Pergamon

Cement and Concrete Research 31 (2001) 455–465

CEMENT AND CONCRETE RESEARCH

The effect of retarders on the microstructure and mechanical properties of magnesia–phosphate cement mortar

D.A. Hall[a],*, R. Stevens[b], B. El-Jazairi[c]

[a]School of Materials, University of Leeds, Leeds LS2 9JT, UK
[b]Department of Materials Science and Engineering, University of Bath, Bath BA2 7AY, UK
[c]Feb MBT, Swinton, Manchester M27 1DT, UK

Received 21 July 2000; accepted 29 November 2000

Abstract

Magnesia–phosphate cement (MPC) mortars based on magnesia and ammonium dihydrogen orthophosphate (ADP) were prepared with additions of sodium triphosphate (STP), boric acid, and borax as set-retarders. The resulting materials were characterised in terms of their setting characteristics, mechanical properties, and microstructures. The retarders were found to increase the setting time and to reduce the intensity of the exothermic reactions during the initial setting and hardening stages. The effectiveness of STP as a retarder was limited by its solubility in the saturated ammonium phosphate solution, determined as 340 g dm^{-3}, which meant that the maximum setting time obtained was approximately 15 min. In contrast, successive additions of boric acid and borax led to a cumulative increase in setting time to a maximum of 1 h for the compositions investigated. The use of retarders also led to an extension of the initial hardening period, as indicated by reductions in the early values of Young's modulus and flexural strength. The microstructural characteristics of the materials produced were very dependent on the type and level of additive employed; for STP, the binding phase was relatively fine grained (<0.5 μm), while for boric acid relatively large-grained (>10 μm) structures were observed as a result of a reduction in the supersaturation of the aqueous solution. Well-aged mortar specimens exhibited a high incidence of microcracks on the fracture surfaces, which were related to the occurrence of a fracture process zone ahead of the main crack tip during fracture. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Retardation; Microstructure; Bending strength; Elastic moduli; MgO

1. Introduction

Magnesia–phosphate cements (MPC), based on the reaction between basic magnesia and an aqueous ammonium phosphate solution, have been employed as concrete repair materials for over 25 years, and known industrially for a good deal longer. In 1947, Every [1] described a general formulation for a rapid setting cement comprising a dry mixture of inert filler (such as silica or zircon), a solid inorganic base, and a soluble inorganic acid salt. Dead-burned magnesite (primarily magnesia) was recommended as the basic material, while the alkali metal or ammonium diacid phosphates were preferred as the acid salt. It was recognised in this first publication that the use of a set-retarder, in this case sodium silico-fluoride, was necessary in order to obtain a material with a reasonably long setting time. The use of such an additive was also reported to increase the strength of the hardened material by a factor of 3.

Subsequently, a "two-part" system comprising solid magnesia and an ammonium polyphosphate solution was proposed as the basis for cold-setting basic refractories [2,3] and rapid repair materials for concrete pavements [4]. In 1976, a "one-part" MPC system consisting of a dry mixture of magnesia, water-soluble ammonium dihydrogen orthophosphate (ADP; $NH_4H_2PO_4$), and a water-soluble polyphosphate, was developed as a concrete repair material [5]. In each of these systems, the incorporation of the polyphosphate component as a set-retarder was necessary in order to control the exothermic setting reactions. Two years later, Stierli et al. [6] patented a method for controlling the setting characteristics of MPCs using soluble oxy-boron compounds such as boric acid (H_3BO_3) or borax ($Na_2B_4O_7 \cdot 10H_2O$).

---

* Corresponding author. Materials Science Centre, University of Manchester and UMIST, Grosvenor Street, Manchester M1 7HS, UK. Tel.: +44-161-200-3577; fax: +44-161-200-3586.

E-mail address: david.hall@man.ac.uk (D.A. Hall).

0008-8846/01/$ – see front matter
PII: S0008-8846(01)00501-9

In dentistry, MPC systems are used as cold-setting refractory moulds for casting molten metal alloys, and therefore several studies have been made of the setting reactions and thermal properties of such “casting investment” materials [7–11]. Allan and Asgar [7] identified the main binding phase as magnesium ammonium phosphate hexahydrate, $MgNH_4PO_4{\cdot}6H_2O$, also known as the mineral struvite. Subsequent studies [8–11] showed that magnesium ammonium phosphate tetrahydrate, $Mg(NH_4)_2(HPO_4)_2{\cdot}4H_2O$, could form under certain conditions, leading to the following overall reaction scheme [11]:

$$MgO + 2NH_4H_2PO_4 + 3H_2O \rightarrow Mg(NH_4)_2(HPO_4)_2 \cdot 4H_2O \tag{1}$$

$$Mg(NH_4)_2(HPO_4)_2 \cdot 4H_2O + MgO + 7H_2O \rightarrow 2MgNH_4PO_4 \cdot 6H_2O. \tag{2}$$

Sugama and Kuckaka [12] published a paper outlining the chemistry and mechanical properties of a magnesia–DAP (diammonium phosphate, $(NH_4)_2HPO_4$)-based cement. Setting was found to occur within 3 min, yielding compressive strengths of 7 and 20 MPa after ageing for 1 and 15 h, respectively. In a subsequent publication [13], it was shown that replacement of the DAP solution by 55% ammonium polyphosphate solution led to an increase in the 1-h compressive strength to 14 MPa.

The characteristic properties of a commercial MPC mortar, developed as a rapid repair material for concrete, were described by El-Jazairi [14,15]. Several areas of application were recognised for the material, including the repair of roads, airport runways, and industrial floors. The chemistry and structure of similar materials were studied by Abdelrazig et al. [16,17]. Several hydrated phosphate compounds were identified as products of the setting reactions, and it was shown that the presence of any one was dependent both on the composition and on the preparation conditions. The hexahydrate was identified as the main reaction product in the commercial MPC mortar, the setting reaction being summarised as follows:

$$MgO + NH_4H_2PO_4 + 5H_2O \rightarrow MgNH_4PO_4 \cdot 6H_2O. \tag{3}$$

Magnesium ammonium phosphate monohydrate ($MgNH_4PO_4{\cdot}H_2O$) and the tetrahydrate ($Mg(NH_4)_2(HPO_4)_2{\cdot}4H_2O$) were detected in some of the systems studied, often in large amounts, which led to the proposal of a reaction sequence involving the formation of the tetrahydrate as an intermediate reaction product in a manner analogous to that suggested by Miyaji et al. [11] (Eqs. (1) and (2)). It was found that a large excess of water caused an increase in porosity and a reduction in the compressive strength of the hardened material [16]. This effect was treated in more depth by the present authors, who showed that the excess water was not chemically bound within the hardened cement and gradually evaporated during ageing to leave a finely porous structure that exhibited poor mechanical properties [19]. In contrast, the use of low water contents yielded a dense material having flexural and compressive strengths of around 10 and 55 MPa, respectively, after ageing for 7 days.

Popovics and colleagues [20,21] carried out a series of investigations into the structure and properties of MPC mortar, including in their studies a comparison of materials incorporating boric acid and borax as retarders. In their work, the monohydrate was reported as being a more significant reaction product than was suggested in the results presented by Abdelrazig et al., being formed preferentially when processing of the materials was carried out at elevated temperatures (around 38°C). It was also noted that the use of higher temperature curing schedules led to reductions in the ultimate strength achieved, which was attributed to the occurrence of a more irregular crystal growth.

Yang and Wu [22] showed that borax is an effective retarder for MPC systems. It was found that the setting time increased almost linearly with borax content, provided that the phosphate content remained constant. Conversely, setting could be accelerated by employing a magnesia powder with a higher specific surface area. The mechanism of retardation by borax was discussed in terms of the precipitation of magnesium borate compounds around the basic magnesia grains, which acted to prevent a continuous reaction with the acidic phosphate solution [22]. A similar retardation mechanism was suggested earlier by Sugama and Kuckaka [13].

For MPC systems, the key to the fabrication of a dense and chemically stable material (i.e., without any of the intermediate and unstable monohydrate or tetrahydrate compounds) lies in controlling the exothermic chemical reactions during the initial setting and hardening period. Both the use of a relatively unreactive fused or dead-burned magnesia as the basic component and the inclusion of inert filler materials help to achieve this goal. In addition, the systems described in the literature usually contain a set-retarder in one form or another; either a water-soluble fluoride, polyphosphate, or oxy-boron compound. In all cases, the use of a retarder was reported to yield an increase in the ultimate compressive strength, often reaching a value of around 70 MPa [6]. The present paper is concerned with the effects of retarders on the structure–property relationships in MPC mortar, with particular emphasis on the significant improvements in strength, which can be afforded by the use of suitable additives.

2. Experimental procedures

MPC mortar compositions were made up according to the commercial formulation [5], the main dry components comprising magnesia, ADP, and inert fillers (mainly silica sand). Excess magnesia was employed in order to ensure that all of the available ADP would react according to the

Table 1
Chemical analysis of raw materials

Component	Chemical analysis
Dead-burned magnesia	90% MgO, main impurities: SiO_2, CaO
ADP ($NH_4H_2PO_4$)	technical grade, >99% ADP
Filler	mainly quartz sand
STP ($Na_5P_3O_{10}$)	22.7–23.6% phosphorus (theoretical 25.3%)
Boric acid (H_3BO_3)	technical grade, >99.9% boric acid
Borax ($Na_2B_4O_7{\cdot}10H_2O$)	technical grade, >99.9% borax

stoichiometry of Eq. (3). The filler content in MPC mortar systems typically comprises approximately 80 wt.% of the dry component; this rather high proportion of inert filler is employed for economic purposes and also to help reduce the temperature rise within the material due to the heat of reaction during setting. Three different retarders were investigated, these being sodium triphosphate (STP), boric acid, and borax. The chemical characteristics of the raw materials employed in the preparation of the mortar are listed in Table 1.

The dry components were weighed out in batches of 1.5 kg, with retarder additions to the basic mix being made according to the amounts listed in Table 2. These particular values were chosen in order to give a range of retarder additions such that the materials produced would exhibit setting times between 8 and 60 min. The amount of water used was calculated as that required to give a water content of 6% (expressed as a mass fraction of the dry component) in material with the commercial composition, this being approximately 90 g for a 1.5-kg batch size. In the case of borax, the weight of water included in the mix was reduced in accordance with the water of hydration chemically bound within the retarder. The dry components were mixed in a Hobart mixer for 10 min and then left to equilibrate in a temperature (20 ± 2°C)- and humidity (60% RH)-controlled laboratory prior to use.

The dry powder mixture was added to the required amount of water contained in a Hobart mixer and mixed for 2 min. The resulting wet mortar was then transferred to the appropriate moulds for subsequent testing. The final setting time was determined using a Vicat needle according to the procedure described in British Standard BS 4550 [23]. Heat evolution during the exothermic setting and hardening reactions was monitored by measuring the temperature rise in a small (150 g) specimen by semiadiabatic calorimetry [24]. The elastic modulus of hardened specimens was measured nondestructively by means of the flexural resonance method, taking an average value from two specimens with dimensions 25 × 25 × 300 mm. Flexural strength was determined by the three-point bend test, using six specimens with dimensions 25 × 25 × 100 mm. Further details of the testing procedures have been given previously [19].

Table 2
Retarder additions for a 1.5-kg batch of MPC mortar

Retarder	Weight added (g)
STP	15, 25, 35, 45, 55
Boric acid	2.5, 5.0, 7.5, 10.0, 12.5
Borax	5, 10, 15, 20, 25

3. Results and discussion

3.1. The effects of retarders on the setting characteristics of MPC mortar

The retarding effects of boric acid and borax were found to be similar; representative results obtained for boric acid by semiadiabatic calorimetry are presented in Fig. 1. Successive additions of each compound caused cumulative increases in the setting time and in the parameters t_1 and t_2, corresponding to the times at which the maximum rate of temperature rise and the maximum temperature, T_{max}, were observed, respectively (Fig. 2). It is of interest here to note that the fractional mass of boron in boric acid is approximately 0.175, while in borax it is 0.113. Therefore, if the effectiveness of these retarders was solely dependent on the boron content, then the mass of borax added to MPC mortar would need to be a factor of 1.55 greater than that of boric acid in order to produce an equivalent retardation effect. In fact, this ratio is quite close to that determined experimentally, indicating that a similar chemical species is responsible for retardation in each case. In the initially acidic solution of the MPC system, with a pH value of approximately 5 [25], this species is likely to be either $B(OH)_3$ or $B(OH)_4^-$ [26].

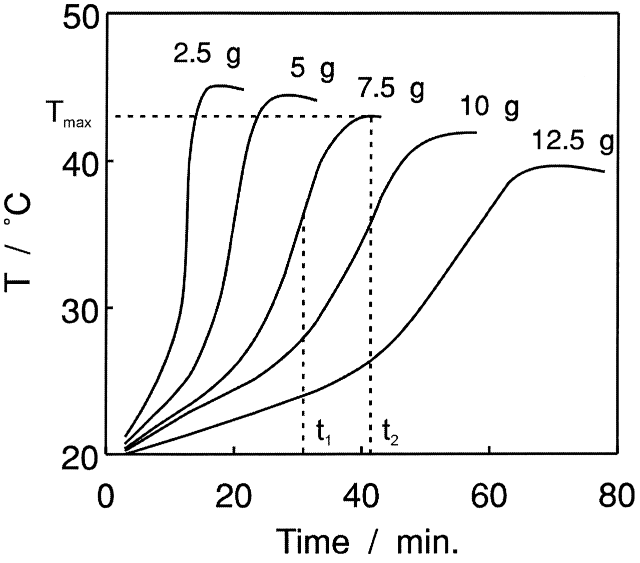
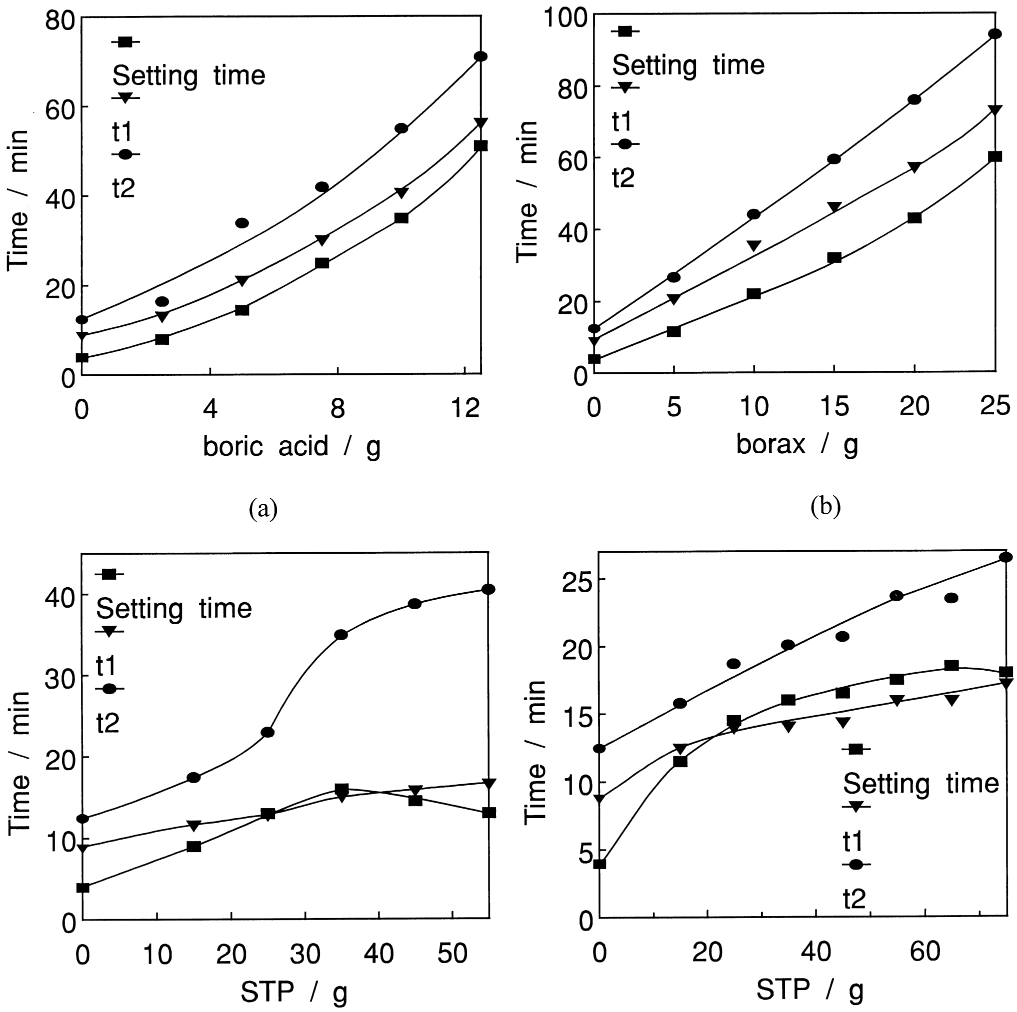


Fig. 1. Calorimetry curves obtained for MPC mortar prepared with various additions of boric acid.



(a) (b)

(c) (d)

Fig. 2. Setting times and calorimetry results for MPC mortar as a function of retarder contents: (a) boric acid, (b) borax, (c) STP (6% water), and (d) STP (10% water).

The effect of STP on the setting characteristics was quite different, as shown in Fig. 2(c). The setting time of the material increased from 4 min (with no additive) to 16 min at a level of 35 g, but decreased again upon further additions. Although flow tests were not performed, it was observed that this acceleration in setting at the high levels of STP was accompanied by a loss in the workability of the wet mix. Similar observations were made by Winbow [27], who suggested that the acceleration in setting at the higher levels of STP might be due to the formation of sodium ammonium phosphate hydrates such as $NaNH_4HPO_4 \cdot 4H_2O$, which could be identified in some hardened MPCs. However, the calorimeter results obtained in the present work showed that there was no acceleration in the rate of heat evolution; in fact it was somewhat retarded, as shown in Fig. 2(c). Since the materials prepared with a high STP content exhibited poor workability, it can be postulated that the retarding action is limited by the *solubility* of STP and that the excess present caused a stiffening of the wet mix that resulted in premature setting. Further experiments were carried out in order to clarify this point.

Firstly, tests were carried out to determine the setting characteristics of materials prepared with a higher water content of 10%. In this case, the setting time continued to increase to a value of around 19 min at an additive level of 65 g (Fig. 2(d)), lending support to the above proposal. One problem with this interpretation is that the maximum useful addition of STP (prior to reaching the solubility limit) cannot be predicted accurately since the solubility of STP in an acid phosphate solution has not yet been published. The solubility in water, presumably at an equilibrium pH of approximately 9 [25], has been given as 145 g dm^{-3} [28], suggesting a maximum addition of just 13.4 g before the solubility limit is reached. However, it is likely that the solubility would be increased considerably in an acidic environment as a result of the formation of acid triphosphate ions according to the following chemical equilibria (Eqs. (4) and (5)) [29]:

$$P_3O_{10}^{5-} + H^+ \Longleftrightarrow HP_3O_{10}^{4-} \quad (4)$$

$$HP_3O_{10}^{4-} + H^+ \Longleftrightarrow H_2P_3O_{10}^{3-} \quad (5)$$

etc.

An experimental determination of the solubility of STP in ADP solutions was made by mixing an excess of STP (15 g) with 25 g of water and with 0–10 g of ADP, the ADP finally being present in excess of its own solubility limit. After mixing for 10 min, the slurry was filtered and part of the filtrate diluted by a factor of 10. This solution was then analysed for sodium, by atomic absorption spectroscopy, and for triphosphate, by the gravimetric method described by McCune and Arquette [30]. The accuracy of the latter method was checked by analysing for known concentrations of STP in saturated solutions of ADP, since the presence of large quantities of orthophosphate ions (PO_4^{3-}) were considered to be a possible source of error in the gravimetric technique.

Both of these analysis techniques indicated a solubility of approximately 0.40 M, or 147 g dm^{-3}, for a pure aqueous solution of STP, which is in close agreement with the figure of 145 g dm^{-3} given in the literature [28]. Following an addition of only 2 g ADP, the increase in the acidity of the solution caused a twofold increase in the solubility to approximately 0.80 M (Fig. 3). Further additions of ADP resulted in a slightly increased solubility, with a value at saturation of approximately 0.925 M, or 340 g dm^{-3}. For the MPC mortar system under investigation, with a water content of 6%, the aqueous component is saturated with respect to ADP within a few seconds of mixing. Under these conditions, given a solubility of 0.925 M for STP in the saturated ADP solution, an optimum useful addition of STP can be calculated as approximately 31 g, which is in reasonable agreement with the experimentally determined optimum level of 35 g. Therefore, it can be concluded that the effectiveness of STP as a retarder for MPCs is limited by its solubility in the acidic phosphate solution.

3.2. The effects of retarders on the mechanical properties and microstructure of MPC mortar

Determination of the elastic moduli of the materials during ageing yielded results that were broadly similar in form for each of the retarder systems investigated, an increase in the retarder content leading to a reduction in the modulus in the early stages of hardening (Fig. 4). All of the materials showed an initial rapid gain in modulus followed by a more gradual increase with time. The main effect of the retarders in this context was to cause an extension of the initial hardening period.

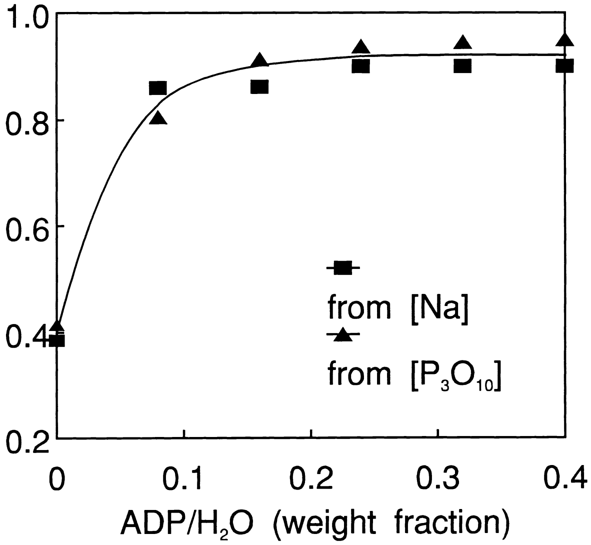
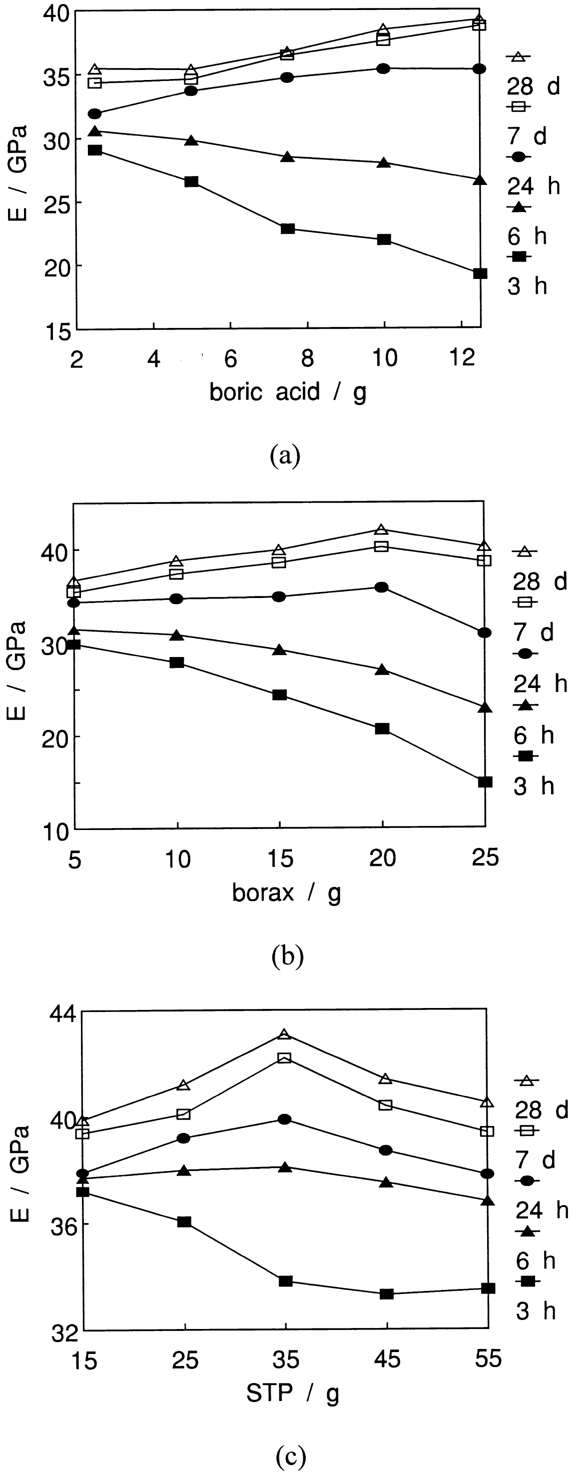


Fig. 3. Solubility of STP in aqueous solutions of ADP.

The ultimate elastic modulus achieved at an age of 28 days increased significantly due to the presence of the retarders. For example, with an addition of 2.5 g boric acid, the modulus value measured after 3 h was 29 GPa, increasing by a factor of 1.2 to give 36 GPa after 28 days. In contrast, when the additive level was increased to 12.5 g, the initial and ultimate modulus values were 19 and 39 GPa, respectively, increasing by a factor of 2 over the ageing period. The results obtained for borax were similar, although the mass of additive required to achieve a given reduction in modulus during the early stages of hardening was higher, in accordance with the lower concentration of boron present.

For STP, the general behaviour was similar in that retarder additions at the higher levels resulted in a retardation in the development of the elastic modulus. However, in this case there was an optimum level of 35 g, beyond which there was a degradation in the ultimate value achieved. Furthermore, the relative increase in modulus during ageing was less than that observed for either of the systems containing the oxy-boron compounds; with an addition of 35 g STP, the modulus increased by a factor of 1.3 over the ageing period, from 34 GPa at 3 h to 43 GPa at 28 days. It is evident that the samples prepared using the higher STP additions exhibited relatively low modulus values during the early ageing period. This supports the suggestion made above regarding the premature setting of these systems, which was attributed mainly to an increase in the viscosity of the wet mix rather than to the precipitation of sodium ammonium phosphate hydrates.

The results obtained for flexural strength, presented in Fig. 5, followed similar trends to those found for Young's modulus, although the statistical variations were larger. Additions of boric acid and borax led to an increasingly pronounced retardation in the development of strength. Materials prepared with an addition of 2.5 g boric acid



(a)

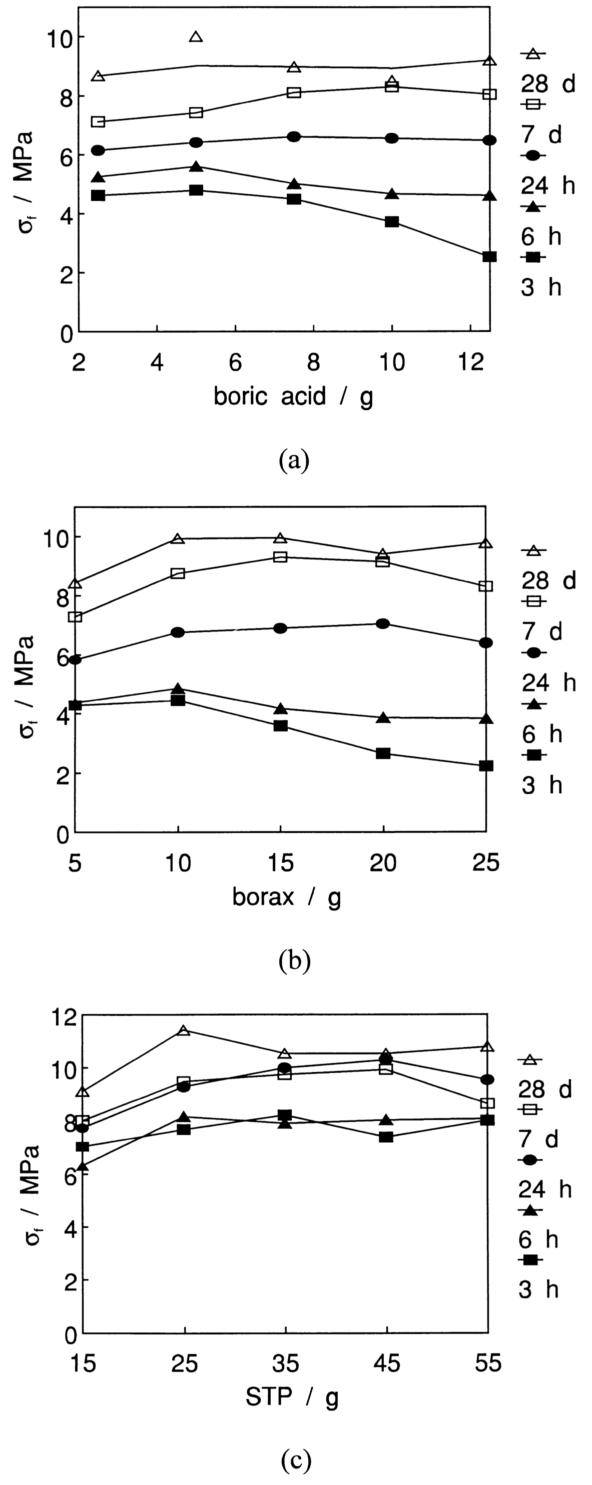
(b)

(c)

Fig. 4. Young's modulus of MPC mortar as a function of retarder content, measured at various ageing times: (a) boric acid, (b) borax, and (c) STP. Typical uncertainties were ±2%.

yielded flexural strengths of 4.6 and 8.7 MPa after ageing for 3 h and 28 days, respectively, showing an overall increase by a factor of 1.9 during this time period. At a level of 12.5 g boric acid, the corresponding flexural strength values were 2.5 and 9.2 MPa, respectively, increasing by a factor of 3.6 during the ageing period.

The trends observed in the flexural strength results obtained for materials prepared with STP were less clear. It is likely that this is due to the statistical variation in the



(a)

(b)

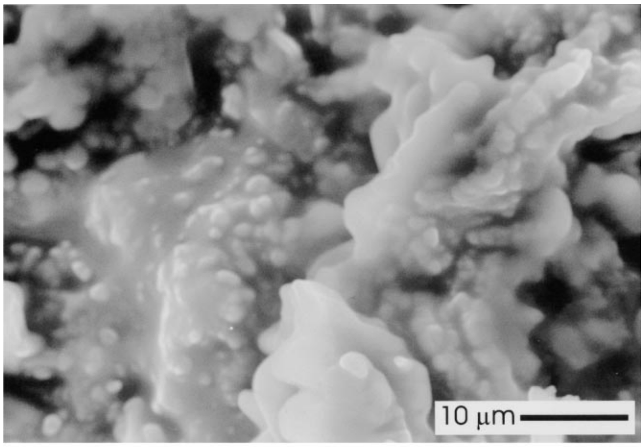
(c)

Fig. 5. Flexural strength of MPC mortar as a function of retarder content, measured at various ageing times: (a) boric acid, (b) borax, and (c) STP. Typical uncertainties were ±8%.

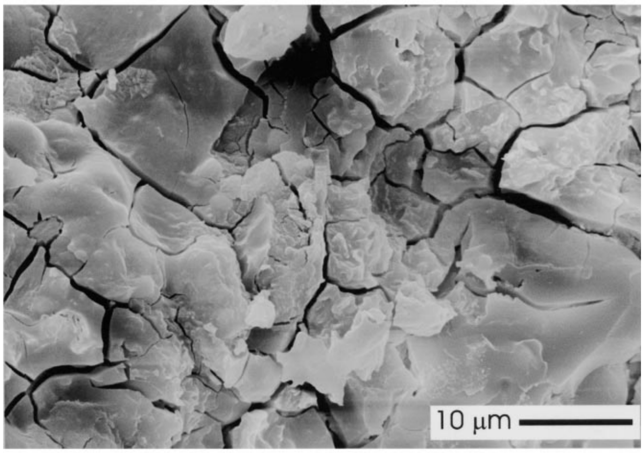
strength measurements, which meant that it was difficult to determine accurately the relatively small changes in strength as a function of retarder content. Nevertheless, it is clear from Fig. 5(c) that the ultimate strength was lowered when the level of STP was below 25 g, and that there was an overall increase in strength by a factor ~1.4 over the time period from 3 h to 28 days.

A representative number of the specimens used in the flexural strength tests were examined after fracture using SEM, in order to provide information on the effects of the retarders on microstructure and on the characteristics of the fracture surfaces. In the specimens prepared with 35 g STP, the appearance of the fracture surface of the binding phase was relatively dense and smooth, as shown by the micrograph presented in Fig. 6(a). Higher or lower levels of STP tended to cause an increased degree of heterogeneity, as shown in Fig. 7. The ultimate Young's modulus and flexural strength values were also significantly reduced as a result of this heterogeneity (Figs. 4 and 5).

For the low retarder contents, this heterogeneity was most likely due to the early setting characteristics (setting times less than 10 min), which would have hindered the compaction of the materials during the casting procedures. It is also possible that the higher temperatures developed during setting and hardening would have led to more irregular crystal growth, as suggested by Popovics and Rajendran [21]. The importance of the deflocculating characteristics of triphosphate ions was recognised by Abdelrazig et al. [16], who suggested that they may play a significant role in enabling improved compaction of the wet mix, thereby reducing the porosity of the hardened material. For the case of the materials prepared with excess (undissolved) STP, which did not exhibit such a strong exotherm on setting, the excess STP resulted in low workability of the wet mix, which was again a source of heterogeneity.



(a)



(b)

Fig. 6. Micrographs of fracture surfaces in specimen prepared with 35 g STP after ageing for (a) 3 h and (b) 28 days.

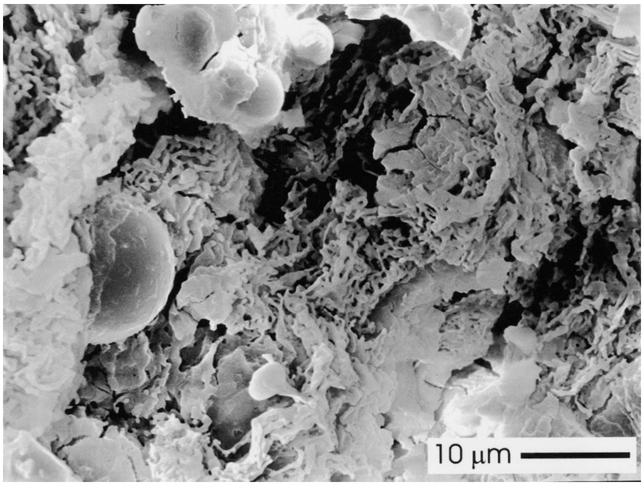


Fig. 7. Micrograph of fracture surface in specimen prepared with 55 g STP after ageing for 28 days.

Significant changes in the mode of fracture within the binding phase were observed as a function of ageing time. The fracture surfaces obtained after ageing for 3 h were relatively smooth and crack-free, as shown in Fig. 6(a). The size of the crystals, identified previously as the hexahydrate $MgNH_4PO_4 \cdot 6H_2O$ [19], was estimated as being of the order of 0.5 μm. After longer ageing periods, the fracture surfaces began to show an increased degree of microcracking until after fracture at 28 days almost all of the surface was covered by a network of fine microcracks (Fig. 6(b)). For this stronger, well-aged material the bonding between individual crystals appears to have developed to such an extent that the major fracture path was transcrystalline and therefore the morphology of the individual crystals was not so easily discernible.

From these observations, it is clear that the extensive microcracking observed on fracture surfaces of the higher-strength specimens was not present in those specimens tested at the earlier ages and therefore cannot be attributed to shrinkage or desiccation in the low pressure environment of the SEM. Furthermore, it can be suggested that such microcracking is a stress-induced phenomenon that occurs

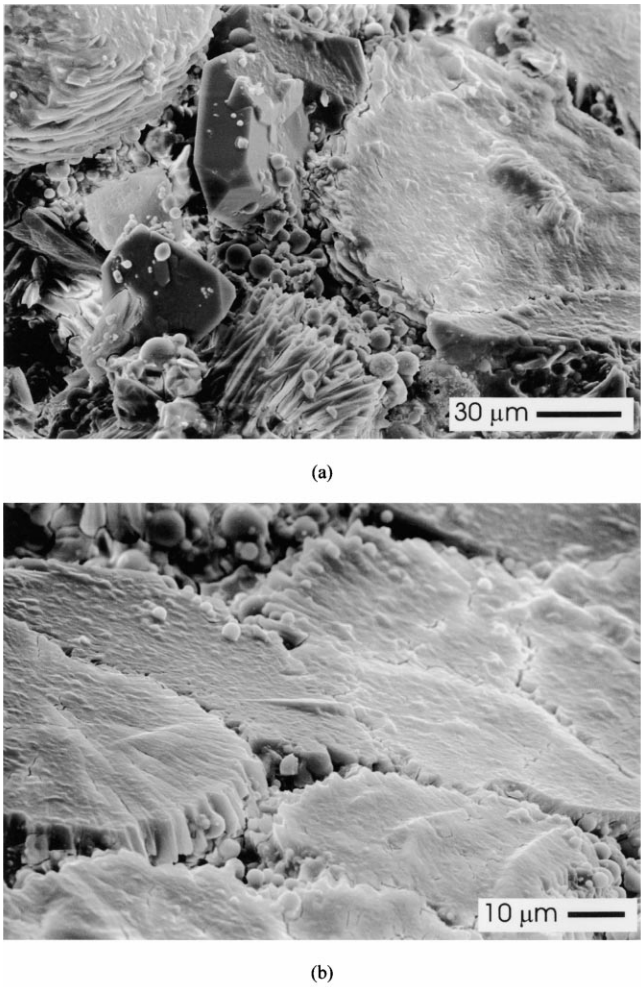


Fig. 8. Micrographs of fracture surfaces in specimen prepared with 12.5 g boric acid after ageing for 24 h, illustrating (a) large crystal size and (b) rosette-type crystal growth.

during fracture, since the incidence of microcracking was observed to increase concurrently with the strength of the materials. The occurrence of microcracks during the fracture of cementitious materials has been discussed by many authors, and is thought to act as a toughening mechanism through the existence of a fracture process zone ahead of the main crack tip [31,32]. Perhaps the most unusual aspect of the present observations is that no special precautions were required in order to observe microcrack-free surfaces in the SEM, i.e., magnesia–phosphate-based cements do not appear to suffer from the desiccation effects that have hindered previous work on the fracture mechanics of Portland cement and concrete. Therefore, MPCs may provide a useful model system for future fundamental studies of crack propagation in cementitious materials.

For materials prepared with boric acid as retarder, there was a pronounced increase in the size of individual crystals as the level of boric acid increased. Some very large, well-formed crystals were observed, as shown in Fig. 8(a). There was also clear evidence of heterogeneous nucleation, resulting in rosette-type crystal growth (Fig. 8(b)). These observations indicate that the presence of boric acid resulted in a lower supersaturation in solution, leading to lower crystal nucleation and growth rates. The pronounced microcracking that was observed at later ageing times tended to obscure the morphology of individual crystals. However, for materials incorporating higher levels of boric acid, in which the crystal size was relatively large, the microcracking was preferentially intercrystalline and so the form of the individual crystals was still evident.

The microstructural development at the cement–aggregate interface is represented by the micrographs given in Fig. 9. There were two major changes with time, firstly a growth in the bonding area and secondly an increase in the degree of microcracking, indicating that higher levels of stress and strain occurred during fracture. This also led to a gradual change in the fracture mode of the coarse silica aggregate with ageing time, from purely intergranular to mixed inter- and transgranular, as shown in Fig. 10,

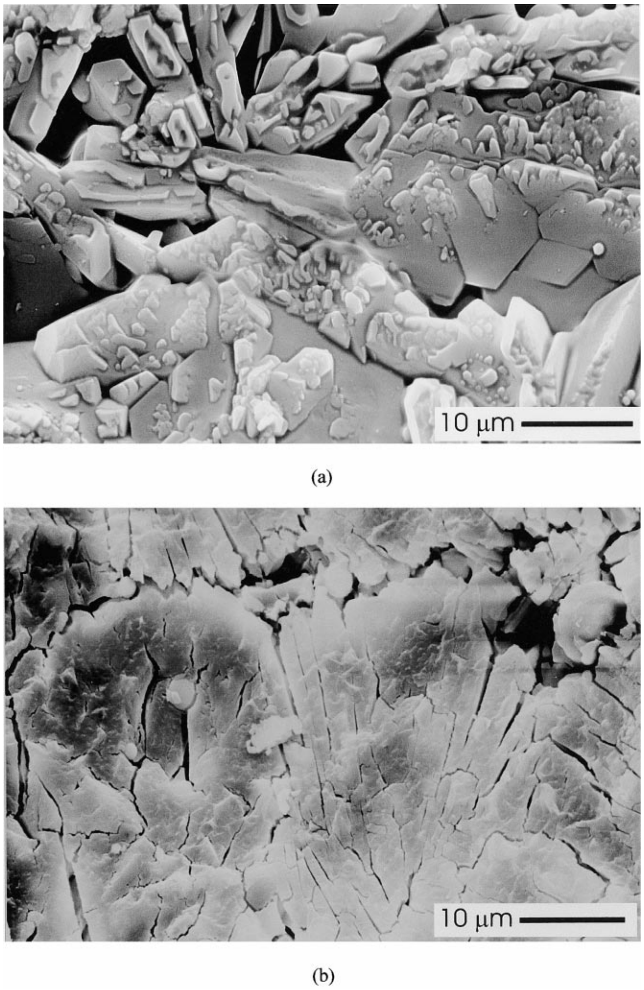


Fig. 9. Micrographs of cement "pull-out" surfaces (from the cement–aggregate interface) in specimens prepared with 12.5 g boric acid after ageing for (a) 3 h and (b) 28 days.

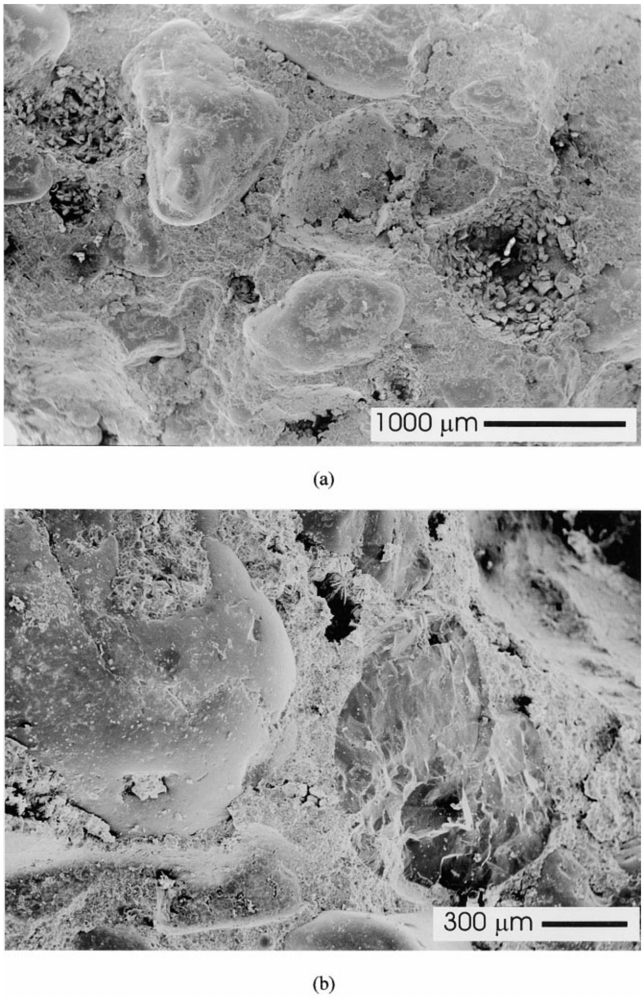


Fig. 10. Low-magnification micrographs illustrating the fracture mode of the coarse silica aggregate: (a) 12.5 g boric acid, 24 h ($\sigma_f = 6$ MPa) and (b) 7.5 g boric acid, 28 days ($\sigma_f = 9$ MPa).

indicating improvements in the strength of the cementitious matrix and of the cement–aggregate bond. It is revealing to make a comparison between the cement "pull-out" surfaces already described (Fig. 9) and those in specimens prepared with a low level of retarder addition (Fig. 11). The latter exhibited a higher porosity and were found to be virtually free of microcracks, even after ageing for 28 days. The fracture surfaces in the binding phase itself were similar in this respect.

For the specimen prepared with the highest level of boric acid, fractured after just 3 h, it was found that the fracture surface was covered by crystals having a very different morphology to that of the underlying bulk material (Fig. 12). The only regions completely free of these crystals were those close to the cast surfaces of the specimen. The most likely explanation for the occurrence of these crystals is that at an age of 3 h there would have still have been a considerable amount of the aqueous solution present in these strongly retarded specimens. Exposing this solution to air (by fracture) would have led to the evaporation of some water, increasing the concentrations of dissolved magnesium, ammonium, and phosphate ions in the remainder and resulting in an increase in the rate of nucleation and crystal growth. The morphology of crystals developing under such conditions would be unlikely to bear much resemblance to the underlying material, which had formed at a lower supersaturation. Near the surfaces of the specimen, most of the free water may have already evaporated more gradually, due in part to the exothermic nature of the setting reaction, and so no such secondary crystal formation would have taken place in those regions.

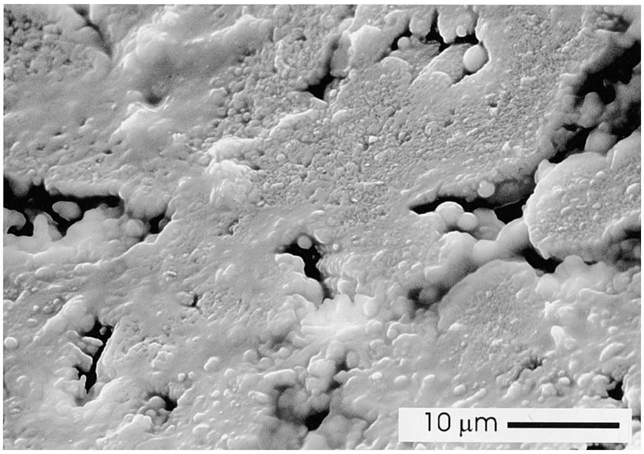


Fig. 11. Micrograph of cement "pull-out" surface (from the cement–aggregate interface) in specimen prepared with 15 g STP, after ageing for 28 days.

In a related study [25], the present authors have shown that the setting reactions in MPCs proceed via the dissolution of basic magnesia particles in the acidic aqueous ammonium phosphate solution, increasing the supersaturation with respect to various magnesium ammonium phosphate hydrates and leading to crystal nucleation and growth. Similar observations were made by Soudee and

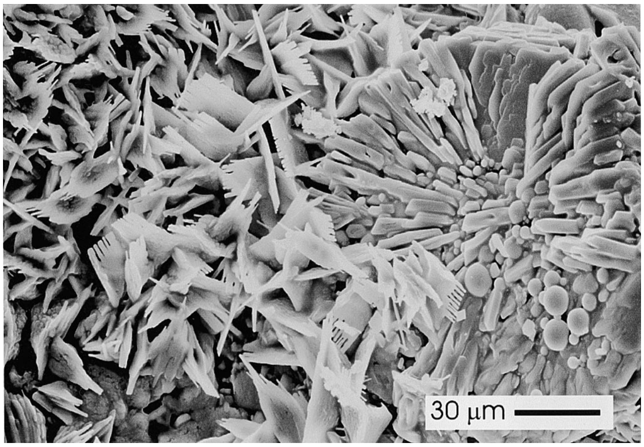


Fig. 12. Micrograph of fracture surface in specimen prepared with 12.5 g boric acid after ageing for 3 h, illustrating the occurrence of secondary crystal growth after fracture.

Pera [33] in a recent publication. In our work, STP and the oxy-boron-type retarders were found to function in different ways; the oxy-boron compounds appeared to retard the dissolution of magnesia, while STP functioned by physical adsorption on crystal nuclei, thereby inhibiting crystal nucleation and growth, and/or by chelation of magnesium ions in a soluble complex, as was suggested by Abdelrazig et al. [16].

The occurrence of large crystals and rosette-type crystal growth patterns in the systems prepared with boric acid (Figs. 8 and 9) are indicative of growth from a solution having a low degree of supersaturation, due to the relatively low magnesium ion concentration. The aqueous solution is likely to have been saturated with respect to ammonium and phosphate ions throughout the setting and initial hardening period, due to the high solubility of ADP. The more uniform and finer crystal sizes observed in the systems containing STP suggest a much higher magnesium concentration, resulting in a homogeneous nucleation process. It is interesting to note that the much larger crystal sizes present in the materials prepared with high boric acid or borax additions did not reduce the ultimate strength values significantly.

Sugama and Kuckaka [13] demonstrated that the addition of borax to a magnesia–ammonium polyphosphate cement (at a level of 20% by weight of polyphosphate) led to a loss in early strength and an extension of the setting time to around 20 min. This effect was attributed to the Mg^{2+} cation-accepting property of the $B_4O_7^{2-}$ ions, which was thought to cause the precipitation of protective amorphous coatings around the magnesia grains in a manner analogous to retardation by "coating" inhibitors in ordinary Portland cement (OPC) systems [34]. Such a mechanism would explain the large crystal sizes observed in the present work, which can be attributed to a low supersaturation in solution. However, although such coatings may occur in the alkaline environment of OPC systems, or within the relatively high pH of a polyphosphate solution, it is unlikely that a significant number of $B_4O_7^{2-}$ ions would remain in the acidic (pH ~ 5), predominantly orthophosphate solution of the present system. Under these conditions, it is likely that the tetraborate ions would dissociate to yield $B(OH)_3$ and $B(OH)_4^-$ [26]. Furthermore, investigations conducted by the present authors indicated that such magnesium–borate precipitates were only stable at pH values greater than 9 [25].

Therefore, it appears to be unlikely that a protective magnesium–borate coating would be formed in the initially acidic conditions of the present MPC system. As an alternative retardation mechanism, it may be suggested that the boric acid species ($B(OH)_3$ and $B(OH)_4^-$) are adsorbed on the magnesia grain surfaces, thereby reducing the dissolution rate in a similar manner to the precipitates proposed by Sugama and Kuckaka [13]. There are many reports of boric acid adsorption on metal oxide surfaces, and in fact this can serve as an effective means of removing borate ions from solution [35]. The adsorption process can be represented by Eqs. (6) and (7) [36]:

$$\mathrm{M-OH+B(OH)_4^- \rightarrow M-O-B(OH)_3^- + H_2O} \tag{6}$$

$$\mathrm{H_2O + B(OH)_3 \rightarrow B(OH)_4^- + H^+}. \tag{7}$$

Here, M–OH represents a protonated site on the surface of the metal oxide and $M{-}O{-}B(OH)_3^-$ represents a "borated" site. It is implied that a covalent bond is formed between the metal ion and the borate ion, and therefore the adsorption process is considered to be one of chemisorption rather than physical adsorption [36].

4. Conclusions

Successive additions of boric acid or borax to MPC mortar gave rise to a cumulative increase in setting time and to a retardation of the exothermic setting reactions. The retardation by STP was more complex, being limited by the solubility of STP in the saturated ADP solution, which was determined as 340 g dm^{-3}. The use of each of these retarders resulted in an extension of the initial hardening period and led to significant increases in the ultimate values of Young's modulus and flexural strength. Microstructural examination revealed that the addition of STP led to a fine (< 0.5 μm) crystal size within the binding phase, indicating a homogeneous nucleation process, while increasing amounts of boric acid gave rise to larger (>10 μm) well-formed crystals, indicating that a heterogeneous nucleation process had occurred due to a relatively low concentration of magnesium in solution. The observation of an increasing density of microcracks on the fracture surfaces as a function of ageing time was attributed to the occurrence of a fracture process zone during fracture, which was presumed to act as a toughening mechanism.

References

[1] C.E. Every, Improvements relating to mouldable compositions, UK Patent 593,172 (1947).
[2] R.W. Limes, D. Ponzani, Basic refractory compositions for intermediate temperature zones, US Patent 3,285,758 (1966).
[3] T. Komac, E.J. Spirko, Process for repairing refractory walls, US Patent 3,413,385 (1968).
[4] R.W. Limes, R.O. Russell, Process for preparing fast setting aggregate compositions and products of low porosity produced therewith, US Patent 3,879,209 (1975).
[5] H.J. Horvitzm, A.P. Gray, Matrix forming composition, UK Patent 1,454,333 (1976).
[6] F.R. Stierli, J.M. Gaidis, C.T. Clayton, Control of setting time in magnesia–phosphate cement, UK Patent 1,512,275 (1978).
[7] F.C. Allan, K. Asgar, Reaction of cobalt–chromium casting alloy with investment, J. Dent. Res. 45 (1966) 1516–1528.
[8] K. Kato, M. Shiba, M. Nakamura, T. Ariyoshi. Study on phosphate bonded investment. On setting mechanism, composition and particle size of raw material and physical properties, Rep. Inst. Med. Dent. Eng. 10 (1976) 45–61.

[9] S. Takeda, H. Kawahara, M. Nakamura, K. Sogawa, S. Maehara, H. Mori, M. Yokohama, H. Takahashi, A. Yata. A study of the thermal changes of the binder in phosphate-bonded investment, Shika Igaku 42 (1979) 429–436.

[10] R. Neiman, A.C. Sarma, Setting and thermal reactions of phosphate investments, J. Dent. Res. 59 (1980) 1478–1485.

[11] T. Miyaji, K. Utsumi, E. Suzuki, Y. Shimizu. Deterioration of phosphate-bonded investment on exposure to 100% relative humidity atmosphere, Bull. Tokyo Med. Dent. Univ. 29 (1982) 53–62.

[12] T. Sugama, L.E. Kuckaka, Magnesium monophosphate cements derived from diammonium phosphate solutions, Cem. Concr. Res. 13 (1983) 407–416.

[13] T. Sugama, L.E. Kuckaka, Characteristics of magnesium polyphosphate cements derived from ammonium polyphosphate solutions, Cem. Concr. Res. 13 (1983) 499–506.

[14] B. El-Jazairi, Rapid repair of concrete pavings, Concrete 16 (1982) 12–15.

[15] B. El-Jazairi, The properties of hardened MPC mortar and concrete relevant to the requirements of rapid repair of concrete pavements, Concrete 21 (1987) 25–31.

[16] B.E.I. Abdelrazig, J.H. Sharp, P.A. Siddy, B. El-Jazairi, Chemical reactions in magnesia–phosphate cement, Br. Ceram. Proc. 35 (1984) 141–154.

[17] B.E.I. Abdelrazig, J.H. Sharp, B. El-Jazairi, The chemical composition of mortars made from magnesia–phosphate cement, Cem. Concr. Res. 18 (1988) 415–425.

[18] B.E.I. Abdelrazig, J.H. Sharp, B. El-Jazairi, Microstructure and mechanical properties of mortars made from magnesia–phosphate cement, Cem. Concr. Res. 19 (1989) 247–258.

[19] D.A. Hall, R. Stevens, B. El-Jazairi, The effect of water content on the structure and properties of magnesia–phosphate cement (MPC) mortar, J. Am. Ceram. Soc. 81 (1998) 1550–1556.

[20] S. Popovics, N. Rajendran, M. Penko, Rapid hardening cements for repair of concrete, ACI Mater. J. 84 (1987) 64–73.

[21] S. Popovics, N. Rajendran, Early age properties of magnesium phosphate-based cements under various temperature conditions, Transp. Res. Rec. 1110 (1987) 34–45.

[22] Q. Yang, X. Wu, Factors influencing properties of phosphate cement-based binder for rapid repair of concrete, Cem. Concr. Res. 29 (1999) 389–396.

[23] British Standard BS4550, Methods of testing cement, 1978.

[24] S.A. Rodger, D.D. Double, The chemistry of hydration of high alumina cement in the presence of accelerating and retarding admixtures, Cem. Concr. Res. 14 (1984) 73–82.

[25] D.A. Hall, Properties and Structure of Magnesia–Phosphate Cement, PhD thesis, University of Leeds, 1987.

[26] P.H. Kemp, The Chemistry of Borates: Part I, Borax Consolidated, London, 1956.

[27] H.D. Winbow, The Chemistry and Properties of Magnesia–Phosphate Cement Systems, PhD thesis, University of Sheffield, 1988.

[28] CRC Handbook of Chemistry and Physics, in: R.C. Weast (Ed.), CRC Press, Boca Raton, FL, 1985.

[29] R.F. Jameson, Chemistry of polyphosphoric acid, in: A.V. Slack (Ed.), Phosphoric Acid vol. 1, Marcel Dekker, New York, NY, 1968 (Part 2).

[30] H.W. McCune, G.J. Arquette, Precipitation of pyrophosphate and triphosphate with tris(ethylenediamine) cobalt(III) chloride and hexamine cobalt(III) chloride, Anal. Chem. 27 (1955) 401–405.

[31] L.J. Struble, P.E. Stutzman, E.R. Fuller, Microstructural aspects of the fracture of hardened cement paste, J. Am. Ceram. Soc. 72 (1989) 2295–2299.

[32] S. Igarashi, M. Kawamura, Detection of failures around main cracks and their relation to the fracture toughness of cement pastes, J. Am. Ceram. Soc. 78 (1995) 1715–1718.

[33] E. Soudee, J. Pera, Mechanism of setting reaction in magnesia–phosphate cements, Cem. Concr. Res. 30 (2000) 315–321.

[34] N.L. Thomas, D.A. Jameson, D.D. Double, The effect of lead nitrate on the early hydration of Portland cement, Cem. Concr. Res. 11 (1981) 143–153.

[35] N.P. Nies, Alkali metal borates: physical and chemical properties, Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry vol. 5, Longman, London, 1980, p. 432 (Suppl. 1, Part A).

[36] M. Blesa, A.J.G. Maroto, A.E. Regazzoni, Boric acid adsorption on magnetite and zirconium dioxide, J. Coll. Int. Sci. 99 (1984) 32–40.