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Mechanisms by which ground granulated blastfurnace slag prevents sulphate attack of lime-stabilised kaolinite

William A. Tasong[a], Stanley Wild[a,*], Richard J.D. Tilley[b]

[a]Centre for Research in the Built Environment, University of Glamorgan, Pontypridd, Mid Glamorgan, CF37 1DL, UK

[b]School of Engineering, University of Cardiff, Cardiff, UK

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Abstract

This paper describes the mechanisms by which ground granulated blastfurnace slag (ggbs) prevents sulphate attack of lime-stabilized kaolinite. Microstructural and mineral phase analyses of compacted cylinders of lime-stabilised kaolinite with different percentages of lime replacement by ggbs have been carried out using scanning electron microscopy (SEM) and x-ray diffractometry (XRD). The cylinders were immersed in 4.2% Na_2SO_4 solution and also in deionised water for various time periods. The exposure data showed that the effect of ggbs in preventing the formation of expansive ettringite in lime-stabilised kaolinite, which had been exposed to 4.2% Na_2SO_4 solution was dramatic. The results also revealed three different growth mechanisms of ettringite in the lime-ggbs-kaolinite systems that were exposed to 4.2% Na_2SO_4 solution. These are: well-formed randomly orientated rods of high aspect ratio growing in pores and cracks, short needles covering surfaces of existing particles, and 'flower-like' needles radiating from isolated points and scattered randomly through the sample.

Keywords: Granulated blastfurnace slag; Sulfate attack; Expansion; Lime-stabilisation; Clay

The possibility of being able to recycle or process waste materials, such as ggbs, to use as a partial replacement for cement in mortar or concrete, or to stabilise soils, has great potential economic benefits in all areas of the construction industry. It is well-known that good quality cement replacement materials, such as ggbs, provide improved resistance to sulphate attack of concrete or mortar in seawater or other aggressive environments.

For example, it has been shown [1] that the resistance of slag blends to sodium sulphate solution attack is favoured by the use of high proportions of ggbs (>65% replacement of Portland cement by ggbs) and ggbs low in Al_2O_3. Related studies on expansion and strength loss on mortars exposed to sodium sulphate solution have also been reported [2]. In this case, damage took the form primarily of expansion and cracking, and was less marked with blended cements, including one containing 70% of ggbs. It was concluded that the deterioration was primarily due to ettringite formation and that the lower contents of calcium hydroxide produced by the blended cements in this case improved the resistance, since this phase provided the Ca^{2+} ions needed to form either ettringite or gypsum. In addition, the slag hydration has been shown [3] to produce a "pore-blocking" effect resulting in increased long-term hardening of cement paste. The blocking of pores leads to higher strength and lower permeability, which besides other improved binding and absorptive effects, enhances resistance of ggbs concrete to attack from sulphates.

Lime stabilisation of clay soils has been widely used in highway and foundation layers as an economic method of providing a suitable pavement and fill material whilst avoiding the generally more expensive process of transporting in large quantities of granular fill. However in a number of reported cases [4,5], serious problems of swelling have occurred where sulphates were present in the soil and this swelling has been associated with ettringite formation.

The well-established sulphate-resistance properties imparted to cements by blending them with ggbs suggest that the ggbs may impart similar sulphate resisting properties to lime-stabilised clays. The use of ggbs in soil stabilisation, however, is still a novel process in the UK, although it has been used in other countries such as South Africa. The beneficial effects associated with the use of ggbs to reduce expansion due to the presence of sulphates, in highway and other foundation layers, has been reported in earlier investigations [6–10]. These findings revealed that small additions of ggbs to sulphate-bearing soils, which are stabilised with lime, reduce substantially the damaging expansion often encountered when lime stabilisation alone is used, and have no

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* Corresponding author. Tel.: +44-1443-482142; Fax: +44-1443-4882140. *E-mail address*: swild@glam.ac.uk (W.A.Tasong)

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significant deleterious effect on strength development. Similar findings have been reported in Australia [11], Japan [12,13], and India [14].

According to Wild et al. [15,16], a colloidal product, which is a precursor to crystalline ettringite formation, initially forms on clay particle surfaces during moist curing in lime-stabilised sulphate bearing clay soils. On soaking, this product imbibes water and swells. The amount of this product that can form is controlled by the relative amounts of free lime, gypsum, and alumina available. At low sulphate contents (up to 1% SO_3) formation of this product is restricted and expansion is very small but at high sulphate contents expansion can be substantial. Progressive replacement of lime with ggbs [7,8] reduces the amount of available free lime, as a result of both dilution and slag hydration, improves cementation due to slag hydration, and must ultimately depress the pH. Thus observed expansions progressively reduce to negligible levels as the ggbs:lime ratio in the soil is increased, even at high sulphate concentrations.

Other beneficial effects of ggbs as a soil stabiliser have also been reported. For example, Yamanouchi et al. [17] reported that the addition of ggbs reduces significantly the permeability of stabilised sandy and soft clay soils that in their natural state were very weak and had unsatisfactory properties in relation to permeability and trafficability. A coefficient of permeability value of 10^{-6} cm/s, which satisfied the required maximum value for water-retaining structures, was obtained by the addition of ggbs. The effectiveness of ggbs as a soil stabiliser against the prevention of accelerated erosion loss has also been reported by Kawamura et al. [18]. Their findings showed that a sandy soil treated with lime, gypsum, and ggbs was highly effective in reducing the erosion loss from early curing time, in comparison with the sandy soil treated with lime only.

The work reported here is part of a large study involving the use of ggbs in the stabilisation of sulphate-bearing and sulphide-bearing soils. During the initial phase of this study [10], an assessment was made of how the lime-ggbs-stabilised material would perform if exposed to external sulphates such as those often present in ground water, after the initial stabilisation process. Various lime-slag-kaolinite compositions, which do not contain sulphates, were exposed to 4.2% sodium sulphate solution and also to deionised water, after an initial moist-curing period of 28 days. Sulphate durability was assessed in the laboratory by means of linear expansion measurements, microstructure, and mineral phase analysis of compacted cylinders of the lime-ggbs-stabilised kaolinite. The results showed that high percentages of replacement of lime with ggbs (in particular 83%), with just enough lime to activate the slag were the most effective in preventing sulphate solution attack. Although the effectiveness of ggbs in controlling expansion of sulphate-bearing clay soils, which are stabilised with lime, has been established, these findings do not fully explain the mechanisms by which ggbs prevents sulphate attack of lime-stabilised soils. Hence, this part of the study was designed to provide further knowledge and understanding about the mechanisms by which ggbs controls the expansion of lime-stabilised soils in the presence of sulphate.

1. Experimental procedure

1.1. Materials

1.1.1. Kaolinite

Kaolinite supplied as "Standard Porcelain" by ECC International Ltd, St. Austell, Cornwall, UK. Its mineralogy comprises 84% kaolinite, 13% mica, 1% feldspar, and 2% other minerals. The chemical and physical properties of the kaolinite are given in Tables 1 to 3.

1.1.2. Lime

The lime used in this investigation is hydrated lime supplied by Buxton Lime Industries Ltd, Buxton, Derbyshire, UK under the trade name 'Limbux'. The chemical and physical properties of the lime are given in Tables 1, 2, and 3.

1.1.3. Slag

The ggbs used in this investigation was supplied by Civil and Marine Slag Cement Ltd, Llanwern, Newport, UK. The chemical and physical properties of the ggbs used are given in Tables 1 and 3, respectively.

1.1.4. Sulphate

A 4.2% sodium sulphate solution, prepared according to European Prestandard - Methods of testing cement, Part X, (Pr ENV 196-X: 1995), was used as an artificial source of sulphate.

1.2. Composition of test samples

Generally, 1–3 wt% lime is needed for modifying soil properties and 2–8 wt% lime for stabilisation, depending on

Table 1
Chemical properties of materials

	Wt %		
Composition	Lime[a]	ggbs[b]	Kaolinite[c]
SiO_2	0.46	35.34	48
Al_2O_3	0.10	11.59	37
Fe_2O_3	0.06	0.35	0.65
TiO_2	—	—	0.02
CaO	—	41.99	0.07
MgO	0.83	8.04	0.30
K_2O	—	—	1.60
Na_2O	—	—	0.10
MnO	—	0.45	—
S_2	—	1.18	—
SO_3	—	0.23	—
$Ca(OH)_2$	96.79	—	—
$CaCO_3$	1.36	—	—
$CaSO_4$	0.06	—	—
H_2O	0.34	—	—
Loss on ignition	—	—	12.50

[a] Data supplied by Buxton Lime Industries Ltd, UK.

[b] Data supplied by Civil and Marine Slag Cement Ltd, UK.

[c] Data supplied by ECC International Ltd, UK.

Table 2
Mineral composition of materials

Material	Mineral composition (wt %) Kaolin	Quartz	Calcite	Mica	Anhydrite	K-feldspar	Calcium hydroxide	Other
Kaolinite[a]	84	—	—	13	—	1	—	2
Lime[b]	—	0.46	1.36	—	0.06	—	96.79	—

[a] Data supplied by ECC International Ltd, UK.
[b] Data supplied by Buxton Lime Industries Ltd, UK.

the clay content. As the current work was carried out on 'pure' clay, a reference value of 6 wt% lime was chosen as a sensible addition to the kaolinite. Kaolinite was selected for this study as an example of pure clay with known mineralogy and chemistry. In order to indicate the relative effect of each component of the lime-ggbs combination, mixes were made, varying the relative proportion of lime to ggbs but maintaining an overall total binder content of 6 wt%. The combinations investigated were, 0L 6S (control), 1L 5S, 3L 3S, 5L 1S, and 6L 0S (control).

1.3. Preparation of test samples

The test specimens were prepared according to the procedure adopted in the earlier phase of this project (Wild et al. [6]). For this, dry materials, enough to produce three compacted cylindrical test samples that were 50 mm in diameter and 100 mm in length, were thoroughly mixed in a variable speed mixer (Kenwood Chef Excel mixer, UK) for two minutes before slowly adding the calculated amount of water. Intermittent hand mixing with palette knives was necessary to achieve a homogeneous mix. A steel mould fitted with a collar so as to accommodate all material required for one sample was used to compress the cylinders to maximum dry density (MDD) at optimum moisture content (OMC) (Table 4). The pre-fabricated mould ensured that material was not over-compressed and also allowed uniform compression for the different test specimens. The cylinders were extruded using a steel plunger after which they were trimmed, cleaned of releasing oil, weighed, and wrapped in several runs of cling film. The cylinders were labeled and placed in polythene bags.

Table 3
Physical properties of materials

Property	Lime[a]	ggbs[b]	Kaolinite[c]
Physical form	Dry white powder	Off white powder	Off white powder
Bulk density (kg/m^3)	480	1200	500
Specific gravity	2.3	2.9	2.57
Specific surface (m^2/kg)	300–1500	425–470	—
Glass content (%)	0	~90	0
Maximum dry density (kg/m^3)	—	—	1530
Optimum moisture content (%)	—	—	25
Solubility in water (g/l sat. sol. at 10°C)	1.76	—	—
pH	12.4 (aq. sol. ~ 2g/l)	10.9	5.0

[a] Data supplied by Buxton Lime Industries Ltd, UK.
[b] Data supplied by Civil and Marine Slag Cement Ltd, UK.
[c] Data supplied by ECC International Ltd, UK.

1.4. Curing of test samples

For each of the mix compositions under investigation, the cylinders, which were to be used for XRD and SEM investigations, were placed in polythene bags before being placed on a platform in sealed plastic containers. Water was always maintained below the platform to ensure that there was no evaporation from samples.

The specimens were moist-cured in this state for 28 days at 30°C, after which cylinders for each mix composition were divided into two groups. One group was partially immersed in 4.2 % sodium sulphate solution, while the other was partially immersed in deionised water in sealed plastic containers. The soaked samples were stored in a constant temperature room maintained at 20 ± 1°C before being analysed for microstructure and mineral phase content. It should be noted that samples, which differ in mix composition, were treated separately to avoid cross contamination (by leaching).

1.5 Analysis of mineral phases and microstructure

Test samples of all the lime-slag-kaolinite combinations were analysed for microstructure and mineral phases using SEM and XRD after 1, 3, 7, and 28 days of exposure to the 4.2% Na_2SO_4 solution or deionised water. Coarse pieces were obtained from the test cylinders, and dried over silica gel and carbosorb in a desiccator. In order to analyse the microstructure, the dried pieces were fractured and the freshly produced surfaces were analysed using SEM (Hitachi S570, Japan). In order to analyse the mineral phases, the dried coarse pieces were ground into fine powder using a mortar and pestle. XRD (Philips PW 1390 with CuKα, Holland) was used to analyse the powders.

Table 4
Proctor results for kaolinite-lime-ggbs systems

Property	Mix composition 6L 0S	5L 1S	3L 3S	1L 5S	0L 6S
Maximum dry density (kg/m^3)	1364	1364	1374	1442	1524
Optimum moisture content (%)	32.0	31.5	31.0	29.0	26.2

2. Results

As Figs. 1 to 5 and Table 5 show, there were significant differences between the various lime-ggbs-kaolinite mixes, which had been moist-cured initially for 28 days before soaking in sulphate solution, in terms of how the ggbs influenced the resistance of the stabilised materials to sulphate attack. XRD examination of all the mixes revealed ettringite as the principal new crystalline mineral formed when the lime-slag-stabilised kaolinite was exposed to the sulphate solution. It should be noted that no gypsum or monosulphate was detected by XRD in any of the compositions studied. As was expected, corresponding samples that were soaked in deionised water did not reveal any disruption or rod-like crystals in SEM. In addition, XRD examination did not reveal the formation of any new crystalline phases. Table 5 below shows the occurrence of ettringite identified on the XRD traces after exposure to sodium sulphate solution for 1, 3, 7, and 28 days. It should be noted that several identical samples of the 1L 5S clay mix that had been exposed to sulphate solution for 28 days were examined in XRD and also in SEM but no ettringite was observed.

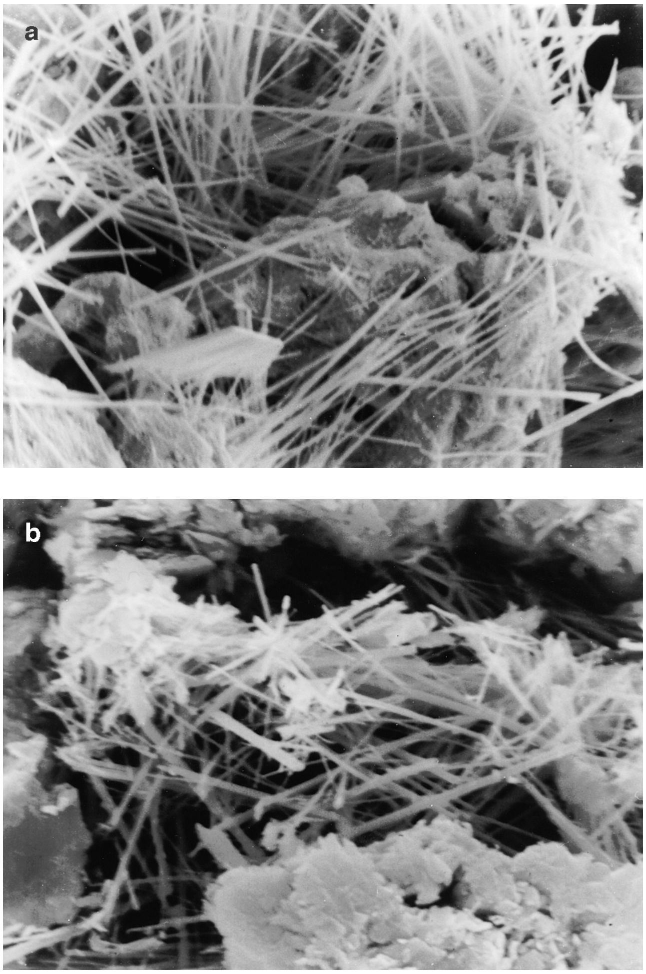

Fig. 1. SEM micrographs (mag. ×2000) of 6L 0S sample after exposure to 4.2% Na_2SO_4 solution: (a) for 3 days and (b) for 28 days.

Fig. 2. SEM micrograph (mag. ×2000) of 3L 3S after exposure to Na_2SO_4 solution for 7 days.

SEM examination of fractured pieces obtained from samples, which had been soaked in sulphate solution for 3, 7, and 28 days revealed abundant ettringite needles in all mix compositions except 1L 5S at 28 days and 0L 6S at 3 and 7 days. However, after only one day of soaking no crystalline ettringite could be observed in any specimen, including the highly expanded specimens (6L 0S and 5L 1S), even though at one day these latter specimens had expanded by one third of their ultimate expansion (see [10]). It should be noted that this initial expansion was not due solely to adsorption of water by the clay itself, as identical specimens soaked in deionised water showed negligible expansion [10]. The mixes with higher lime content (6L 0S and 5L 1S) in particular were severely disrupted, and at extended ages (3–28 days) consisted of extensive regions of well-formed, rod-like crystals of ettringite (Fig. 1). This degree of disruption was observed to reduce with a decrease in the lime content. These observations were consistent with the results of the linear expansion measurements [10]. Three different categories of ettringite needles were observed based on their

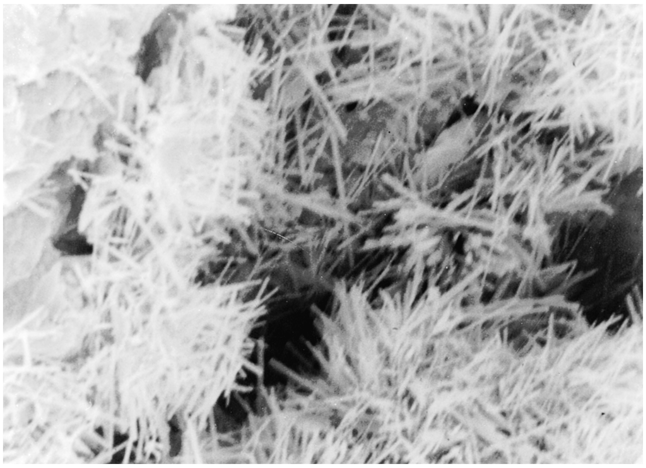

Fig. 3. SEM micrograph (mag. ×2000) of 1L 5S after exposure to Na_2SO_4 solution for 7 days.

Fig. 4. SEM micrograph (mag. ×2000) of 1L 5S sample after exposure to deionised water for 28 days.

mode of occurrence and morphology. These appeared to relate to the variations in mineralogy and composition of the different lime-ggbs-kaolinite mixes and the resulting variation in their interaction with the 4.2% Na_2SO_4 solution. The categories are:

1. Category A: Well-formed and randomly orientated rod-like crystals of ettringite of high aspect ratio that appeared to grow into pre-existing pores and cracks.
2. Category B: Very short ettringite needles that appeared to cover the surfaces of existing particles.
3. Category C: Flower-like radiating needles of ettringite at isolated points, scattered all over an entire sample.

2.1. Lime-stabilised kaolinite (6L 0S)

SEM examination of fractured pieces obtained from samples that had been soaked in 4.2% Na_2SO_4 solution for 1, 3, 7, and 28 days revealed severe disruption of the sample associated with formation of ettringite and showed the category A mode. The degree of disruption was observed to increase with soaking period. As previously noted the samples that were soaked in 4.2% Na_2SO_4 solution for one day did not reveal any ettringite in SEM. At the 3rd and 7th day of soaking, rod-like crystals of ettringite could be seen (Fig. 1*a*). By the 28th day of soaking, well-formed and randomly orientated rod-like crystals were observed with much clearer evidence that they appeared to have grown into pre-existing pores and cracks that later extended, accommodating further growth of ettringite crystals. This is apparent from comparison of Figs. 1*a* and 1*b*. The category A mode of occurrence of ettringite observed for this mix suggests a mechanism of formation that appears to be associated with the precipitation of ettringite from the pore fluid, which was saturated in SO_4^{2-}, Ca^{2+}, Al^{3+} and OH^- ions. In this case, the Ca^{2+} and OH^- ions were supplied by the lime whilst the aluminium and sulphate ions were derived from kaolinite and the sulphate solution, respectively.

Fig. 5. SEM micrograph of 0L 6S sample after exposure to Na_2SO_4 solution for 28 days.

Table 5
Ettringite identified by XRD

	Occurrence of ettringite			
Composition	1 day	3 days	7 days	28 days
6L 0S	–	+	+	+
5L 1S	–	+	+	+
3L 3S	–	+	+	+
1L 5S	–	+	+	–
0L 6S	–	–	–	+

Note: – = absence and + = presence of ettringite.

2.2. 17% replacement of lime by ggbs (5L 1S)

SEM examination of fractured pieces obtained from samples that have been soaked in 4.2% Na_2SO_4 solution for 1, 3, 7, and 28 days showed the microstructure of this mix to be more or less the same as that of the 6L 0S mix. This observation suggests small replacements of lime by ggbs are ineffective in preventing sulphate attack of the stabilised material.

2.3. 50% replacement of lime by ggbs (3L 3S)

The amount of ettringite crystals was observed in SEM to reduce (Fig. 2) compared with the 6L 0S and 5L 1S mixes. Only isolated spots of rod-like crystals of ettringite were seen and they were of the category A type. The category A type of ettringite observed suggests a similar mechanism of formation of ettringite as in the 6L 0S and 5L 1S mixes. The decrease in lime content is considered the main reason for the reduced amount of ettringite observed for this mix, since this phase provides the Ca^{2+} ions needed to form ettringite [2].

2.4. 83% replacement of lime by ggbs (1L 5S)

SEM examination did not reveal any signs of disruption for this mix compared with the previous mixes described above. This observation was consistent with the observations made previously in linear expansion measurements [10], for which no linear expansion in 4.2% Na_2SO_4 solution was experienced for this mix.

However, SEM examination of the 1L 5S specimens that had been exposed to 4.2% Na_2SO_4 solution revealed very tiny needles of ettringite crystals (Fig. 3) that appeared to grow over the surfaces of the clay particles (category B type) at an early age (i.e. during the first 3 to 7 days of exposure to 4.2% Na_2SO_4 solution) but were not observed in the specimens that had been exposed for longer periods (over 28 days).

When the specimens, after 28 days of initial moist-curing were exposed to Na_2SO_4 solution, there was clearly sufficient calcium available in the pore solution to promote ettringite formation and growth after three days, although the growth of ettringite was very greatly suppressed relative to the high lime composition specimens. The complete disappearance of this ettringite by 28 days indicates that the environment created by the pore solution was no longer sufficient to maintain ettringite stability. It is suggested that the unstable environment was produced by the reduced availability of calcium at extended ages. It is known that Na_2SO_4 accelerates slag hydration [7], that slag hydration after initial release of calcium will subsequently consume calcium in the development of hydration products, and that Na_2SO_4 depresses the amount of calcium in solution and increases the pH. Thus the limited supply of Ca^{2+} ions in this system is probably the main factor limiting the growth in size of the ettringite crystals to produce the category B type of ettringite and to subsequently lead to its breakdown. SEM examination of corresponding specimens of the 1L 5S mix that had been moist-cured initially for 28 days and then soaked in deionised water for 28 days revealed the formation of fibrous material tentatively identified as C-A-S-H gel (Fig. 4) due to slag hydration. This process has been shown [3] to produce a 'pore blocking' effect resulting in increased long-term hardening of cement paste. The blocking of pores leads to higher strength and lower permeability, which besides other improved binding and reduced absorptive effects, also enhances resistance of ggbs concrete to attack from sulphates.

2.5. 100% replacement of lime by ggbs (0L 6S)

SEM and also XRD examination revealed no disruption or ettringite during the first week of soaking in the 4.2% Na_2SO_4 solution. However, by the 28th day, disruption was apparent and this was due to the formation of ettringite that was detected on XRD traces. This ettringite occurred in the form of flower-like radiating needles in isolated spots (Fig. 5), scattered all over an entire sample (category C type). This observation was consistent with the swelling data obtained for this mix, which experienced significant expansion (although less than the 6L 0S and 5L 1S compositions) when exposed to 4.2% Na_2SO_4 solution [10].

This composition contained no lime. Thus during the initial 28 day moist-curing period, there would have been no slag activation and hydration. It has been reported that under these conditions a silica/alumina gel coating forms over the surface of the slag particles. The formation of ettringite, apparent after 28 days of exposure to Na_2SO_4 solution (but not observable at 7 days), implies the release of calcium, the only source in this case being the slag. It is proposed that the exposure of the slag to Na_2SO_4 solution initiates slag hydration and rupture of the colloidal layers [19]. The release of calcium, together with alumina and silica from the slag, and sulphate in the pore solution, promotes the precipitation of ettringite, the crystals of which, grow from the sources that are releasing the primary components (i.e. slag particles). It is again of interest to note that a substantial part of the expansion of these specimens occurs (7 days of exposure) prior to the appearance of crystalline ettringite [10].

3. Discussion

Previous results by the authors [10] show that high percentages of replacement of lime with ggbs, in particular 83% were the most effective in preventing attack by the sulphate solution. The hydration of ggbs produces C-A-S-H gel and hydrotalcite-type phases containing magnesium. Unlike the pozzolanic reaction of lime with clay, which is very slow, slag hydration activated by lime is much more rapid. This reaction is also (depending on the slag composition) known to consume lime [20]. In addition, there will be competing reactions (i.e. slag hydration activated by lime to give C-A-S-H gel and hydrotalcite and the much slower kaolinite-lime aqueous reaction to give C-A-S-H gel and calcium aluminates, and alumino-silicates). Thus, a possible explanation for the increase in resistance to sodium sulphate solution attack, with increasing ggbs/lime ratio is that most of the lime is consumed during the initial 28 days of moist-curing before the samples are exposed to the sulphate solution. Therefore, high percentage replacement of lime with ggbs, with just enough lime to activate slag hydration results in high resistance to sulphate attack. In this case, the slag reaction becomes the dominant reaction and there is little or no lime left for the precipitation of ettringite.

Whether or not ettringite formation results in expansion is dependent on a number of factors, which are related to its mode of formation and immediate chemical environment. Swelling is normally associated with absorption of water during ettringite formation [4,16,21,22]. For example in the kaolinite-lime-gypsum system [15] where expansion has been shown to be related to ettringite formation, expansion increases with an increase in sulphate content and also increases linearly with water absorption. For 7-day moist-cured kaolinite-6wt% lime-6wt% gypsum mixtures, ultimate linear expansion (after 28 days soaking) is 15% and water absorption is 22 wt%. For similar specimens containing 2 wt% gypsum expansion is less than 1% and water absorption is 3 wt%. If it is assumed in the former case, that all the gypsum present forms ettringite (which is unlikely) then

5.4 wt% water absorption would be needed to provide the structural water for the highly hydrated ettringite. However, the water absorption associated with the swelling and with ettringite formation [15,16] is several times greater than this percentage. The additional water absorption could result from capillary action drawing water into voids that are created as a result of crystal growth pressure by the growing ettringite crystals [23]. Alternatively, it could result from absorption of water by swelling colloidal calcium sulphoaluminate product as postulated by Wild et al. [15,16]. The evidence presented by Wild et al. strongly supports the latter mechanism. In addition, the propensity to swell appears to depend upon the chemical environment during growth, which in turn determines its resultant morphological character. From observations [22,24–28] on ettringite formation and expansion, calcium sulphoaluminate hydrates begin to form by precipitation from solution at pH 10.5–10.7 and at higher pH ($\sim$11.6), monosulphate may begin to precipitate from solution. At low pH ($<$10), ettringite is unstable with respect to gypsum, calcium aluminates, and alumina gel. The precipitate fibres get finer, more rounded, and less faceted with a rising pH, and beyond a pH of 12.5, the fibres start to disappear and at pH $>$13, no fibres are generally observed. According to Deng et al. [27], at low pH (i.e. in the absence of free lime), ettringite tends to form large, chunky, widely scattered crystals within the bulk solution whereas at the higher pH ($\sim$12.5), ettringite crystals are fine and needle-like, and form on the aluminum-bearing particle surfaces. This agrees with previous reports by Mehta [22,24] that ‘ettringite’ formed in the presence of free lime (high pH) produces fine rods that are colloidal in nature, whereas ‘ettringite’ formed in the absence of free lime produces much thicker crystals. At very high pH, ‘ettringite’ becomes extremely fine and may even dissolve [28,29]. This latter situation may arise if sodium sulphate is present together with lime. In this situation, the solubility of Ca^{2+} ions in the pore solution is seriously suppressed and pH values can approach 14. It is suggested that this type of environment is produced for low lime-high slag compositions at extended curing times.

In the current work for specimens where significant swelling did take place (6L 0S & 5L 1S) a substantial proportion of that swelling occurred during the initial exposure period when no crystalline ettringite had visibly formed (detectable either in SEM or XRD). This confirms as previously reported by Wild et al. [15,16] that the swelling process occurs by water absorption during the initial stages of ettringite nucleation and growth. It is suggested that the ability of the ettringite precusor to hydrate is dependent on its composition. As the lime to slag ratio decreases, the amount of calcium available for reaction in the pore solution during slag hydration and exposure to Na_2SO_4 solution will be severely depressed (as explained above) and growth of ettringite will be severely inhibited. Also, the composition of the ettringite precusor would be expected to be low in calcium. Although formation of monosulphates is expected under these conditions, no monosulphates were detected on XRD traces. In this situation, there is very little water absorption, whereas for the high lime-low slag compositions where calcium is abundant substantial swelling occurs. The composition (0L 6S) is a special case in that hydration of the slag is delayed, activity is localised and confined principally to the slag particles, and calcium is rapidly released into the pore solution at a particular stage.

4. Conclusions

Lime-stabilised kaolinite shows severe disruption when exposed to 4.2% Na_2SO_4 solution and this disruption is associated with the formation of ettringite.

The progressive replacement of lime by slag resulted in a progressive modification of the microstructure, with respect to ettringite morphology. Three different categories of ettringite were observed in the lime-ggbs-kaolinite systems that had been exposed to 4.2% Na_2SO_4 solution, indicating three different growth conditions that appear to be determined principally by the availability of calcium in the pore solution and its distribution within the specimen.

The swelling of these specimens (reported in a previous paper [10]) appears to be associated with the initial stages of ettringite formation. It is suggested that the potential for water absorption by the ettringite precusor and for swelling, is dependent on its composition, and in particular on its calcium content.

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