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Enhancing the mechanical behaviour of cement based materials

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Abstract

A mechanism for the toughening of ceramic materials has been successfully developed in the refractories industry using residual stresses at the microstructural scale. This paper addresses the application of this approach to cement-based systems. In the cement case, the growth of expansive phases has been controlled, along with the set characteristics of the paste, to establish internal stresses which, while significant, have not been sufficient to cause expansive failure. Macro-crack propagation, initiated by external loading, has been suppressed either by the release of residual stresses which act to close the crack or by grain bridging. Because such stresses are dispersed throughout the matrix, this toughening mechanism would add to the value of steel reinforcement in the strengthening of concrete structures. This paper describes some early work concerning the factors which control internal stresses in cement microstructures and the experimentally measured stress–strain and fracture behaviour of pastes and mortars which confirm the dramatic effect of microstructural engineering. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Cement; Microstructure; Structural applications; Mechanical properties

1. Introduction

Dual phase refractories, in particular magnesia-spinel composites, have been recently developed specifically to withstand severe thermal shock without the propagation of major cracks. This has been achieved by the subtle manipulation of residual stresses within the microstructure such that the applied tensile stresses trigger microcracking. This has two effects.

(i) It releases these residual stresses producing a permanent overall volume expansion[1,2] which in turn suppresses the growth of major cracks in a similar way to transformation toughening in zirconia containing ceramics.[3]
(ii) It also produces a complex network of microcracks ahead of the main crack which can lead to grain bridging across the major crack.

Fig. 1 shows the stress–strain properties of magnesia and magnesia-spinel refractories and highlights the enhanced energy absorption (represented by the area under the stress–strain curve) of the dual phase refractory. Whilst the residual strains may seem small, the magnesia-spinel material exhibits increasing toughness as the crack propagates (R-curve behaviour) compared to the magnesia material which has a constant value of toughness.[4] Mathematical modelling of the refractory materials indicates that microstructures, where the included phase is in residual tension, and the matrix phase in residual compression, offers the best opportunities for improving the mechanical behaviour of these systems. The present study explores the possibility of exploiting this beneficial effect in cement mortars. The key to transferring this mechanism of toughening from fired ceramic to cement based materials is the development and control of residual stresses within the mortar.

1.1. Development of residual stresses in Portland cement pastes, mortars and concretes

Under normal conditions, the formation of hydration products during the hydration of Portland cement results in a net shrinkage, as water is lost from the pore structure into products or to the atmosphere. However, addition of certain additives can cause components of the paste to expand. By appropriate combination of rate

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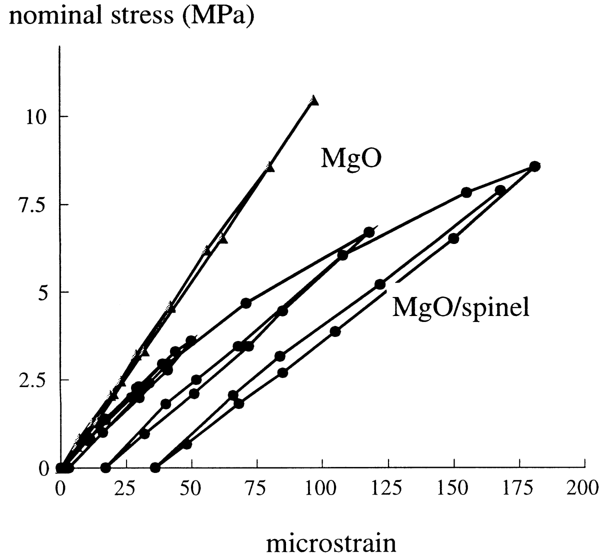

Fig. 1. Stress–strain properties of MgO and MgO-spinel refractories highlighting the influence of residual stresses. The energy absorption is represented by the area inside the hysteresis loop.

of expansion and set time, internal stresses in the microstructure can be generated by the growth of expansive phases within the confined porosity (see Fig. 2). Expansion, causing internal stresses, is said to be 'active' expansion, whereas expansion occurring while the paste is plastic or accommodated for in the available porosity after the paste has set, is considered to be 'passive'.[5] By manipulation of mix design and set times, expansion characteristics can be engineered to optimise the distribution and level of internal stresses.

1.2. Expansion in cement-based systems

Expansive cements are not new. Existing products aimed at shrinkage compensation and self-stressing cements all rely on the same chemistry. The expansion is associated with the rapid development of ettringite, a calcium aluminosulphate hydrate of approximate composition $Ca_6Al_2(SO_4)_3.(OH)_{12}.26H_2O$. There has been much discussion on the chemistry that causes ettringite expansion. Two main theories have been proposed.[6] According to the crystal growth theory, expansion is caused by the growth of ettringite crystals on solid surfaces or from solution, resulting in a crystallisation pressure. Alternatively, the incorporation of water into an ettringite gel, causing an overall expansion, is the basis of the swelling theory. A number of factors influence both models, not least the chemistry of the solution, in which the concentration of calcium ions is thought to play an important role in defining the size and aspect ratio of ettringite crystallites.[7–9]

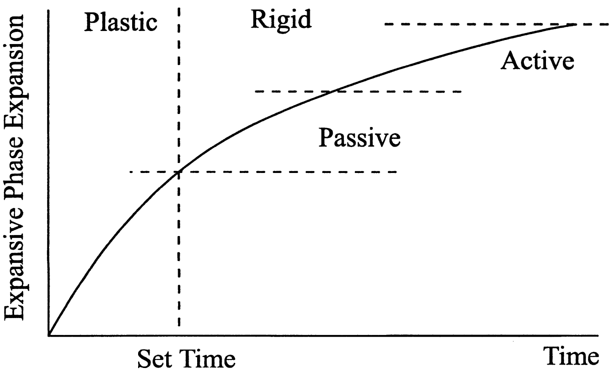

Fig. 2. Influence of phase expansion on the development of internal stresses.

Portland cement pastes develop ettringite quickly, due to the presence of gypsum, deliberately added to retard the tricalcium aluminate hydration reactions. While the sulphate concentration in solution remains high, ettringite remains the stable phase. This may be achieved by the addition of a soluble sulphate salt during mixing. At very high sulphate concentrations, gypsum ($CaSO_4.2H_2O$) will precipitate. This is also an expansive reaction contributing to pore filling and paste expansion. Sulphate additions not only stabilise and promote ettringite formation (assuming an adequate supply of aluminium), but they also can significantly shorten setting times. This paper describes the effect of sulphate additions on Portland cement paste set times and dimensional properties, and on the mechanical performance of the associated mortars.

2. Methodology

2.1. Sample preparation, curing and set time measurement

Portland cement pastes were made from ordinary Portland cement (OPC),* of composition given in Table 1, and various additions of sodium sulphate (see Table 2 for mix compositions). These were mixed with water to a water/cement ratio (w/c) of 0.35. Sodium sulphate was used in this study because it is a convenient source of soluble sulphate but, in practice, an alternative such as calcium sulphoaluminate cement would be used to minimise the addition of alkalis to the cement.

Pastes were throughly mixed using a domestic food blender and cast into perspex moulds of dimensions 10×10×100 mm. Five bars were cast for each composition. A portion of the paste was retained for set time determination using the Vicat needle method (BS 4550). After approximately 15 min, the top surface of the moulded bars were screeded to produce smooth paste

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* Supplied by Blue Circle Industries plc, Dunbar Works, East Lothian, Scotland.

Table 1
Portland cement (OPC) composition

Oxide	Wt%
SiO_2	20.1
Al_2O_3	5.07
Fe_2O_3	3.3
CaO	64.21
MgO	2.27
SO_3	3.14
Eq. Na	0.43

Table 2
Mix proportions for the preparation of the cement binder

Cement/g	Na_2SO_4/g	Water/g
292	8	105
285	15	105
278	22	105
270	30	105

bar surfaces and the moulds, with bars, were placed on a tray above water in a sealed desiccator for 24 h at 23°C. The bars were then demoulded and Demec studs were fitted to the ends using fast-setting Araldite. The bars were then weighed and their dimensions recorded using a digital comparator (Mitutoyo Digimatic Indicator) and a measuring jig, to ensure reproducable positioning of the bar each time. The bars were then returned to the above curing regime to await further measurements.

Mortar bars, made with a sand:binder ratio of 1:1, were also prepared. The preparation technique was similar to that for paste bars except that the river sand (<1 mm) was saturated with water prior to mixing with the binder (OPC) so that the w/c of 0.35 would be preserved on mixing. Additional mortar bars were prepared using a well-graded sand[†] ($0.3\ \text{mm} < d_{50} < 0.5\ \text{mm}$). Plates of dimensions 75×25×150 mm, with a notch of 50 mm, were cast for fracture toughness testing, as determined by the test configuration.[9]

2.2. Mechanical property measurements

The stress–strain behaviour of an OPC mortar (graded sand) with (7.5%) and without sodium sulphate additions was investigated using 4 point flexure tests on the fabricated bars. The strain was measured directly on the specimen by strain gauges attached to the tensile face of the specimen. The nominal stress was calculated from the applied moment and dimensions of the specimen assuming linear elasticity. The specimens were loaded and unloaded, the maximum load being increased every cycle, until failure occurred.

The fracture toughness behaviour of OPC mortars (graded sand) with (7.5%) and without sodium sulphate additions were measured on the pre-notched plates.[10] A crack was initiated at the notch-tip and propagated down the middle of the plate as the load was increased. The fracture toughness was calculated using the following formula:

$$K_{\text{app}} = \frac{F}{\sqrt{w}}\left(\frac{x}{w} - \frac{1}{4}\right)\sqrt{2}\sqrt{\frac{12}{1-\nu^2}}\frac{1}{B} \tag{1}$$

where F is the applied load, x is the distance between the loading points, w is the width of the plate, ν is the poissons ratio and B is the thickness of the plate.

3. Results and discussion

Figs. 3 and 4 show the dimensional and weight changes, respectively, on ageing of cement paste and mortar bars as a function of time. The exhibited trends are derived from averages of the readings from five bars per composition at each measurement time. All dimensional and weight changes reported are referenced against the initial dimensions and weights recorded on demoulding. The data show an expansion and weight increase with time for all specimens, but these changes are exaggerated as the sulphate additions are increased, at least up to 7.5%. The combination of weight increase and expansion suggests that moisture is absorbed from the curing environment to enable the continuing development of ettringite or gypsum. This would be consistent

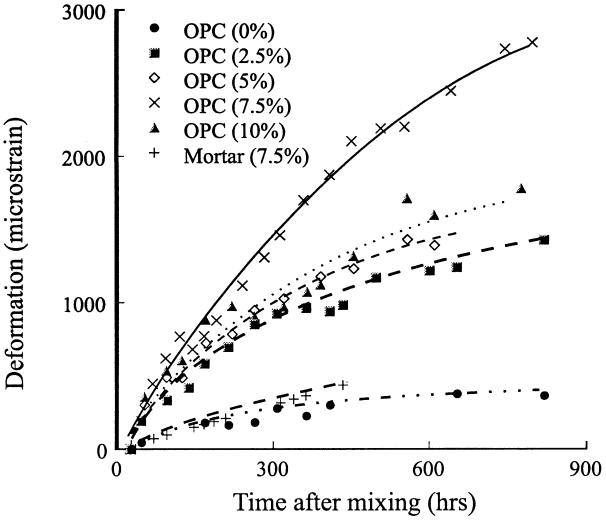

Fig. 3. Deformation vs time for OPC paste and mortar bars aged in a high humidity environment.

[†] Chelford 30, supplied by Hepworth Minerals and Chemicals, Sandbach, Cheshire, England.

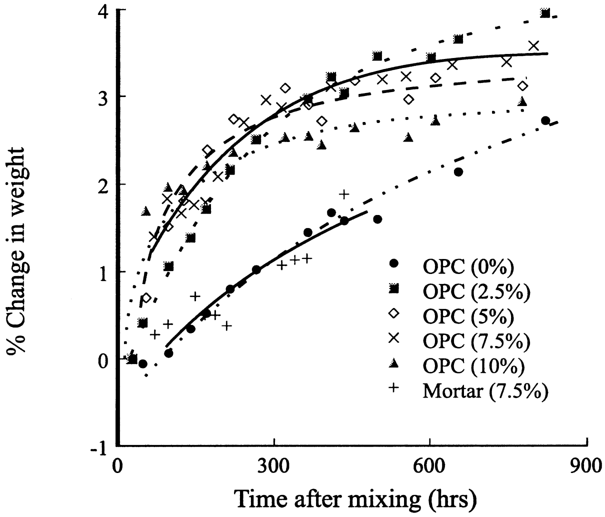

Fig. 4. Weight change vs. time for OPC paste and mortar bars aged in a high humidity environment.

with expectations. The higher addition (10%) actually demonstrates a lower expansion than for the 7.5% addition at longer ages.

As expected, there is less expansion in the mortar than in the corresponding OPC paste (i.e. both containing 7.5% sulphate addition), due to the dilution of cement by the aggregate.

Fig. 5 shows the accelerating effect of sulphate additions on the setting time of the cement pastes. This acceleration may account for the reduced expansion measured for the sample containing 10% relative to the 7.5% sulphate additions. Assuming it has attained a final set, the paste is no longer able to yield to expansion unless expansion is accommodated for in available porosity. While this occurs, macroscopic expansion stops. Further phase expansion internally places the microstructure under stress until its tensile strength is exceeded and cracking is observed. Indeed, macroscopic cracking was observed on the bars containing the highest sulphate loading suggesting that on-going expansion was sufficiently 'active' to crack the matrix. This is an example where the mix composition was unsuitable although the generation of internal stresses is quite evident.

The final and most convincing argument for the existence and effectiveness of internal stresses in these cement pastes and mortars comes from the mechanical performance measurements which show non-linear stress–strain characteristics consistent with those observed for the MgO-spinel ceramic system in Fig. 1. Fig. 6 shows the characteristics of mortars made from OPC and OPC with added sulphate (7.5%). The Portland cement mortar without sulphate addition exhibits some non-linear behaviour but this is greatly enhanced by the addition of sulphate. After the peak load was reached, these samples remained intact and, on reloading, were capable of withstanding 50% of the initial maximum stress. This indicates extensive microcracking rather than the propagation of one large crack and consequently a toughened matrix.

In addition to the non-linear stress–strain characteristics Fig. 7 shows the R-curve behaviour of mortars made from OPC and OPC with added sulphate (7.5%). This provides clear evidence of the toughening behaviour, caused by the introduction of sodium sulphate. The release of the residual tensile stresses created by the expansive matrix phase has two effects. Firstly there is a 50% increase in the resistance to the onset of macrocrack propagation. Secondly, as the macro crack propagates the toughness of the material increases rapidly with crack extension when compared to the small increase in toughness observed for the OPC mortar.

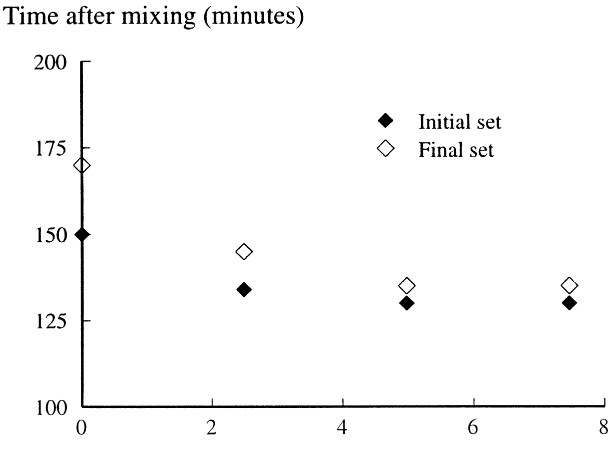

Fig. 5. Set time characteristics of OPC pastes with and without sulphate additions.

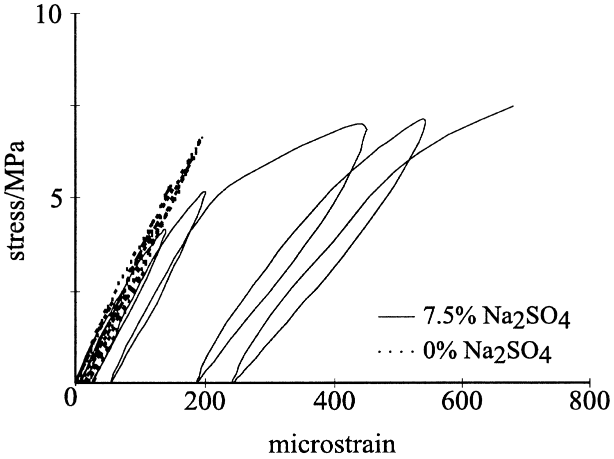

Fig. 6. Influence of sodium sulphate addition on the stress–strain properties of Portland cement mortars (w/c = 0.30), aged 28 days under high humidity conditions.

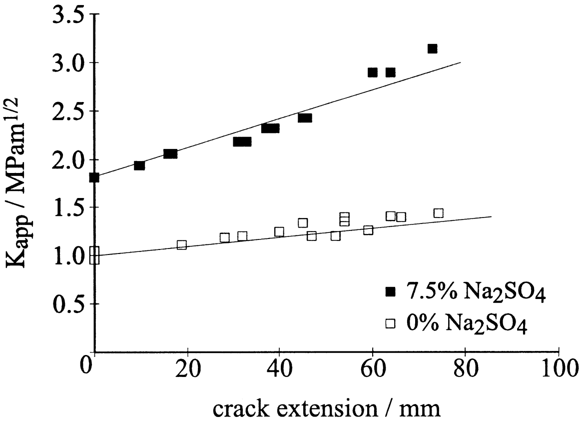

Fig. 7. Influence of sodium sulphate addition on the toughness behaviour of Portland cement mortars (w/c = 0.30), aged 28 days under high humidity conditions.

Most failures are a result of tensile loading, either arising from excessive expansion of phases within the concrete or as a result of impact. In either case, concretes with better resistance to catastrophic cracking would provide enhanced protection against surface deterioration and spalling. In addition, a consequence of the toughening mechanism is a lower porosity microstructure. This will improve durability because the matrix modifications, whilst reducing porosity overall, will shift the emphasis from interconnected porosity, which permits material transport throughout the interior of the microstructure, to isolated porosity. The latter cannot contribute to internal degradation of the matrix so that the exposed surfaces are primarily restricted to the geometric surface of the concrete structure and deterioration rates will be reduced. However, this would require confirmation by experimentation.

4. Conclusions

A few simple experiments with conventional cement mortars have shown that residual stresses can also be manipulated in hydraulically bonded systems and the tensile mechanical properties dramatically enhanced (see Figs. 6 and 7). Thus, by suitable mix design, products with enhanced toughness can be manufactured without the use of reinforcing fibres. This is an important observation especially relevant to high strength concrete where the low toughness is particularly noticeable.

References

1. Henderson, R. J. and Chandler, H. W., A model for non-linear mechanical behaviour of refractories. *Brit. Ceram. Trans.*, 1997, **58**, 85–96.
2. Henderson, R. J., Thermomechanics of dual-phase refractories, PhD thesis, University of Aberdeen, UK, 1997.
3. Swain, M. V., R-curve behaviour and thermal shock resistance of ceramics. *J. Am. Ceram. Soc.*, 1991, **73**(3), 621–628.
4. Henderson, R. J. and Chandler, H. W., The fracture behaviour of dual phase composite refractories. In *Engineering with Ceramics*, ed. W. E. Lee, and B. Derby. British Ceramic Proceedings 59, The Institute of Materials, 1999, pp. 225–231.
5. Panchenko, A. I., Control of expansion and structure formation of expansive cement. *Cem. Concr. Res.*, 1990, **20**(3), 602–609.
6. Cohen, M. D., Theories of expansion in sulfoaluminate-type expansive cements-schools of thought. *Cem. Concr. Res.*, 1993, **13**, 809–818.
7. Ogawa, K. and Roy, D. M., $C_4A_3\bar{S}$ hydration, ettringite formation, and its expansion mechanism. 1. Expansion-ettringite stability. *Cem. Concr. Res.*, 1981, **11**, 741.
8. Ogawa, K. and Roy, D. M., $C_4A_3\bar{S}$ hydration, ettringite formation, and its expansion mechanism. 2. Microstructural observation of expansion. *Cem. Concr. Res.*, 1982, **12**, 101–109.
9. Ogawa, K. and Roy, D. M., $C_4A_3\bar{S}$ hydration, ettringite formation, and its expansion mechanism. 3. Effect of CaO, NaOH and NaC1 — conclusions. *Cem. Concr. Res.*, 1982, **12**, 247–256.
10. Chandler, H. W., Henderson, R. J., Al-Zubaidy, M. N., Saribiyik, M. and Muliaidi, A., A fracture test for brittle materials. *J. Eur. Ceram. Soc.*, 1997, **17**, 759–763.