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Preparation of magnesium phosphate cement by recycling the product of thermal transformation of asbestos containing wastes☆

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ABSTRACT

Asbestos containing wastes have been employed for the first time in the formulation of magnesium phosphate cements. Two samples were mixed with magnesium carbonate and calcined at 1100 and 1300 °C. Under these conditions, complete destruction of asbestos minerals is known to occur. The product, containing MgO, after reaction with water-soluble potassium di-hydrogen phosphate, led to the formation of hydrated phases at room temperature. Crystalline and amorphous reaction products were detected, with the latter being likely the metastable precursor of the former. Measured strengths were found to be in line with data from the literature, suggesting that this material may be used as cement. The process here described represents a viable recycling opportunity for this class of hazardous wastes. Simultaneous destruction of asbestos minerals and formation of reactive MgO during thermal treatment, bring benefits in terms of energy requirements and preservation of natural resources in cement manufacturing.

1. Introduction

Magnesium phosphate cements (MPCs) are classified as chemically-bonded phosphate ceramics [1,2]. Like most periclase (MgO)-based binding materials, they are capable of giving high strengths at early ages as well as over the long-term; good water resistance, high adhesive properties and affinity for cellulose materials [3,4]. These properties make them attractive for applications like fast repairing of damaged structures, waste encapsulation, bone repair, natural fibre composites, sealing of bore holes [5–14].

When periclase reacts with either di-ammonium hydrogen phosphates or ammonium di-hydrogen phosphate, insoluble magnesium ammonium phosphates are formed.

The final product is struvite ($MgNH_4PO_4 \cdot 6H_2O$) with schertelite [$(NH_4)_2MgH_2(PO_4) \cdot 4H_2O$)] and dittmarite ($MgNH_4PO_4 \cdot H_2O$) sometimes occurring as intermediate reaction phases. They invariably convert to struvite when enough water is available. Release of ammonia with time has however limited their use to outdoor applications.

When potassium di-hydrogen phosphate (KH_2PO_4) (KDP) is employed, crystallization of the isomorphous potassium equivalent of struvite (MKP) occurs, according to the reaction:

$$MgO + KH_2PO_4 + 5H_2O \rightarrow MgKPO_4 \cdot 6H_2O \quad (1)$$

This acid–base reaction is rapid and exothermic, and its mechanism has been explained through the dissolution, up to saturation, of KDP after addition of water to the mix [15]. As periclase is wetted, it starts to dissociate; $Mg(H_2O)_6^{2+}$ complexes form and replace water molecules at the magnesia surface. Together with PO_4^{3-} ions in solution, they supply the structural units required for crystallization of MKP. From this, it follows that the reaction is controlled by the reactivity of periclase powder, the amount of $Mg(H_2O)_6^{2+}$ complexes formed at the grain surface (preventing water molecules from further wetting magnesia), and the relative amount of each reactant.

Factors affecting reaction kinetics and mechanical properties of the mortar have been investigated by several authors. Calcination temperature of magnesite ($MgCO_3$), the primary source of magnesium oxide, has proven to be critical in determining the reactivity of the periclase formed [2,16–18]. At temperatures above 1300 °C, less reactive well crystallized periclase crystals of higher mean grain size and without amorphous coatings, are formed [2]. Such dead-burnt magnesia is generally employed in commercial MPCs in order to slow down reaction rate.

An excess of magnesium with respect to potassium was observed to yield shorter setting times and higher compressive strength [19]. Under

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these conditions amounts of KDP and water are the limiting factors for the reaction [20].

As a general rule, KDP should be enough to cover periclase grains with phosphate complexes, thus, in theory, the optimal KDP/MgO molar ratio should be less than unity [21]. However, a KDP/MgO molar ratio equal to unity was considered adequate to reach good performance and low porosity in hardened samples [6]. High compressive strengths have been observed up to very low values of KDP/MgO molar ratio (0.25), in conjunction with a consistent fraction of unreacted periclase grains [18]. This means that periclase grains also act as inert fillers, opening the way for the introduction of fillers and/or aggregates, with a positive impact on costs. Fly ash (high silica), silica sand, fluvial sand, slags, limestone, granitic sand and alumina sand have been tested. Increasing the aggregate/cement weight ratio up to one led to a net reduction of paste porosity, improving performance [4,5,8,13,17,19]. Fast setting of MPC mortars has been controlled with set retarders such as borax [5,6,8,9,14,21,22].

Due to their peculiar mechanism of setting, decreasing the water/solid (*w/s*) ratio reduces porosity of the mortar improving performance [3,20,21], on the other hand, the increase of *w/s* allows better workability. In order to ensure wetting of the surface of periclase grains, the optimal *w/s* ratio will be dependent on particle size distribution of periclase and amount of filler/aggregate fraction. In any case, grain size of periclase, is known to strongly affect setting time [21].

From the above considerations, it follows that direct comparison between experiments conducted under different conditions is not straightforward, because of difficulties in achieving a complete control over these factors, and absence of standardization in experimental procedures.

Although calcination of magnesite can be accomplished at temperatures well below those needed for ordinary Portland cement clinker, claims of ecological labels for MPCs, such as low-energy, low-CO_2, or green cements [8], have been questioned [23].

A completely different scenario can be disclosed if magnesite calcination and thermal inertization of hazardous wastes were integrated within the same industrial process, developing a novel binding material. In this view, asbestos-containing materials (ACMs) could be recycled in the production of MPC. Once overall benefits inherent to such a process are considered, energy balance issues become less stringent.

ACMs, widely used in the past in many European countries, are a class of hazardous wastes of great concern. Thanks to the need for the safe disposal and/or inertization of ACMs, several industrial inertization processes involving thermal treatment have been proposed so far [24–28]. Investigations on the transformation of minerals in ACMs during prolonged annealing in the temperature range 1200–1300 °C led to the development of an innovative process [28–31]. During thermal treatment, ACMs undergo a series of solid state reactions leading to global structural changes of the matrix and to the complete crystal chemical transformation of asbestos minerals as well [32]. The newly-formed phases are mainly calcium–magnesium silicates, calcium silicates and aluminates in variable proportions, depending on the chemical composition of the corresponding pristine raw material [33,34].

Recently, a class of thermally-treated cement-asbestos (CA), containing up to 70 wt.% of phases possessing good hydraulic properties, such as β-C_2S, C_3S, C_4AF, $C_{12}A_7$, ye'elimite ($Ca_4Al_6O_{12}(SO_4)$, $C_4A_3\overline{S}$), and lime, resembling a C_2S-rich clinker, has been used successfully to replace cement in concrete [35] and for the preparation of calcium sulfoaluminate cements [36]. The use of CA as a raw material for cement clinker production, following other industrial processes, has been proposed by other authors as well [37–40].

ACMs can be of interest for obtaining MPC because calcination of magnesite and thermal inertization can be exploited together in the same process. Furthermore, during thermal treatment, the magnesium content of ACMs could yield an extra fraction of periclase that will add to the one obtained from magnesite.

Chrysotile, with ideal formula $Mg_3(OH)_4Si_2O_5$, is the most common form of asbestos and the main source of magnesium in ACMs. In CA slates, its content usually ranges between 5 and 14 wt.%, whereas may be nearly 100 wt.% in some friable ACMs.

During thermal treatment of ACMs, a fraction of magnesium is hosted in the newly formed silicates, but it can also crystallize as periclase, as in some thermally-treated CAs, where it ranges between 5 and 8 wt.% [34].

A synoptic view of the compositions of ACMs and mixes of ACMs and magnesite can be obtained by plotting data as molar fractions in the simplified CaO–SiO_2–MgO (CMS) triangular phase diagram, depicted in Fig. 1 [34]. Here, stability fields at equilibrium of phases were indicated, and compositional ranges of CAs and high-chrysotile ACMs have been reported as grey shadowed areas. Industrial magnesite, having only a small amount of contaminants, falls very close to the MgO vertex. Any mix of ACM with magnesite shifts bulk composition along a line joining these two components. In this work, a CA sample and a friable ACM sample have been mixed with magnesite and thermally treated at two different temperatures (1100 and 1300 °C) in order to obtain materials suitable to be used as components of MPCs. After addition of KDP, hydration tests have been performed and mineralogical composition has been monitored at different times. Basic analysis of reaction kinetics was attempted, and flexural tests were conducted in order to follow the development of mechanical properties of the pastes.

2. Experimental

2.1. Materials and sample preparation

Two different samples of ACM representing the most common forms of asbestos-containing wastes were employed as starting raw materials. The sample named CAT was taken from a CA slate removed from the environment; its full characterization has been reported elsewhere [33]. The sample named CHR is a friable thermal insulation material high in chrysotile.

Other raw materials were commercial magnesite ($MgCO_3$) (Bal–Co Spa, Sassuolo, Italy) with 95.7% purity, and reagent grade KDP. Analytical data for the raw materials (except KDP) are reported in Table 1.

The weight fraction of magnesite to be added to each sample was computed making use of the CMS phase diagram previously described (Fig. 1), employing for magnesite the chemical composition calculated from the mineralogical analysis. In order to enhance periclase yields

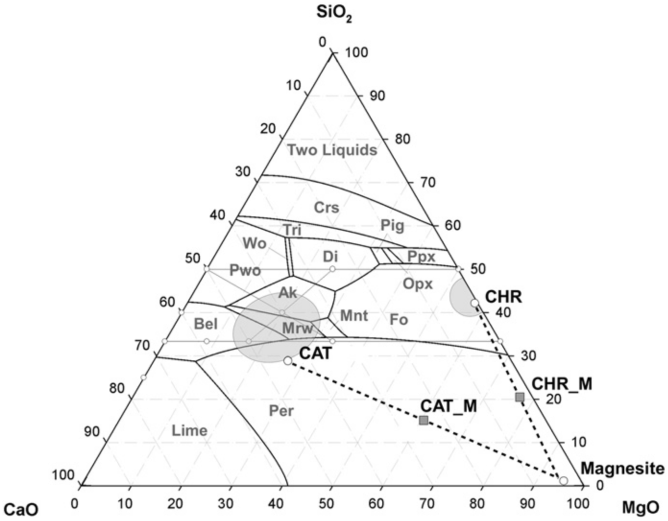

Fig. 1. Points corresponding to bulk chemical compositions for samples CAT, CHR, magnesite, CAT_M and CHR_M, plotted as mol.% of oxides in the CaO–MgO–SiO_2 system. Compositional ranges of CAs and high-chrysotile ACMs, are depicted as grey shadowed areas. Stability fields of phases are depicted. Ak, akermanite; Bel, Belite; Crs, cristobalite; Di, diopside; Fo, forsterite; Mnt, monticellite; Mrw, merwinite; Opx, orthopyroxene; Per, periclase; Pig, pigeonite; Ppx, protopyroxene; Pwo, pseudo-wollastonite; Tri, tridimyte; Wo, wollastonite.