Mg-Phosphate Ceramics Produced from the Product of Thermal Transformation of Cement-Asbestos

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Summary

According to recent European directives, the need for environmentally friendly alternative solutions to landfill disposal of hazardous wastes, such as asbestos-containing materials, prompts their recycling as secondary raw materials. In this work, magnesium phosphate ceramics were prepared using the product of inertization of cement-asbestos. Magnesium phosphate ceramics show interesting properties like good water resistance and high strength that make them attractive materials for several applications. Asbestos containing materials were mixed with magnesium carbonate and annealed at two different temperatures (1100 and 1300 ^{o}C). During thermal treatment complete destruction of asbestos minerals with their transformation into new phases, and crystallization of MgO from magnesium carbonate decomposition, occurs. Upon addition of potassium di-hydrogen phosphate and water, the magnesium oxide in the product of thermal treatment, contributes to the onset of a setting reaction whose product is magnesium potassium phosphate hydrate. The reactivity of periclase was found to be dependent on the calcination temperature. Lower reaction rates were observed for the MgO obtained at lower temperature. The setting reaction of the magnesium phosphate ceramic has been followed in time up to 6 months by means of the X-rays powder diffraction trechnique. Quantitative phase analysis was performed using the Rietveld method and both crystalline and amorphous phases were quantified. The amount of magnesium potassium phosphate was found to increase with time, and was accompained by a decrease in the amount of the amorphous fraction. This fact supports the hypothesis of the formation of an amorphous precursor of the crystalline MKP during the hydration reaction.

SEM images showing elongated magnesium potassium phosphate hydrate crystals emerging from what appears as an amorphous matrix, further confirms this view.

Since the mechanical properties of magnesium phosphate ceramics are known to increase with time, we can conclude that the main contribution to the development of strenght comes from the crystalline magnesium potassium phosphate hydrate. In this work, we describe a procedure for simultaneous destruction of asbestos minerals and formation of cementitious compounds, which represents a recycling opportunity for this class of hazardous wastes, bringing benefits in terms of energy requirements and preservation of natural resources in cement manufacturing.

Keywords: cement-asbestos, magnesium phosphate ceramics, amorphous

Introduction

Asbestos containing materials (ACMs) have been extensively used in the past in many European countries. Thanks to the need for safe disposal of this hazardous waste, several inertization processes of ACMs have been conceived (Abruzzese et al., 1998; Gualtieri et al., 2008; Leonelli et al., 2006). High temperature treatment leads to transformation of ACMs into stable crystalline silicates thanks to recrystallization processes in which the morphology of the original fibres is preserved. According to the chemical composition of the raw materials different phases such as calcium-magnesium silicates, calcium silicates and aluminates are formed.

There are several examples of recycling the product of inertization of ACMs into cementitious materials. For the preparation of calcium sulfoaluminate cements a thermally-treated cement-asbestos (CA) has been successfully used (Gualtieri and Boccaletti, 2011; Viani and Gualtieri, 2013). Recently magnesium phosphate cements have been produced using the same raw materials (Viani and Gualtieri, 2014). The use of CA as a raw material for cement clinker production, following other industrial processes, has been also proposed by other authors (Gleichmar et al., 1997; Sprung et al., 1998).

Magnesium phosphate ceramics (MPCs), classified as chemically-bonded phosphate ceramics (Roy, 1987; Wagh, 2004), are periclase (MgO)-based binding materials. Their properties, like high strength and good water resistance, make them attractive for many applications.

Insoluble magnesium phosphate forms through the reaction of potassium di-hydrogen phosphate (KH2PO4) (KDP) with periclase. The product is the isomorphous potassium equivalent of the mineral struvite (MKP):

$$MgO + KH_2PO_4 + 5H_2O \rightarrow MgKPO_4{\cdot}6H_2O \tag{1}$$

The primary source of magnesium oxide is magnesite ($MgCO_3$). It has been proven that the calcination temperature of magnesite is critical in determining the reactivity of the formed periclase (Ding et al., 2012; Soudée and Péra, 2002; Wagh, 2004). Dead-burnt magnesia, which is forming at temperature above 1300°C, is generally employed in commercial MPCs in order to slow down the reaction rate.

If magnesite calcination is accomplished together with inertization of hazardous waste, the ecological impact of the resulting MPC is reduced. ACMs can be recycled during the production of MPC, with substantial benefits in terms of energy content of the product. During thermal treatment of ACMs, a fraction of magnesium is integrated into the newly formed silicates, but it can also crystallize as periclase, adding to the amount obtained from magnesite.

The use of CaO-MgO-SiO_2 (CMS) triangular phase diagram for plotting compositions of raw materials has been proved useful (Viani et al., 2013). In Figure 1 points corresponding to bulk chemical compositions of raw materials are plotted as mol% of oxides in the CaO-MgO-SiO_2 system. Any mix of ACM with magnesite shifts bulk composition along a line joining these two components.

In a previous paper MPC with composition corresponding to the point labeled CHR_M in Figure 1, was produced starting from an industrial magnesite and a material rich in chrysotile (CHR). Flexural strength was found to increase with time. The sample showed the presence of an amorphous fraction which has been tentatively interpreted as a precursor of crystalline MKP. In order to explain the relationship between the amorphous phase and MKP, further investigations are needed. To this aim, in this paper the phase composition of the CHR sample was followed in time, up to 6 months.

Materials and methods

The ACM employed in this work, named CHR, is a friable thermal insulation material high in chrysotile. Other raw materials were commercial magnesite ($MgCO_3$) with 95.7% purity, and reagent grade KDP. They have been already characterized elsewhere (Viani and Gualtieri, 2014) and relevant analytical data are reported in Tables 1 and 2.

The CMS phase diagram previously described was used to calculate the amount of magnesite to be added to the CHR material in order to have the final composition falling inside the stability field of periclase. This choice was dictated by the need of obtaining a high amount of periclase. Magnesite chemical composition was calculated from the mineralogical analysis (Table 2). The resulting raw mix contained 60.3 wt% of magnesite. Figure 1 depicts the points corresponding to magnesite, CHR and the raw mix, named CHR_M. The raw mix was homogenized in an agate shatterbox for 20s and subsequently pressed into pellets (40mm of diameter and approximately 10mm of height), weighting 30g. The pellets were placed into Pt crucibles and calcined at 900°C for 30 min. Afterwards, the temperature was raised to the final temperature. We used two different temperatures 1100°C and 1300°C, which were maintained for 40 min. The samples were then quenched with air flow. The resulting products were milled in a steel shatterbox for 10s and then ground together with

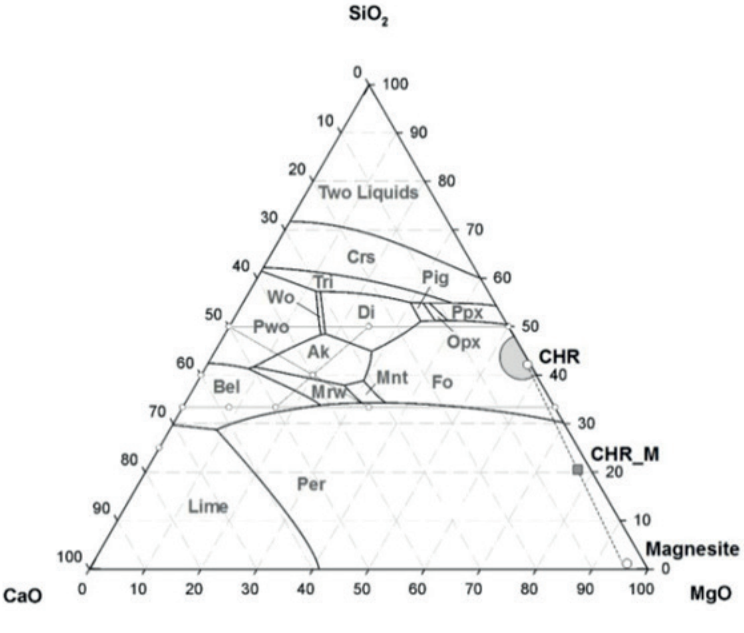

Fig. 1 Points corresponding to bulk chemical compositions for samples CHR, magnesite and CHR_M, plotted as mol% of oxides in the CaO-MgO-SiO2 system. Compositional range of high-chrysotile ACMs, is depicted as grey shadowed area. Stability field of phases is depicted. Ak, akermanite; Bel, Belite; Crs, cristobalite; Di, diopside; Fo, forsterite; Mnt, monticellite; Mrw, merwinite; Opx, orthopyroxene; Per, periclase; Pig, pigeonite; Ppx, protopyroxene; Pwo, pseudo-wollastonite; Tri, tridimyte; Wo, wollastonite (modified after Viani and Gualtieri, 2014)

Rys. 1 Punkty odpowiadają masie składu chemicznego dla próbek CHR, magnezyt i CHR_M wykreślono jako %molowy tlenków w układzie CaO-MgO-SiO2. Skład wysoko-chryzolitowy ACM jest przedstawiony jako szary. Przedstawiono pole stabilności faz. Ak, akermanit; Bel, Belit; Crs, cristobalit; Di, diopsid; Fo, forsterit; Mnt, monticellit; Mrw, merwinit; Opx, orthopyroxen; Per, peryklaz; Pig, pigeonit; Ppx, protopyroxen; Pwo, pseudo-wollastonit; Tri, tridimyt; Wo, wollastonit (modified after Viani and Gualtieri, 2014).

KDP (KDP/MgO molar ratio of 1) in an agate mortar. Hydration was conducted using deionized water, employing a water/solid ratio of 0.3. After mixing with water for 10s, a fraction was placed in a sealed sample holder for X-rays powder diffraction (XRPD) analysis. A further set of samples was prepared to perform quantitative phase analysis (QPA), through XRPD, after 7 days, 3 and 6 months. XRPD data were collected using a Bragg–Brentano θ-θ diffractometer (Bruker D8 Advance, Cu Kα radiation, 40 kV and 40 mA) equipped with a real time multiple strip (RTMS) detector. The virtual step scan of the measurement was 0.010° (2θ).

QPAs were performed using the Rietveld method (Rietveld, 1969). Refinements were accomplished with the GSAS package (Larson and Von Dreele, 1999) and its graphical interface EXPGUI (Toby, 2001). Both crystalline and amorphous fraction (AF) were determined with the combined Rietveld–RIR method (Gualtieri, 2000). To this aim, samples were added 10 wt% of NIST676a corundum as internal standard and homogenized in agate mortar.

Scanning electron microscopy (SEM) study was accomplished with a SEM FEI Quanta 450 FEG instrument equipped with an energy dispersive X-rays fluorescence spectrometer (EDS). A tiny amount of sample was loaded on an aluminium stub and coated with a gold 5 nm thick film. Observations were performed using secondary electrons with 40 kV accelerating voltage.

Results and discussion

As already reported elsewhere (Viani and Gualtieri, 2014), the mineralogical composition of the sample after thermal treatment is dominated by forsterite (Mg_2SiO_4), spinel ($MgAl_2O_4$) and periclase. Other minor phases, such as monticellite ($CaMgSiO_4$), magnetite (Fe_3O_4) and quartz (SiO_2) accounted for less than 2 wt%. The weight fraction of periclase is 34.3 and 28.2 wt% in the sample annealed at 1100°C (CHR_1100) and 1300°C (CHR_1300), respectively.

In accordance with the literature, samples annealed at higher temperature showed a coarser grain size. Both samples can be considered as composed of two phase fractions: periclase, ready to react with KDP, and oxides and silicates, basically acting as inert material.

Table 3, reporting the results from QPA, shows that the amount of forsterite, quartz and spinel, are more or less constant with time. Periclase is slightly decreasing in the sample CHR_1100, whereas, no trend is recognizable for the sample CHR_1300. The most important changes involve the phase fractions of MKP and amorphous. As depicted in Figure 2, they show opposite behavior; MKP increases with time, and the amorphous phase decreases with time. Considering the sample CHR_1100, 8.7 wt% of MKP formed after 6 months compared with the 7 days measurement. This change is compensated by the decrease of periclase and amorphous fraction. The same happens

Tab. 1 Chemical composition of CHR and magnesite in weight fraction (wt%)

Tab. 1 Skład chemiczny CHR i magnezytu w procentach wagowych (wt%)

	CHR	Magnesite
SiO_2	33.7	2.43
Al_2O_3	4.60	-
CaO	0.57	0.61
Na_2O	1.40	-
K_2O	0.16	-
MgO	35.7	46.1
Fe_2O_3	4.61	-
TiO_2	0.06	-
P_2O_5	0.01	-
L.O.I	19.2	50.8

Tab. 2 Mineralogical composition of CHR and magnesite in weight fraction (wt%)

Tab. 2 Skład mineralogiczny CHR I magnezytu w procentach wagowych (%wt)

	CHR	Magnesite
Chrysotile	70.8 (3)	-
Calcite	-	0.1 (1)
Dolomite	-	1.8 (1)
Quartz	0.3 (1)	2.4 (1)
Chlorite	21.4 (5)	-
Biotite	1.5 (2)	-
Gypsum	0.4 (1)	-
Magnesite	-	95.7 (1)
Talc	4.1 (3)	-
Magnetite	1.7 (1)	-

Tab. 3 Results from QPA for the samples under study

Tab. 3 Wyniki analizy QPA badanych próbek

	CHR_1100			CHR_1300		
	7 days	3 months	6 months	7 days	3 months	6 months
MKP	31.1 (1)	37.4 (1)	39.8 (1)	25.4 (1)	31.8 (1)	32.3 (1)
Periclase	2.2 (1)	2.0 (1)	1.3 (1)	2.8 (1)	2.2 (1)	2.5 (1)
Forsterite	18.9 (1)	20.1 (1)	20.2 (2)	23.5 (1)	22.2 (1)	23.7 (2)
Spinel	1.1 (1)	1.3 (1)	1.3 (1)	4.4 (1)	4.2 (1)	4.6 (1)
Magnetite	0.5 (1)	-	-	-	-	-
Quartz	0.4 (1)	0.1 (1)	0.1 (1)	0.2 (1)	0.2 (1)	-
Amorphous	45.9 (3)	39.1 (3)	36.5 (3)	43.6 (3)	39.3 (3)	37.0 (3)

to sample CHR_1300. The phase fraction of MKP after 6 months is 6.9 wt% higher than after 7 days, and this difference is accounted for by the decrease showed by periclase and amorphous phase fractions.

In a previous work (Viani and Gualtieri, 2014), the amorphous phase was supposed to be the precursor of crystalline MKP. Our data support this view because, apart from a small contribution coming from periclase, all the new crystalline MKP forms at the expenses of the amorphous phase. This result is of great importance for understanding the mechanism of the MPC reaction and the development of the mechanical properties with time. The strength development of MPC mortars was previously supposed to be substantially increased by the precipitation of an amorphous phase, possessing the chemical composition of MKP and filling voids between the network of crystalline phases (Ding et al., 2012). Our results suggest the opposite: that is, since fexural strength increases with time (Viani and Gualtieri, 2014) and the amorphous fraction decreases with time, MKP is the main responsible for the improvement of mechanical properties with time. This will be further clarified by observing the microstructure of hardened pastes, as discussed below.

If we compare the two datasets, the lower amount of MKP detected and the lower increase in MKP phase fraction with time in the sample CHR_1300 with respect to the sample CHR_1100, are confirming previous results, indicating that the MPC reaction is faster in samples heat treated at lower temperature.

SEM micrographs, reported in Figure 3, show typical features observable in our MPC samples. In a) elongated MPK crystals surrounded by irregularly and/or round shaped particles (likely inert minerals) are filling the space, forming a dense network. This undoubtedly positively affects the mechanical properties of the hardened paste. When looking at the samples in more detail (i.e. at higher magnification), areas like the one depicted in b) can be found. Here, MKP crystals, whose chemical nature was assessed by EDS microanalysis, are emerging from the matrix. The aspect of the matrix suggests a non crystalline or poorly crystalline nature. Its chemical composition was found to be that of MKP by EDS point analysis. If we accept that the amorphous phase is the precursor of MKP, this picture shows MKP crystals forming from the amorphous. The fact that a matrix with this aspect was not observed in areas where MKP crystals are bigger and fill the available space as in a), further support our conclusion. Thus, at least a fraction of MKP crystallizes from this amorphous precursor, and, as these crystals grow bigger, a texture like the one depicted in Figure 3 a) is produced.

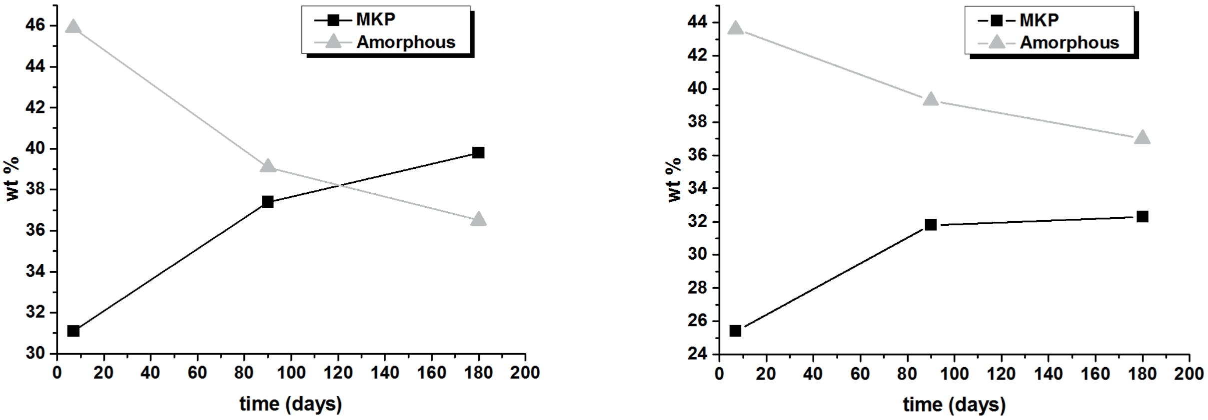

Fig. 2 Points corresponding to the phase fractions at different times of MKP and amorphous phase for the samples CHR_1100 on the left (a), and CHR_1300 on the right (b).

Rys. 2 Punkty odpowiadają frakcjom fazy przy różnych czasach MKP i fazie amorficznej dla próbek CHR_1100 po lewej (a), a CHR_1300 po prawej stronie (b)

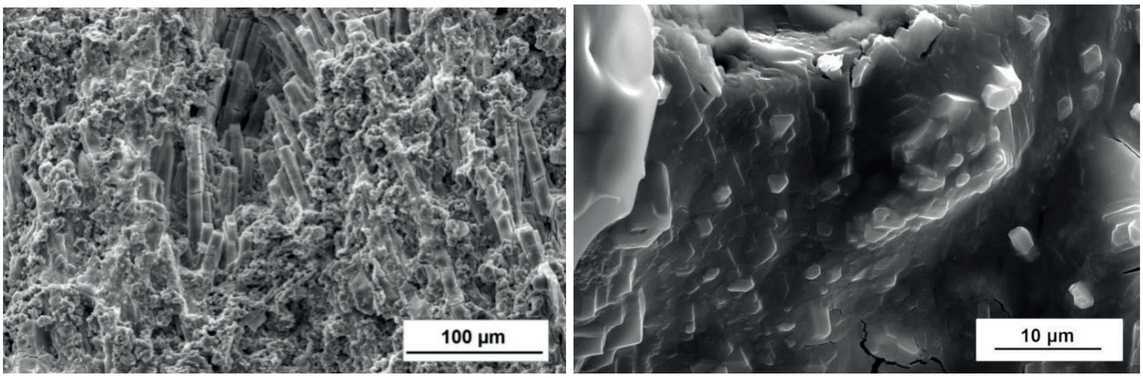

Fig. 3 SEM micrographs of the samples CHR_1300 on the left (a), and CHR_1100 on the right (b) 14 days after hydration

Rys. 3 Mikrograf SEM próbek CHR_1300 z lewej (a) i CHR_1100 z prawej (b) 14 dni po hydracji

Conclusion

Magnesium phosphate ceramics have been successfully produced by adding KDP and water to a mix of magnesite and ACM annealed at 1100 and 1300°C.

After thermal treatment, samples can be described as composed of a fraction of periclase, suitable to react with KDP, and various inert phases, acting as fillers during setting.

Reactivity of periclase showed to be dependent on the calcination temperature, resulting in lower reaction rates for samples heat treated at higher temperature.

For the first time it was proved a direct relationship between the amount of MKP formed at different times after hydration and the amorphous phase detected in the samples.

This suggests that the amorphous phase acts as a precursor of crystalline MKP and that MKP is the main responsible for the development of strength in MPC pastes.

The solution presented here is an example of the safe recycling of hazardous wastes into secondary raw materials. Destruction of asbestos minerals and formation of reactive periclase occur simultaneously during thermal treatment of asbestos/magnesite mixtures as long as sufficient magnesite is added. This may have advantages in terms of energy requirements and preservation of natural resources.

Acknowledgements

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Magnezowo-fosforanowe wyroby ceramiczne wytwarzane z produktów termicznej transformacji cementu - azbestów

Zgodnie z niedawnymi dyrektywami europejskimi, potrzeba przyjaznego dla środowiska alternatywnego rozwiązania usuwania odpadów niebezpiecznych, takich jak materiałów zawierających azbest, pobudza ich ponowne wykorzystanie jako surowców wtórnych. W tej pracy, magnezowo fosforanowe wyroby ceramiczne zostały wytworzone z użyciem produktów inertyzacji cementu – azbestu. Magnezowo fosforanowe wyroby ceramiczne wykazują interesujące właściwości takie jak dobry opór wodny oraz duża wytrzymałość, co sprawia, że są atrakcyjnym materiałem dla wielu aplikacji. Materiały zawierające azbest zostały zmieszanie w węglanem magnezu i wyżarzone w dwóch różnych temperaturach (1100°C i 1300°C). Podczas obróbki cieplnej następuje całkowite zniszczenie minerałów azbestu wraz z ich transformacją w nowe fazy, oraz krystalizacja MgO z rozpadu węglanu magnezu. Podczas dodawania diwodorofosforanu magnezu do wody, tlenek magnezu jako produkt obróbki cieplnej, przyczynia się do rozpoczęcia reakcji wiązania, której produktem jest hydrat fosforanu magnezu i potasu. Odkryto, że reaktywność peryklazu zależy od temperatury kalcynacji. Niższa szybkość reakcji została zaobserwowana dla MgO uzyskanego w niższej temperaturze. Reakcja wiązania wyrobów ceramicznych magnezowo fosforanowych została przeprowadzona w czasie do 6 miesięcy za pomocą techniki rentgenowskiej dyfrakcji proszkowej. Ilościowe analizy fazowe zostały wykonane z użyciem metody Rietvelda i obliczono zarówno fazę krystaliczną jak i amorficzną. Zauważono, że ilość fosforanu magnezowo potasowego zwiększa się w czasie, i że towarzyszy jej spadek ilości części amorficznej. Fakt ten potwierdza hipotezę powstawania amorficznego prekursora krystalicznego fosforanu magnezowo potasowego podczas reakcji hydracji.

Obrazy SEM przedstawiają wydłużone kryształy hydratu fosforanu magnezowo potasowego wyłaniające się, z wyglądającej na amorficzną, macierzy, następnie ten wygląd się potwierdza.

Ponieważ wiadomo, że właściwości mechaniczne fosforanu magnezu zwiększają się z czasem, możemy wnioskować, że główny wpływ na zwiększenie się wytrzymałości ma krystaliczny hydrat fosforanu magnezowo potasowego. W pracy tej opisano procedurę jednoczesnego rozpadu minerałów azbestu i tworzenia się związków cementytowych, co wskazuje na możliwość powtórnego przetworzenia tego rodzaju odpadów niebezpiecznych, co przynosi korzyści w kategoriach zapotrzebowania energetycznego i ochrony zasobów naturalnych w przetwórstwie cementu.

Słowa kluczowe: cement-azbest, magnez, fosforyty ceramiczne, bezpostaciowość