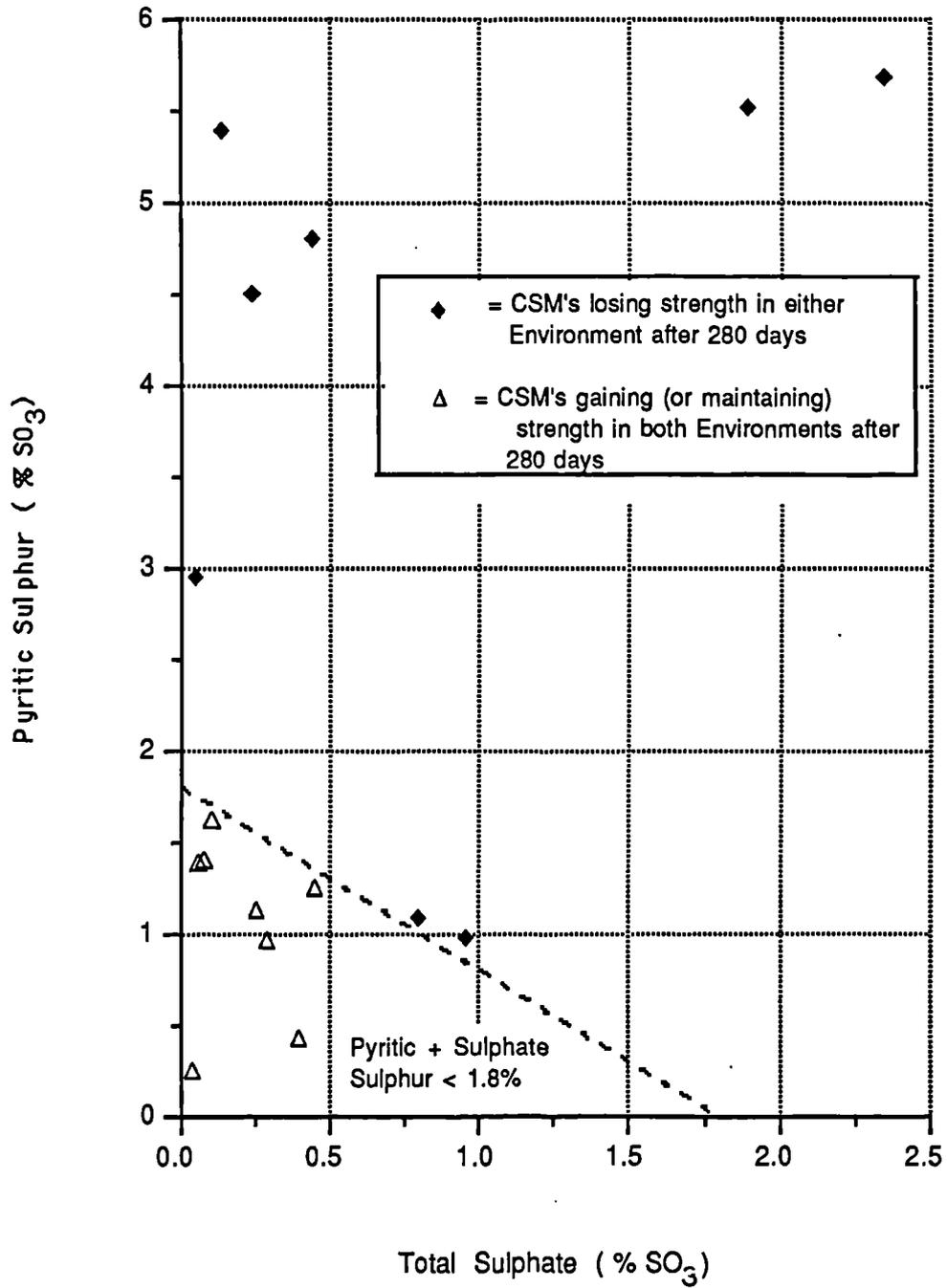
The loss of strength of specimens in Environment 3 appears to be virtually unaffected by the sulphate sulphur contents (total and water soluble) of the raw material. This concurs with the findings for the expansion of the same specimens and the same arguments are applicable.

8.8.5 Suggested Sulphur Limits for CSM.

The expansion of CSM can, within reasonable limits, be tolerated provided it does not result in significant strength reduction or render the structure unserviceable. The eight CSMs that appear to continue to lose strength beyond the duration of this study can not be classed as "durable" materials unless ingress of moisture into the CSM is prevented. The other eight specimens do not suffer any further strength loss beyond the initial loss following exposure to moisture in Environments 2 and 3 and may, therefore, be considered as "durable". Since the long-term performance of CSM is related to its sulphur bearing mineralogy it should be possible to separate these "durable" CSMs on the basis of the chemistry of the raw minestone.

From the relationship between long-term strength and pyritic sulphur content, Figure 8.32, a pyrite limit can be calculated on the basis of strength loss. If CSMs are to maintain strength in Environment 3 the pyrite content should not exceed 1.9% (as SO_3). The multiple regression equation (Equation 8.3) gives maximum limits of 1.8% pyrite and 1.7% sulphate to ensure zero strength loss during long-term immersion. In addition the sum of the pyritic sulphur and sulphate sulphur must not exceed approximately 1.8% (from Equation 8.4). Figure 8.33 shows a plot of pyritic sulphur against sulphate sulphur for the sixteen minestones studied. It can be seen that the CSMs that maintain their strength throughout the 410 day exposure period to both environments have a pyritic and sulphate sulphur

Figure 8.33 Effect of Sulphur Contents on Long-term Strength Development.



content sum of less than 1.8% (as SO₃).

Since the organic sulphur content of minestone is relatively small it may be possible to utilise the total sulphur content of the raw minestone to assess long-term durability. A maximum total sulphur content of 1.9% is given from Equation 8.5 to ensure strength maintenance in Environment 2. However, it should be noted that minestones with the majority of their total sulphur being present as sulphate minerals are not represented by the samples in this study. An examination of Figure 8.33 shows a large unrepresented region below the 1.8% pyrite plus sulphate line. A linear regression was performed on the ten minestones with pyritic sulphur below 1.8% to establish the role of the total sulphate on the long-term strength of immersed CSM. The relationship given by the regression is:-

$$LS = 10.9 - 18.7 AS \quad \text{Equation 8.7}$$

The null hypothesis, that the correlation is equal to zero, may only be rejected at the 5% level of statistical significance. The relationship suggests that a sulphate sulphur content of more than 0.6% may be sufficient to cause strength loss in CSM.

8.9 Summary

The expansion and moisture uptake of CSM specimens exposed to increased moisture content continues well beyond the first seven days. Therefore, the degree of damage to CSM can not be fully realised by utilisation of a simple seven day immersion test. The use of raw minestone indices, such as those suggested in Chapter 7 can provide a better assessment of the full extent of disruption likely to be suffered by CSM during early periods of exposure. However, no correlation was found between these

indices and the long-term performance of the CSM.

Beyond the early exposure periods the performance of CSM is largely determined by the sulphur bearing mineralogy of the raw minestone. The oxidation of pyrite minerals and the action of the sulphates produced, together with those already present, continued to cause expansion of CSM throughout the duration of this study. Consequently, chemical indices of raw minestone must also be utilised together with physical indices if a strong and durable material is to be produced by cement stabilisation.

9. CONCLUSIONS

This study is basically comprised of three separate investigations. Firstly an examination was undertaken of CSM pavements sites, where CSM had suffered distress. The second phase was a laboratory investigation which was principally concerned with the short-term durability of CSM and the statistical reliability of the raw material indices that could be used to predict this performance. A rapid method of predicting this durability was assessed. A second laboratory study was set up to examine the long-term durability of CSM and to test the hypotheses resulting from the investigation of distressed CSM pavements.

9.1 Examination of Distressed Pavements

Three CSM pavements examined during this examination had suffered disruption consistent with the horizontal expansion of the CSM layers. A fourth pavement, Thannington Diversion, had provided adequate performance up to the time of sampling but samples had since deteriorated when subjected to long-term immersion in water in the laboratory. The raw minestones used in these four constructions had been tested prior to use and appeared to be suitable for use as cement stabilised pavement layers. Tests on the stabilised material also suggested a strong and durable material.

Compressive strength determinations, performed on samples from three of the sites, gave evidence that the CSM had lost strength when compared to measured and specified 7 day strengths.

Microscopic investigation of thin sections cut from CSM placed in the Horden Lorry

Park and Thannington Diversion was carried out and cracks were identified both within and surrounding minestone particles. A large proportion of the wider cracks were associated with dark, sulphide rich particles. Examination by scanning electron microscopy showed the minerals gypsum and ettringite precipitated in the larger pores of two of the Snowdown CSMs and this was verified by X-Ray diffraction analysis of the pore infill material.

The results of these examinations culminated in the development of a hypothesis which explains the disruption of these pavements following at least twelve months of service life in which no distress was noticeable. The hypothesis is that the action of the sulphate minerals on the products of cement hydration together with the possible oxidation of sulphide minerals result in the formation of minerals of lower density producing expansion and disruption of the CSM.

9.2 Short-term Durability of CSM

Sixteen minestones were sampled from colliery spoil tips around the United Kingdom. The physical characteristics of these minestones show a high degree of variation. The chemical properties determined were limited to those of the sulphur bearing minerals and pH and these properties show a similar degree of variation to the physical properties. However, there is generally little contrast in the clay mineral proportions with one exception, minestone 93 which has a substantially higher kaolin content than the other minestones.

The air-dry moisture content, sub-63 microns content and the plasticity characteristics of these raw minestones are all reliably and positively intercorrelated. The modified slaking index is able to distinguish between shale types and despite being determined for a completely different size fraction, the

index has a reliable negative correlation with the plasticity index. In summary, minestones with higher proportions of fines display increased plasticity and hygroscopic moisture demand and lower resistance to the action of "slaking". The clay and sulphur bearing mineralogy and the grading indices do not show any intercorrelation with the other properties determined for the raw minestones.

From these results, seven minestones appear to have acceptable physical and chemical characteristics for cement stabilisation as determined by the Department of Transport Specification (1977). These are: Minestones 32, 61, 62, 71, 72, 91, and 93. Of particular interest is the fact that only minestones 31 and 92 have sulphate contents in excess of the specified limit of 1% (as SO_3), the remainder satisfying this limit, although their physical characteristics make them unsuitable for cement stabilisation.

The sixteen minestones, mixed with 10% (by mass of dry minestone) cement at their respective optimum moisture contents were successfully compacted to 95% of their maximum dry density. Relationships between the air-dry and optimum moisture contents and between the dry density and optimum moisture contents are presented with correlation coefficients of 0.935 and 0.898 respectively. Consequently, a prediction of the compaction characteristics can be made from air-dry moisture contents with a precision which may prove acceptable.

The required 7 day compressive strength of 3.5MPa (for cubical specimens) is equivalent to 2.03 MPa for the cylindrical specimens of reduced dry density used in this study. The following CSMs fulfil the strength requirements :- 32, 61, 62, 71, 72, 73, 91, 93, 94 and 95. Minestones 73, 94 and 95 fit into this category despite unsuitable plastic limits although they only exceed the specified maximum

by a mere 2%.

Although the plasticity characteristics and fines contents affect the strength, the coarse-grained, less plastic minestones generally produce stronger CSM at 7 days. The finer minestones had generally suffered some breakdown and/or weathering and an interesting correlation was found between the modified slaking index and the 7 day strength (a correlation coefficient of 0.719 being calculated for these two variables).

Criteria based on raw material indices are suggested to isolate the CSMs that achieved satisfactory strength at 7 days. These are:-

Modified slaking index	greater than 55%
Plastic limit	less than 22%
Plasticity index	less than 15%
Sub-63 microns content	less than 25%

Seven minestones produce CSM that achieved Immersion Ratios in excess of 80%, these being:- 52, 61, 62, 72, 91, and 93. With the exception of 52 the minestones also have acceptable plastic limits, i.e. less than the specified 20% maximum permitted by the Department of Transport (1977).

All CSMs immersed for 7 days imbibed water, expanded and lost strength in relation to specimens cured for 14 days at constant moisture content. A non-linear relationship between the volume and mass increases and a linear relationship between the 7 day expansion (expressed as a diametrical strain) and Immersion Ratio of immersed CSM specimens are presented.

Relationships between the Immersion Ratio and the physical properties, sub-63 microns content, plastic limit and modified slaking index are presented and these have correlation coefficients of - 0.838, - 0.877 and 0.837 respectively. None of these indices is alone capable of selecting minestones to produce CSM with a specified minimum Immersion Ratio.

By using a limiting value for each index it is possible to identify the CSMs with an IR greater than 80%. These limits are:-

Sub-63 microns content	less than 20%
Plastic limit	less than 25%
Modified slaking index	greater than 60%

However, these criteria fail to preclude CSM 71, which had an IR of only 60%. A further criterion based on either the water or acid soluble sulphate contents is required to eliminate coarse grained minestones with deleterious sulphate contents. The existing sulphate limits do not appear to be sufficiently low to prevent strength loss of cement stabilised minestones under immersion conditions. Whilst, sufficient data are not available for coarse-grained minestones, a total sulphate limit between 0.6% and 0.8% or a water soluble sulphate limit of 0.3% appears reasonable.

For strength and durability criteria (2.03 MPa at 7 days and IR of 80%) the following criteria are suggested from the results of this study.

Sub-63 microns content	less than 20%
Plastic limit	less than 22%
Plastic index	less than 15%
Modified slaking index	greater that 60%

Acid soluble sulphate content	less than 0.8% (as SO ₃)
Water soluble sulphate content	less than 0.3% (as SO ₃)

No reliable correlation was found between the clay mineralogy proportions and the behaviour of immersed specimens. This is thought to be mainly due to the similarity in the clay mineralogy of the samples studied rather than the absence of a clay mineral expansion mechanism in CSM.

A multiple regression analysis performed on the data presented in Tables 7.1 to 7.4 produces a model for predicting the Immersion Ratio. The equation is:

$$IR = 115 - 3.62 PL + 0.529 MSI - 34.3 WS$$

where; IR = Immersion Ratio (%)
 PL = Plastic limit (%)
 MSI = Modified slaking index (%)
 WS = Water soluble sulphate (% SO₃)

The independent variables, PL, MSI and WS explain 87% of the variation in the value of the Immersion Ratio.

The performance of CSM in the vacuum saturation test was similar to that during 7 days immersion. Despite specimens failing to reach a saturated state at the termination of the test, sufficient moisture uptake and swelling had occurred to promote a loss in strength. An excellent correlation ($r = 0.974$) exists between the strengths following vacuum saturation and 7 day immersion, the strengths being almost equal.

The Vacuum Saturation Ratio provides an adequate rapid assessment of the effects of immersion on CSM. However, the prediction of IR was statistically improved by incorporating a variable representing the sulphate contents, the final multiple regression equation being:-

$$IR = 0.971 VSR - 33.7 WS - 4.75$$

where VSR = Vacuum Saturation Ratio (%)

The independent variables VSR and WS explained 95.1% of the variation in Immersion Ratio.

The expansion of CSM specimens had not ceased following 7 days immersion and consequently the full damage sustained by CSM due to the effects of moisture uptake are not realised. However, if the Immersion Test is to be included in the specifications for cement stabilised materials, then the use of simple indices may provide an adequate prediction of the behaviour of CSM in this testing regime.

9.3 Long-term Durability of CSM

CSM specimens reach a state of equilibrium relatively quickly when sealed from the atmosphere in polythene. The strength of these specimens continues to increase with time due to the continued hydration of the cement. No significant changes in the sulphur bearing mineralogy were detected in these specimens. A gradual reduction of the calcium hydroxide peak was noticed on X-Ray diffractograms throughout the duration of the study and this is probably the result of carbonation. Further evidence of this is provided by the small reduction in the alkalinity in CSM stored at constant moisture content.

The CSM specimens exposed to Environments 2 and 3 continued to swell throughout the study although the rate of swelling decreased with time. After the initial loss of strength due to exposure all CSMs underwent a period of strength recovery. However, by the end of the study eight of the sixteen CSMs had shown signs of further strength loss and were deteriorating badly.

The long-term expansion rate (determined after 240 days exposure) for CSM exposed to Environment 2 is related to both the pyrite and sulphate sulphur contents of the raw minestone by the equation:-

$$\text{Expansion} = 5.3 + 7.2 \text{ AS} + 1.6 \text{ PS} \quad \text{Equation 8.1}$$

Where; Expansion is measured in microns/100 days

AS = acid soluble sulphate (% SO_3) of raw minestone

PS = pyritic sulphur (% SO_3) of raw minestone

For CSM exposed to Environment 3 the long-term expansion rate is related linearly to the pyrite content of the raw minestone by the equation:-

$$\text{Expansion} = 4.4 + 5.7 \text{ PS} \quad \text{Equation 8.2}$$

The long-term strength development (determined as the rate of strength change after 240 days exposure expressed as a percentage of the 240 day strength) for CSM exposed to Environment 2 is again largely dependent on both the pyrite and sulphate sulphur contents of the raw minestone. The multiple regression equation for specimens in Environment 2 being :-

$$LS = 17.1 - 10.2 AS - 9.3 PS$$

Equation 8.3

Where; LS = long-term strength development (% change/100 days)

For CSM exposed to Environment 2 its strength performance is again only dependent on the pyritic sulphur content of the raw minestone, the linear regression equation being :-

$$LS = 17.5 - 9.3 PS$$

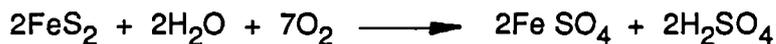
Equation 8.6

Equation 8.1 explains 84% of the variation in the long-term expansion rate and Equation 8.3 explains 83% of the variation in the long-term strength development of CSM exposed to Environment 2. The relationships between the pyritic sulphur content of raw minestone and the long-term expansion rate and strength development of CSM exposed to Environment 3 have correlation coefficients of 0.883 and 0.777 respectively. These four relationships are statistically significant at the 1% level.

Further evidence of the role played by sulphur chemistry is provided by the microscopic study of cracks and disrupted material and the X-Ray diffraction analysis of crack infill material. Sulphide rich mudstone particles in an advanced state of degradation are also readily identified in CSM. In addition CSMs produced from high sulphate minestone were prone to disruption due to the formation of expansive sulphate minerals. In particular, the minerals gypsum and ettringite were associated with the areas of disrupted CSM and this is consistent with both sulphate attack and sulphide oxidation.

The long-term performance (durability) of CSM appears to be largely controlled by

the sulphur bearing mineralogy of its component minestone. Sulphate attack due to the sulphate minerals available at the time of mixing is likely to continue until the supply of reactive sulphates is exhausted. Consequently , expansion due to this attack will also continue, making disruption and strength loss more likely with the passage of time. The oxidation of pyrite by the reaction :-



not only results in expansion due to reaction products of lower mineral density but, in addition, provides a further supply of sulphate for attack on the cement hydration products and clay minerals.

It has been suggested (Rainbow, 1986) that adequate sealing of the exposed CSM surface by a bituminous wearing course would prevent pyrite oxidation. This is unlikely, in view of the results presented here, unless the CSM structure was completely sealed from the environment surrounding it. The application of an asphalt or bituminous layer to the CSM surface may well exacerbate the problem as the conditions under the blacktop are likely to approach those experienced in Environment 3 of this study, namely; undersaturation, high humidity, oxygen availability and periodically, an elevated temperature.

Limits on the sulphur content of minestone suitable for use as CSMs, suggested on the basis of these investigations, are:-

Sum of pyrite and sulphate sulphur	- 1.8% (as SO ₃)
Total sulphate sulphur	- 0.6% (as SO ₃)

The minestones with sulphate and pyrite contents within these limits all produced CSM that showed no signs of strength loss throughout the remainder of their period of exposure once strength recovery in Environments 2 and 3 had started.

Current specifications controlling the use of soil cement (Department of Transport, 1977) do not impose a sulphide sulphur limit. The existing criteria together with the proposed inclusion of a minimum Immersion Ratio (Rainbow and Sleeman, 1984) may preclude most "unsuitable" minestones. However, CSM 93 had a 7 day strength of 3.16MPa and an Immersion Ratio of 91% and despite this suffered considerable disruption during long-term exposure (Figure 8.22). This emphasises the importance of the pyrite content (5.4% as SO₃ for minestone 93) of the raw minestone in assessing its suitability for cement stabilisation. Other cement stabilised materials may also require an examination of their sulphur bearing mineralogy if high pyrite or sulphate contents are suspected.

Thus by a careful selection of raw material parameters such as a fines index, plasticity characteristics, slaking index, sulphate and sulphide contents it may be possible to select a minestone capable of producing a cement bound material of satisfactory strength and durability both in the short-term and-long term.

9.4 Limitations of Study and Recommendations for Future Work

The content of this study was limited largely by the constraints of time. Future studies based on a larger sample size would produce more reliable statistics. In addition the examination of other soil parameters such as point load strength, absorption and other short-term durability tests, e.g. cyclic freeze/thaw, could be carried out.

However, the results of this study have shown that short-term durability is not an adequate guarantee of the satisfactory performance of CSM throughout its design life. CSM is not necessarily in chemical equilibrium with its environment and the geochemical alteration of sulphide minerals can result in the disruption of the structure. Consequently, it is recommended that future research be concentrated on the chemistry and mineralogy of minestone and their engineering implications.

The long-term durability study presented here was terminated after 410 days exposure. Studies of longer duration may be required to ensure that the "acceptable" CSMs continue to provide adequate performance beyond this period. In addition, minestones with high sulphate and low pyrite contents need to be examined as these were absent from this study.

The oxidation of pyrite by chemical or biological means is a combination of complex processes. A fuller understanding of the processes involved in cement stabilised mudrocks is undoubtedly required to extend the use of these materials.

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APPENDIX A

Chemical Composition of Cement

<u>Element</u>	<u>Chemical Oxide</u>	<u>Percentage</u>
Calcium	CaO	63.8
Silicon	SiO ₂	20.4
Aluminium	Al ₂ O ₃	7.3
Iron	Fe ₂ O ₃	2.3
Sulphur	SO ₃	2.5
Magnesium	MgO	1.2
Sodium	Na ₂ O ₃	0.4
Potassium	K ₂ O	0.5
Loss on Ignition		0.9

Bogue Compounds

C ₃ S	43
C ₂ S	25
C ₃ A	15
C ₄ AF	7

APPENDIX B

Grading Index

In order to subject normal particle size distribution curves to a statistical treatment a numerical representation of the grading is required. Grading indices can be calculated to represent an entire grain size curve (Hale, 1979)¹. To calculate the index the curve is divided into several size groups and the percentage of the material within each group is multiplied by the equivalent mean mesh size of that range. These weighted fractions are then summed and the numerical value may then be used to represent the material in subsequent numerical treatments (Hale, 1979)¹.

Ten size groups were chosen for the study of minestones. These are given below in an example calculation of the grading index of minestone sample 92. The final indices were divided by 100 for convenience.

1. HALE, B.C. 1979. "The Development and Application of a Standard Compaction-Degradation Test for Shales", Joint Highway Research Project, JHRP-79-21, Purdue University, Indiana.

Calculation of Grading Index Example for sample 92

Size Range mm	Mean Equivalent Sieve Size (a) mm	Proportion of Sample in Size Range (b) %	Weighted Fraction (a)*(b)
50 - 28	39	10	390
28 - 14	21	10	210
14 - 6	10	7	70
6 - 3	4.5	7	31.5
3 - 1.18	2.09	10	20.9
1.18 - 0.600	0.89	6	5.34
0.600 - 0.300	0.45	3	1.35
0.300 - 0.150	0.225	4	0.9
0.150 - 0.075	.1125	1	0.1125
passing 0.075	0.0375	42	1.575
Sum of weighted fractions			731.6775

Grading Index of minestone sample 92 = 7.32

APPENDIX C

Slake Durability Test

The apparatus used for the determination of the Modified Slaking Index was designed in accordance with the critical dimensions suggested by Franklin and Chandra (1972)¹. These are summarised in Figure C1, and are:-

- 1 Drum comprising a 2mm mesh cylinder of unobstructed length 100mm and diameter 140mm. The drum has a solid base and a solid removable lid.

- 2 Trough to contain the drum and support its horizontal axis whilst allowing free rotation. The trough must be capable of containing sufficient slaking fluid to provide a fluid level 20mm below the drum axis. A clearance of 40mm between the base of the trough and the base of the mesh must be provided.

An electric motor was used to drive the drum with suitable gearing to provide 20 rpm. The test procedure of Franklin and Chandra (1972)¹ was found to be incapable of distinguishing between minestones and the frequency distributions of the indices determined by both this and the modified procedure outlined in Chapter 6 are shown in Figure C2.

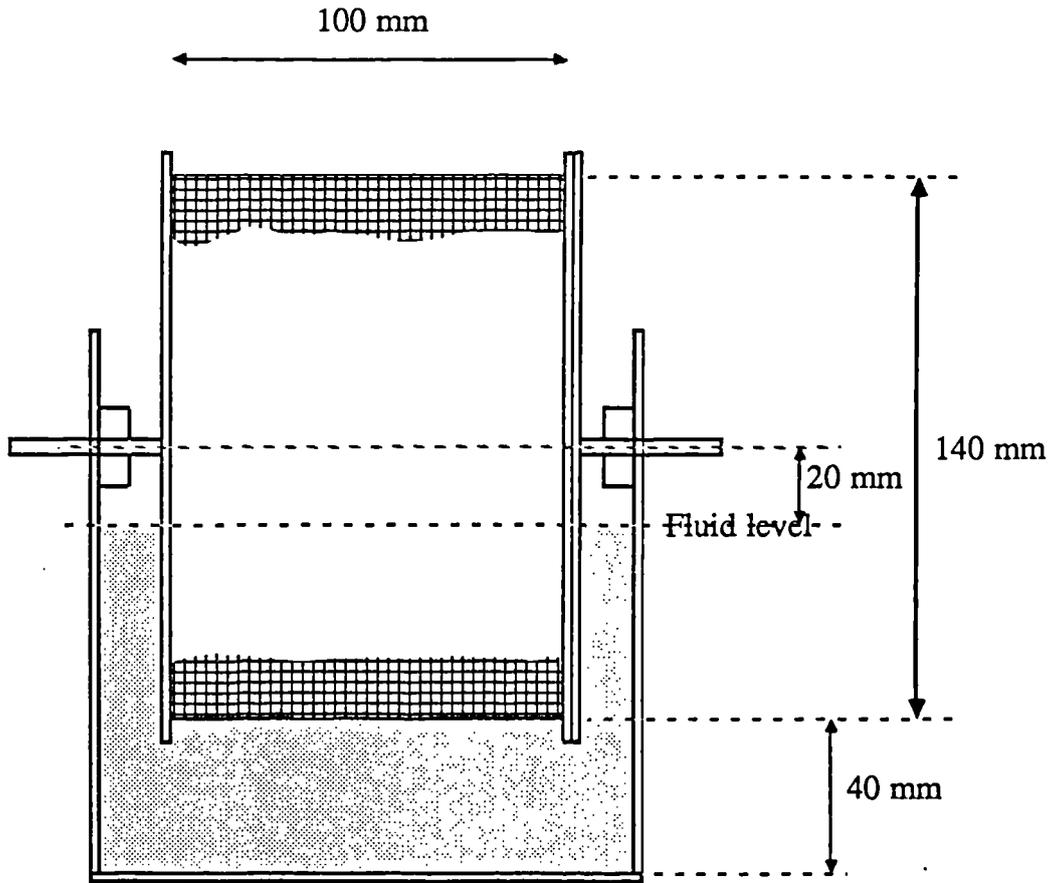


Figure C1 Slake Durability Apparatus

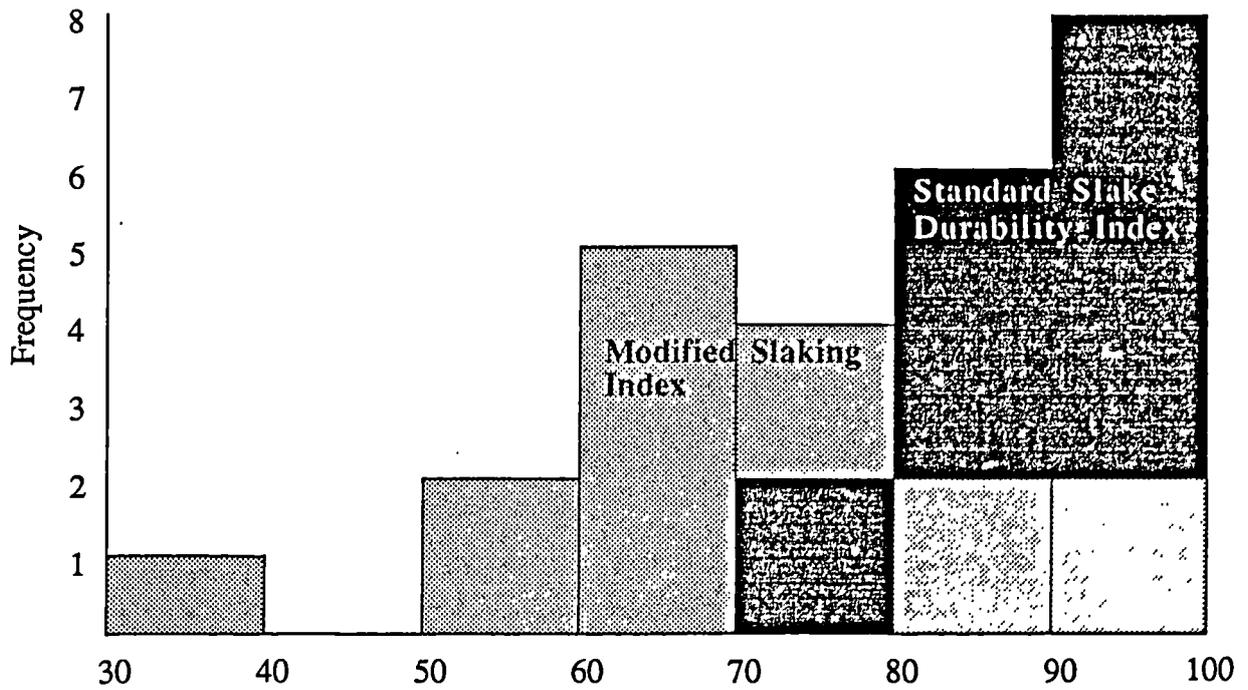


Figure C2 Frequency Distribution of Standard and Modified Slaking Indices.

1. FRANKLIN, J.A. and CHANDRA, R. 1972. "The Slake Durability Test", *Int. J. Rock Mech. Min. Sci.*, Vol. 9, pp 325-341.

APPENDIX D

Spec. No.	Days in Environment 2					Days in Environment 3										
	1	7	70	140	240	280	360	410	1	7	70	140	240	280	360	410
31	710	1230	1730	1800	1833	1841	1868	1886	560	1090	1200	1310	1365	1377	1401	1418
32	50	70	150	160	192	198	208	215	0	60	160	200	230	237	244	249
41	600	940	1910	1960	2054	2054	2060	2064	300	950	1550	1670	1681	1684	1691	1694
51	10	40	95	98	122	130	133	138	10	50	120	130	164	160	169	173
52	30	40	150	170	188	193	206	215	50	110	200	240	279	285	304	317
61	10	30	70	80	100	107	111	116	0	0	70	75	93	94	101	105
71	30	200	580	620	642	652	662	672	40	100	540	610	633	638	642	647
81	50	210	310	315	338	348	358	367	40	240	280	350	374	379	386	391
62	45	80	85	85	90	96			40	50	95	105	120	133		
72	5	10	48	50	52	55			10	30	63	73	95	113		
73	25	40	50	53	59	67			10	25	93	98	100	103		
91	0	10	53	50	53	55			5	10	40	40	45	51		
92	390	685	1080	1113	1138	1158			350	655	1160	1200	1235	1266		
93	15	35	223	275	295	308			20	50	245	288	318	346		
94	45	55	78	78	90	100			15	60	120	143	161	179		
95	75	100	120	123	127	135			60	85	188	228	250	272		

Dimensions in microns

Table D.1 Linear Dimension Changes for CSM s Exposed to Environments 2 and 3

CSM	Environment	Exposure Period in Days (following 7 days cure at constant moisture content)											
		0	7	40	70	100	140	180	210	240	280	360	410
31	1	1.4	1.6	2.5	3	3.1	3	3.5	2.8	3.1	3.2	3.5	3.5
	2	0	0.1	0.2	0.2	0.7	0.9	1.4	1.5	1.7	0.8	0.8	0.4
	3	0.2	0.3	0.8	0.8	1.4	1.9	1.9	1.4	1.1	0.9	1	0.8
32	1	2.3	2.6	4	5	5.2	4.3	5.1	5.6	6	8.3	5.8	5.7
	2	1.9	1.9	2	2.1	3.2	1.9	4.1	4.1	5	4.5	4.8	5.1
	3	2.2	2.8	2.8	4	3.9	4.1	4.4	4.5	4.8	4.3	4.7	5
41	1	1.3	1.6	2.2	2.3	3	2.5	1.6	2.3	2.4	1.8	2.5	2.3
	2	0.3	0.3	0.1	0.2	0.1	0.5	0.5	0.5	0.6	0.4	0.6	0.6
	3	0.4	0.6	0.6	1.3	1	0.6	0.8	1.4	1.3	0.9	1.2	1.5
51	1	1.2	1.9	2.8	2.6	3.1	3.5	3.3	4.1	3.7	3.2	4	3.8
	2	1.3	1.8	1.8	2.1	3.2	2.1	3	2.8	3.2	3.6	3.5	3.8
	3	1.4	1.7	1.7	1.9	2.5	2.6	2.5	2.6	2.8	3.6	4.1	3.9
52	1	1.6	2.1	2.7	2.9	4.5	4.4	4.8	4	4.3	4.5	4.7	4.3
	2	1.7	2.5	2.5	3.2	3.8	4.4	3.8	1.5	2.9	3.1	2.2	1.9
	3	2	3.3	3.3	3.5	3.6	2.7	3.5	3.1	3	3	2.7	2.8
61	1	2.4	2.6	4.5	7	5.2	5	5.5	5.4	5.7	6.2	6	5.8
	2	2.1	2.1	3	2.3	3.2	3.3	3.3	4.4	4.4	4.3	4.5	4.4
	3	2.4	2.4	3.5	3.5	3.8	4.6	3.5	4.5	4.5	4.4	4.7	4.7
71	1	2.4	2.9	2.8	4.2	4.4	4.4	5.3	4.5	5	5	5	5.3
	2	1.7	1.7	1.8	3	3.4	4	3.5	2.7	2.3	2.6	2.3	2.2
	3	1.9	1.9	1.6	2.1	3.2	3.5	2.9	3	3.3	3.1	3	2.9
81	1	1.5	2.2	3.6	5	5	5.1	5.3	5.6	6	7.1	6.6	6.2
	2	1.3	1.3	2	2.1	4.3	3.6	3.6	3.4	3.5	3.5	2.7	3.1
	3	0.9	0.9	0.8	1.4	1	3.1	3	4.2	4.3	4.1	4	3.8

Strengths in MPa

Table D.2 Compressive Strengths of CSM s Following Exposure to Environments 1, 2 and 3.

CSM	Environment	Exposure Period in Days (following 7 days cure at constant moisture content)												
		0	7	40	70	100	140	180	210	240	280	360	410	
62	1	2.1	2.3	3.2	4	3.4	3.6	3.5	4	3.8	4			
	2		1.9	2.5	2.6	2.3	3.8	3.4	3.9	3.4	3.9			
	3		1.6	1.5	1.7	2.8	2.9	3	3.5	3.5	3.7			
72	1	5.6	5.9	6.8	6.5	7.5	6.8	6.5	7	6.9	7.5			
	2		5.8	6.4	6.6	6.4	7.1	6.8	7	7.1	9			
	3		5.5	6.7	7	7	7.4	7	6.8	7.2	9			
73	1	3.8	4.4	6	5.7	7	6.4	6.6	6.3	6.4	6.5			
	2		3.7	4.2	5.1	5	5.7	5.7	5.9	6.1	6.3			
	3		4	5.3	5.5	6.2	7.4	6	6.4	6.3	6.9			
91	1	4.1	4.2	5.5	5.9	5.7	5.6	5.9	5.8	6.2	6.5			
	2		3.9	4.6	4.6	5.2	6.4	5.2	5.5	5.7	6.1			
	3		3.7	4.4	4.6	4.9	6.7	5.1	5.2	5.7	5.6			
92	1	0.7	0.8	1.1	1.5	1.5	1	1	1.5	1	1.7			
	2		0.3	0.8	0.7	1	1	0.8	0.7	0.3	0.3			
	3		0.2	0.3	1	1.1	1	1	0.5	0.5	0.5			
93	1	3.2	3.6	4.4	4	4.7	3	5	4.3	4.5	4.6			
	2		3.3	3.5	4.2	4.2	3.3	3.7	3	3.3	2.1			
	3		3.2	4	4.1	3.6	2.6	2.8	3.3	2.2	1.9			
94	1	2	2.4	3.5	4.5	5	4.6	5	4.7	5	5.3			
	2		1.7	1.9	2.6	3.7	2.5	3.5	3.1	2.5	2			
	3		2	2.5	2.1	3.2	3.5	3.8	3.5	3.6	3.1			
95	1	4	3	3.7	4.1	3.8	3.3	3.7	4.3	4.9	4.4			
	2		2.1	2.6	3.1	2.8	4.4	3.6	3.6	3.4	3.3			
	3		2	2.5	3.3	3.6	3.3	3.3	3.4	3.5	2.6			

Table D.2 Continued.

CSM	Days in Environment 1				Days in Environment 2				Days in Environment 3							
	7	140	280	410	70	140	210	280	360	410	70	140	210	280	360	410
31	8.76	8.8	8.69	8.79	8.69	8.76	8.5	8.55	8.49	8.02	8.76	8.55	8.75	8.64	8.59	7.99
32	1.75	1.77	1.71	1.75	1.66	1.68	1.65	1.4	1.58	1.6	1.75	1.76	1.73	1.66	1.8	1.92
41	0.6	0.58	0.63	0.61	0.55	0.56	0.6	0.52	0.53	0.55	0.58	0.64	0.52	0.53	0.6	0.61
51	1.94	1.96	1.9	1.99	1.95	1.92	1.93	1.69	1.9	1.71	1.94	1.95	1.92	1.89	1.82	1.86
52	3.21	3.21	3.17	3.2	3.2	3.2	3.18	3.1	3.25	3.09	3.15	3.17	3.2	3.13	3.49	3.1
61	1.42	1.44	1.36	1.41	1.43	1.39	1.4	1.3	1.33	1.35	1.41	1.36	1.33	1.29	1.45	1.31
71	2.18	2.1	2.2	2.19	2.15	2.07	2.11	2	2.21	2.09	2.12	2.14	2.1	2.18	2.09	2.16
81	2.1	2.11	2.15	2.14	2.07	2.04	2.06	1.93	2.1	1.93	2.07	1.91	1.98	2.01	2	1.91

Table D.3 Total Sulphur Content (as %SO₃) for First Phase CSM s Exposed to Environments 1, 2 and 3.

CSM	Days in Environment 1				Days in Environment 2				Days in Environment 3							
	7	140	280	410	70	140	210	280	350	420	70	140	210	280	350	420
31	5.1	5.15	5.13	5.1	5.07	4.96	4.78	4.78	4.69	4.43	5.15	4.89	5.02	4.8	4.7	4.25
32	1.36	1.31	1.33	1.36	1.29	1.23	1.21	0.99	1.16	1.14	1.32	1.3	1.28	1.19	1.25	1.3
41	0.26	0.24	0.2	0.28	0.23	0.25	0.27	0.18	0.2	0.17	0.25	0.33	0.19	0.21	0.24	0.2
51	1.48	1.47	1.48	1.45	1.5	1.44	1.48	1.28	1.3	1.26	1.47	1.45	1.42	1.36	1.22	1.28
52	2.68	2.6	2.66	2.6	2.64	2.55	2.58	2.45	2.51	2.33	2.62	2.54	2.54	2.48	2.61	2.24
61	0.86	0.88	0.89	0.85	0.89	0.82	0.84	0.66	0.74	0.72	0.85	0.8	0.66	0.62	0.69	0.73
71	0.93	0.9	0.95	0.93	0.9	0.75	0.79	0.65	0.85	0.72	0.9	0.82	0.82	0.74	0.73	0.78
81	0.95	0.95	0.99	0.92	0.92	0.8	0.81	0.69	0.79	0.61	0.95	0.71	0.78	0.72	0.84	0.69

Table D.4 Pyritic Sulphur Content (as %SO₃) for First Phase CSM s Exposed to Environments 1, 2 and 3.

CSM	Days in Environment 1				Days in Environment 2				Days in Environment 3							
	7	140	280	410	70	140	210	280	360	410	70	140	210	280	360	410
31	2.39	2.35	2.4	2.35	2.42	2.5	2.53	2.56	2.56	2.5	2.38	2.42	2.5	2.71	2.65	2.71
32	0.3	0.32	0.32	0.31	0.34	0.39	0.39	0.37	0.38	0.42	0.33	0.36	0.39	0.4	0.47	0.43
41	0.27	0.25	0.28	0.26	0.28	0.27	0.27	0.31	0.29	0.35	0.26	0.25	0.27	0.26	0.31	0.39
51	0.34	0.35	0.33	0.35	0.35	0.36	0.34	0.37	0.41	0.44	0.36	0.4	0.38	0.4	0.47	0.48
52	0.28	0.29	0.25	0.31	0.32	0.4	0.37	0.4	0.45	0.55	0.31	0.38	0.43	0.4	0.5	0.64
61	0.52	0.51	0.55	0.5	0.5	0.55	0.55	0.6	0.58	0.68	0.53	0.54	0.63	0.63	0.72	0.75
71	1.11	1.11	1.09	1.13	1.1	1.2	1.19	1.26	1.2	1.31	1.09	1.19	1.17	1.23	1.24	1.33
81	1.04	1	0.99	1.02	1.05	1.09	1.17	1.26	1.25	1.26	1.02	1.1	1.12	1.19	1.3	1.25

Table D.5 Total Sulphate Sulphur Content (as %SO₃) for First Phase CSM's Exposed to Environments 1, 2 and 3.

CSM	Days in Environment 1				Days in Environment 2				Days in Environment 3							
	7	140	280	410	70	140	210	280	350	420	70	140	210	280	350	420
31	0.59	0.51	0.5	0.51	0.28	0.31	0.26	0.28	0.2	0.21	0.28	0.26	0.25	0.2	0.2	0.18
32	0.03	0.03	0.01	0.01	0.02	0.01	-	-	0.01	0.01	0.02	0.01	-	0.01	-	0.01
41	0.01	0.01	-	0.01	0.01	-	0.01	-	-	-	0.01	0.01	0.01	0.02	-	0.01
51	0.06	0.04	0.04	0.03	0.02	0.03	0.02	0.01	0.02	0.01	0.01	0.01	-	0.02	-	-
52	0.01	-	0.01	0.01	0.03	0.03	0.04	0.01	0.02	0.03	0.02	0.02	0.03	-	0.01	0.02
61	0.09	0.08	0.1	0.08	0.03	0.05	0.01	0.03	0.04	0.01	0.01	0.04	0.05	0.01	0.02	0.02
71	0.3	0.28	0.25	0.23	0.21	0.15	0.19	0.11	0.13	0.1	0.23	0.2	0.15	0.19	0.2	0.15
81	0.25	0.26	0.23	0.22	0.15	0.14	0.15	0.1	0.1	0.12	0.19	0.1	0.15	0.16	0.1	0.1

Table D.6 Water Soluble Sulphate Sulphur Content (as %SO₃) for First Phase CSM's Exposed to Environments 1, 2 and 3.

CSM	Days in Environment 1					Days in Environment 2					Days in Environment 3						
	7	140	280	410		70	140	210	280	360	410	70	140	210	280	360	410
31	1.27	1.3	1.16	1.34		1.2	1.3	1.19	1.21	1.24	1.09	1.23	1.24	1.23	1.13	1.24	1.03
32	0.09	0.14	0.06	0.08		0.03	0.06	0.05	0.04	0.04	0.04	0.1	0.1	0.06	0.07	0.08	0.19
41	0.07	0.09	0.15	0.07		0.04	0.04	0.06	0.03	0.04	0.03	0.07	0.06	0.06	0.06	0.05	0.02
51	0.12	0.14	0.09	0.19		0.1	0.12	0.11	0.04	0.19	1.0E-2	0.11	0.1	0.12	0.13	0.13	0.1
52	0.25	0.32	0.26	0.29		0.24	0.25	0.23	0.25	0.29	0.21	0.22	0.25	0.23	0.25	0.38	0.22
61	0.04	0.05	-0.08	0.06		0.04	0.02	0.01	0.04	0.01	-0.05	0.03	0.02	0.04	0.04	0.04	-0.17
71	0.14	0.09	0.16	0.13		0.15	0.12	0.13	0.09	0.16	0.06	0.13	0.13	0.11	0.21	0.12	0.05
81	0.11	0.16	0.17	0.2		0.1	0.15	0.08	-0.02	0.06	0.06	0.1	0.1	0.08	0.1	-0.14	-0.03

Table D.7 Organic Sulphur Content (as %SO₃ assumed by difference) for First Phase CSM s Exposed to Environments 1, 2 and 3.