



# Effect of phosphoric acid on the properties of magnesium oxychloride cement as a biomaterial



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## ABSTRACT

Magnesium oxychloride cement (MOC) has been used in civil engineering for more than 100 years, but its application has been limited by its poor water resistance. This property, however, could be exploited in the formulation of a resorbable orthopaedic biomaterial. In this study,  $H_3PO_4$  was added to control the degradation process of MOC to provide a predictable and clinically appropriate resorption time. The effects of  $H_3PO_4$  on the phases, microstructures, mechanical properties, hydration and degradation of MOC have been evaluated. The results revealed that the crystalline phases in MOC before and after adding  $H_3PO_4$  were the same, but that the needle-like phase 5 ( $5 Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$ ) crystals were formed more extensively in MOC with  $H_3PO_4$  than that in MOC without  $H_3PO_4$ . Furthermore, the addition of  $H_3PO_4$  was shown to retard the hydration process.  $H_3PO_4$  did significantly improve the water resistance of MOC though its addition resulting in a reduction in compressive strength.

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## 1. Introduction

Magnesium oxychloride cement (MOC) was discovered by a French scientist, Sorel, in 1867 [1]. MOC has attracted much attention since in many ways it exhibits properties superior to standard Portland cement. It sets quickly to enable rapid repair and exhibits a high early strength. Furthermore, it exhibits rheological properties that enable the material to flow into irregular cavities. It also exhibits comparatively high flexural strength ( $\geq 4$  MPa) and compressive strength ( $\geq 69$  MPa), and elastic modulus (70–85 GPa) [2]. Despite these advantageous properties the application of MOC is not widespread because it reduces in strength rapidly on prolonged exposure to water [3]. The durability of MOC could be improved by modifying composition and introducing various additives [2,4,5]. One of the additives that can greatly improve the water resistance of MOC is phosphoric acid ( $H_3PO_4$ ) [6]. Although poor water resistance has limited the utility of MOC in civil engineering, after modification, steady degradation when immersed in aqueous media, along with excellent early-mechanical properties and non-toxicity to bone marrow stromal cells [7], make it an excellent candidate as a resorbable bone replacement.

During the last several decades, much work has been done to study the microstructure, reaction products and strength development in the system  $MgO-MgCl_2-H_2O$  [3,8–12]. It is generally considered that the main phases in MOC are  $3 Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$  (phase 3) and  $5 Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$  (phase 5) at room temperature. It is also

accepted that maximal formation of phase 5 crystals is desirable as it is widely reported that this phase provides the bulk of the mechanical integrity [13]. The water sensitivity of the cement is as a result of the instability of both phase 5 and phase 3 in water. Each phase can transform to  $Mg(OH)_2$  by the action of water. As a result of this, the hardened paste becomes a highly porous structure consisting of only  $Mg(OH)_2$  [14]. Deng [6] has studied and discussed the mechanism of  $H_3PO_4$  for improving the water resistance of MOC. Systematic information about the effect of  $H_3PO_4$  on the properties of MOC, however, cannot be found in the literature. In this study, we have systematically studied how  $H_3PO_4$  concentrations influence the physicochemical properties of the hardened cement, including crystal phases, microstructures, mechanical properties, hydration and the degradation.

## 2. Materials and methods

The magnesia (MgO) powder was produced by calcination of magnesium carbonate hydroxide hydrate (Sigma-Aldrich, UK) in a furnace at 800 °C for 20 hours. The cement samples were made by mixing the MgO with magnesium chloride solution (4 M) at a liquid to powder ratio (L/P) 1.0 ml/g. The  $MgCl_2$  solution was made by mixing magnesium chloride anhydrous (Sigma, UK) with distilled water. In order to improve the water resistance of the hardened MOC,  $H_3PO_4$  (Fisher, UK) of different concentrations (Table 1) was added to magnesium chloride solution. The mixtures were stirred to form homogeneous pastes which were then packed into the cylindrical molds to form samples of diameter about 6 mm and height 12 mm. After hardening for 24 hours, the samples were removed from the molds.

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**Table 1**

Setting time of MOC without and with different concentration of  $H_3PO_4$  (0.5 M, 1.0 M, 1.5 M, 2.0 M).

Content of $H_3PO_4$ (M)	L/P (ml/g)	Initial setting time (min)	Final setting time (min)
0	1.0	86	175
0.5	1.5	270	400
1.0	1.5	240	365
1.5	1.7	220	308
2.0	1.7	180	285

The setting time was estimated using the Gillmore needles according standard ASTM C266-89. To find the initial setting time a needle of 2.13 mm in diameter and 113.4 g in weight was applied to the surface. The final setting time was determined using a needle of diameter 1.05 mm and mass 454 g. The point at which the needles no longer made an impression on the surface was deemed to be the setting time.

For the hydration study, the samples were demolded 30 min, 1 h, 2 h, 6 h, 18 h, 24 h after mixing and, then crushed and immersed in acetone for 1 h to stop hydration [15]. Then the samples were dried at 60 °C overnight. X-ray diffraction (XRD; D8, Bruker, UK) analyses were conducted to determine the crystal phases of the cement set for different times. The powders were scanned with  $Cu K\alpha$  X-ray (40 kV, 40 mA) from 5 to 60° 2 $\theta$  degrees with a step size of 0.02° for 20 min.

For mechanical testing, 10 samples of each group were measured after one-day setting at a stroke rate of 0.5 mm/min using a universal testing machine (Zwick/Roell Z030, Germany). The porosity was calculated in Eq. (1). The apparent density was calculated by weight divided by volume as determined from geometric measurement; the strut density (skeleton density or true density) was determined using a

micromeritics helium pycnometer using 3 purges and 3 measurements (AccuPyc II 1340, Micromeritics, UK).

$$\text{Porosity}\% = \left(1 - \frac{\text{Apparent density}}{\text{Strut density}}\right) \times 100\% \quad (1)$$

For the degradation studies, three samples for each group were soaked into 20 ml phosphate buffered saline (PBS) solution separately and stored in a 37 °C shaker. The samples were weighed on a daily basis and the PBS refreshed.

The composition of the aged cement samples was characterized by XRD and Fourier Transform Infrared Spectroscopy (FTIR, NICOLET 380, USA). The FTIR was performed in the wavenumber range of 400–4000  $cm^{-1}$ , and the samples were formed in KBr pellets. The microstructures were observed by Environmental Scanning Electron Microscopy (ESEM, Phillips XL30, Germany).

Means and standard deviations (STD) of all the experimental groups data reported were calculated. The results were statistically analyzed by one-way analysis of variance (ANOVA) at a significance level of 0.05.

### 3. Results

#### 3.1. Phase composition

The XRD patterns (Fig. 1) showed that each of the cements contained the magnesium chloride hydroxide hydrate phase ( $5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$ , PDF-07-0420) and a small amount of residual MgO (PDF-45-0946). The XRD pattern does not show any evidence of a crystalline phosphate phase. The FTIR spectra, however, demonstrate that treatment with  $H_3PO_4$  had an influence on the composition of the material (Fig. 2). The peaks from 1000 to 1100  $cm^{-1}$  are indicative of P–O bonds, and as the concentration of  $H_3PO_4$  was increased, so was the intensity of these peaks. The material formed with no  $H_3PO_4$  exhibited no peak in the 1000–1100  $cm^{-1}$  region, this proves the incorporation of phosphate based phase into the cement matrix. The bands at 3670  $cm^{-1}$  also correspond to stretching vibrations of OH in P–OH groups [16]. All spectra exhibit a very strong band from 3000 to 3600  $cm^{-1}$ , which is due to OH group vibrations. The bands in the region 1600–1650  $cm^{-1}$  are due to the H–O–H bending motion. These bands suggest the presence of more water of crystallization when the cements were made at higher L/P ratios.

#### 3.2. Microstructures

The microstructure of the fracture surface is shown in Fig. 3. There were some large pores (about 20–50  $\mu m$ ) on the surface of the MOC made without  $H_3PO_4$  (Fig. 3(a)) and the microstructure within these pores (Fig. 3(b<sub>1</sub>)) was different to that outside (Fig. 3(b<sub>2</sub>)). In the holes, there were needle-shaped crystals, which were not seen on the

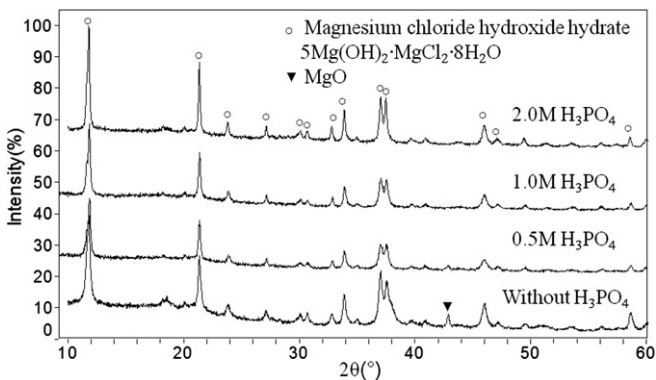


Fig. 1. XRD patterns of MOC without and with different concentration of  $H_3PO_4$  (0.5 M, 1.0 M, 2.0 M), magnesium chloride hydroxide hydrate crystals were formed in all the samples.

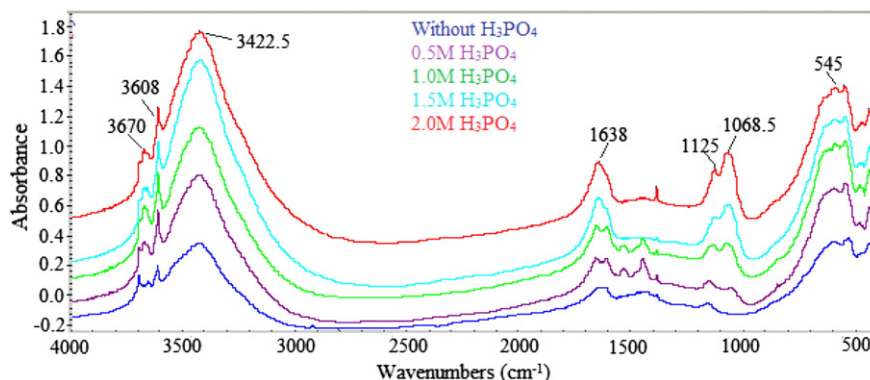


Fig. 2. FTIR patterns of MOC without and with different concentration of  $H_3PO_4$  (0.5 M, 1.0 M, 1.5 M, 2.0 M).

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