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Adu-Amankwah, S orcid.org/0000-0002-0568-2093, Ajambo, T, Chen, T et al. (1 more author) (Accepted: 2022) A comparative study on retarders for magnesium phosphate cements. In: 41st Cement & Concrete Science Conference, 12-13 Sep 2022, Leeds, UK. (Unpublished)

This is an author produced version of a conference paper originally presented at 41st Cement & Concrete Science Conference, 12–13 September 2022, Leeds, UK.

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A comparative study on retarders for magnesium phosphate cements

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Keywords: Boric acid, citric acid, hydration, microstructure, MKPC, set retarder.

ABSTRACT

Magnesium potassium phosphate cements (MKPC) are chemically bonded ceramics with potential biomedical, construction and nuclear waste management applications. These are formed from acid-base reaction between magnesium oxide and hydrogen phosphate source, leading to struvite (-K) as the main reaction product. The dissolution and precipitation reactions occur rapidly, generating significant heat and causing fast setting. Routinely, boric acid, a reproductive toxin is added to control the reaction of MKPC. This study investigated the activity of citric acid as alternative retarder. MKPCs with MgO/PO₄ molar ratio of 4 and 0.5 w/s ratio with or without 2.5% boric or citric acid by weight of solids were investigated by isothermal calorimetry, XRD, and SEM. The results demonstrate effectiveness of citric acid in modifying reaction kinetics and MKPC microstructure. This is significant for safe production of MKPC.

INTRODUCTION

MPC and MKPC are based on the dissolution and precipitation reactions involving charge transfer between a base and an acid at room temperature. Promising applications including dental and bone cements, repair material and nuclear waste encapsulation have been demonstrated [1-3].

In the presence of water, MgO and the phosphate source, often ammonium or dihydrogen phosphate undergo hydrolysis, releasing Mg²⁺, OH⁻, HPO₄²⁻ and H⁺ species. These precipitate into struvite or its potassium variant. The reactions are fast and exothermic, typically achieving final set within 30 minutes. The magnesium to phosphate ratio (herein M/P) controls setting time and mechanical properties of MKPC. Hou *et al.* [4] noticed faster setting but reduced strength when the M/P ratio exceeded 6 due to formation of potassium-free precipitates [5]. MKPCs are thus prepared at 4 ≤ M/P ≤ 8 for optimized performance [2, 5].

For most applications, the reaction rate of MgO and phosphate and hence setting time must be controlled through set retarders. Boron-based retarders including borax and boric acid are the most common [2-4]. These are believed to form protective complexes around magnesium oxide slowing down further dissolution. However, concerns exist about reproductive toxicity of borax, which is banned in the UK and EU since 2010. Alternative retarders for MKPC is pertinent if their application is to become widespread. Suitability of organic compounds such as glacial acetic acid was suggested in [6], who postulated an unstable complex formation between Mg²⁺ and -COOH. Suitability of citric acid is evaluated here.

MATERIALS AND METHODS

Three MKPC paste samples were investigated at 0.5 w/s ratio. The control was MKPC without a retarder, designated ref. The rest had 2.5% by weight of the MgO and KH_2PO_4 mix as retarder, viz. boric acid and citric acid herein B and C respectively. The precursors were light-burnt magnesium oxide powder (96% purity) and dihydrogen potassium phosphate. Reagent grade boric and citric acids were used as retarders.

In preparing the paste samples, the MgO powder and KH_2PO_4 granules were blended in the mixing container before adding the mixing water. Where used, the retarder was pre-dissolved in the mixing water and hand-mixed.

Heat of reaction was measured continuously on a TAM calorimeter using 9g paste. XRD scans were performed on fresh pastes. The scans commenced 5 minutes after mixing and thereafter scanned at 30 minutes interval for 24 hours. The sample holder was covered with a Kapton film to prevent evaporation. Data were acquired on a Phillips Emyrean diffractometer using a $\text{CuK}\alpha$ anode operated at 45 kV and 40 mA and equipped with a PIXcel3D detector without a monochromator. A high-resolution monochromatic FEI Helios G4 Dual beam SEM was used to identify the microstructures in the fractured specimens after reacting for 30 minutes and 24 hours. The crushed samples were spread on a sticky carbon tape and coated with 10nm carbon. The SEM was operated in low vacuum at 2Kv AV.

RESULTS AND DISCUSSION

The calorimetry data (Fig 1) reveals instantaneous exothermic reaction in the reference MKPC such that the main reaction peak occurred during wetting of the constituents. Similar kinetics is reported elsewhere for these systems [6]. Boric and citric acid as retarders modified kinetics of the reaction differently. An extended induction period (~10 mins.) was observed in the boric acid mix. Despite noticeable but shorter induction in the citric acid mix, occurrence of the main reaction peak coincided with the reference (at ~15 mins). However, cumulative heat of the citric acid mix was asymptotic after this whilst the boric acid mix peaked at ~ 50 mins with increasing cumulative heat. This indicates different controlling mechanisms.

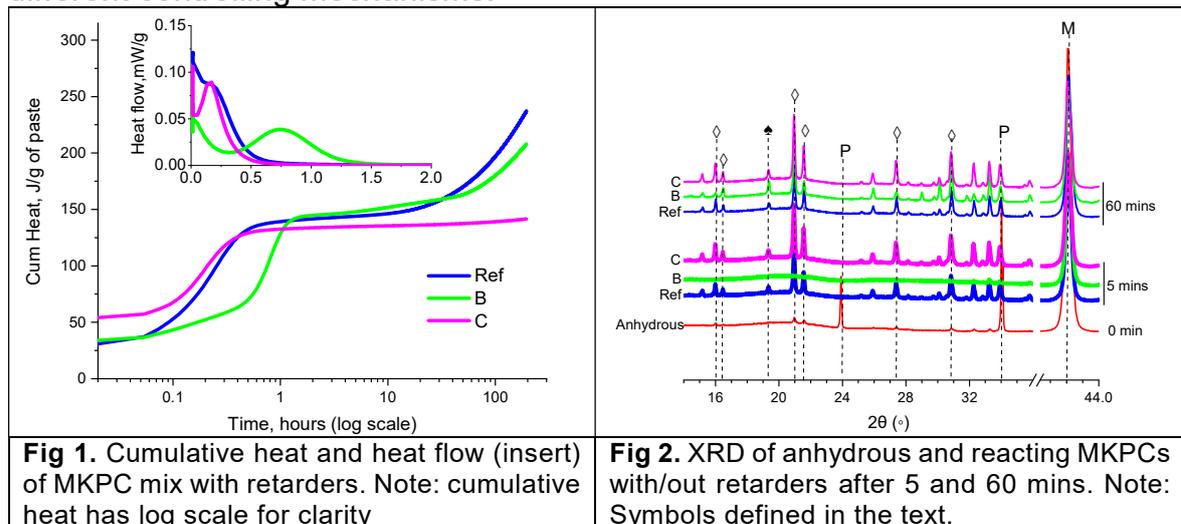


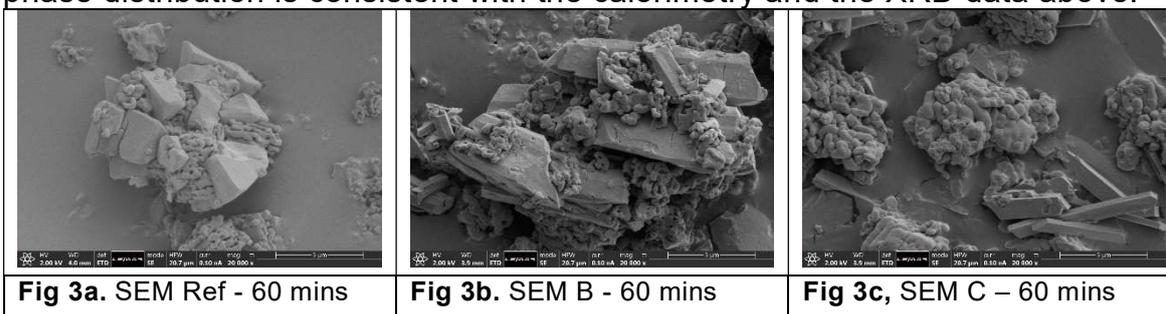
Fig 1. Cumulative heat and heat flow (insert) of MKPC mix with retarders. Note: cumulative heat has log scale for clarity

Fig 2. XRD of anhydrous and reacting MKPCs with/out retarders after 5 and 60 mins. Note: Symbols defined in the text.

The XRD scans provide insight into the mechanisms. With or without set retarder, potassium dihydrogen phosphate (P) dissolved completely within 5 mins of

mixing. Struvite was the main phase assemblage in all mixes, agreeing with the literature [3, 5]. However, crystalline assemblages identified as brucite (\spadesuit) and struvite-K (\diamond) were only seen in the reference and the citric acid mixes. This is consistent with a greater MgO (M) peak intensity, indicating retarded dissolution by boric acid.

The morphology and distribution of phase assemblages play a critical role in the early age microstructure and performance. The secondary electron images in Figures 3 (a – c) highlight the distinctive effect of the retarders. In the reference mix, short prismatic crystals of struvite-K forms (3a). These were much broader and longer in the presence of boric (3b). Citric acid causes longer but thinner sized struvite-K which incidentally precipitates away from the reacting MgO. The phase distribution is consistent with the calorimetry and the XRD data above.



CONCLUSIONS

1. Struvite-K is the main reaction product in all investigated MKPC systems. However, traces of brucite was identified, plausibly as intermediate product
2. Boric and citric acids modify kinetics and microstructure differently. Boric acid suppresses crystalline precipitates whilst citric acid alters their size and distribution. These may have potential implications on performance.

Acknowledgment: The authors would like to express appreciation to the TFI Network+ and UKRI for funding this research project.

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