Pergamon

Cement and Concrete Research 32 (2002) 675–682

CEMENT AND CONCRETE RESEARCH

Magnesia–phosphate bond for cold-setting cordierite-based refractories

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Received 31 January 2001; accepted 26 October 2001

Abstract

A cold-setting refractory material was developed using the magnesia–phosphate reaction. A cement paste based on alumina, silica fume, magnesia and orthophosphoric acid or monoaluminum phosphate was designed to form cordierite–mullite during heating. This cement paste set at room temperature and $MgHPO_4 \cdot 3H_2O$ phase (newberyite) was observed, but amorphous phases were predominant. Two exothermic effects were detected during the setting process corresponding to the acid–base reaction of magnesia with phosphates and to the formation of bonding hydrates. At 1100 °C, C-$AlPO_4$ was formed by reaction of alumina with orthophosphoric acid or monoaluminum phosphate. At 1350 °C, the principal crystalline phases were cordierite and mullite. A refractory concrete with the obtained cement paste and a cordierite–mullite aggregate (scrap refractory material) was prepared. At 1350 °C, this concrete had a thermal expansion coefficient of 1.0×10^{-6} °C^{-1} and a flexural strength of 10 MPa. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Magnesia–phosphate cement; Cold-setting; Cordierite; Chemically bonded ceramics; Calorimetry

1. Introduction

The bonding properties of a large number of phosphate materials have been recognized for many years. Phosphate bonds are usually employed in dental cements, rapid repairs to damaged concretes and refractories. Early literature on phosphate bonding was reviewed by Kingery [1,2], then by Cassidy [3] and Sarkar [4]. The phosphate bonding can be cold- and thermal setting. In refractory applications, acid salt or derivatives of phosphoric acid react at ordinary temperatures with many oxides of weakly basic or amphoteric nature, but not all of them form bonding products. For optimum bonding, a moderately small cationic radius is required so that a nonordered or glassy structure can be formed. Similar products are formed, producing cement-like materials. All these products are mono- and dibasic phosphates. Aluminum, chromium, magnesium and zirconium oxides react chemically with phosphoric acid to form a bonded material. Among these cations, magnesium and aluminum are the most readily available, and then the most commonly used with phosphoric acid or phosphates.

The base in all magnesia–phosphate cement (MPC) [5] is dead-burned magnesia, but various acid sources have been used: H_3PO_4, $NH_4H_2PO_4$, $(NH_4)_2HPO_4$, $Al(H_2PO_4)_3$, $Na_5P_3O_{10}$, etc. Compositions with ammonium phosphates had been the most used in patents and researches [6–20] for the quick-setting and high-strength properties of the mixtures. Monoaluminum phosphate, $Al(H_2PO_4)_3$, was also employed [11,21,22]. An acid–base reaction between magnesia and phosphates in aqueous solution is responsible for the cold-setting characteristics of the MPC. The reaction product, usually a salt or a hydrogel, forms the cement matrix in which the fillers are embedded. In order to obtain good materials, the reactivity and the solubility of magnesia must be controlled as much as the concentration of the phosphoric acid or the phosphate. The setting time is controlled by means of the type of magnesia, phosphate concentration, magnesia/phosphate ratio and retarders.

Phosphates can be employed in cordierite-based refractories due to the high fusion temperature of many phosphates. Cordieritic materials are extensively used as kiln furniture because of their low thermal expansion and outstanding thermal shock resistance. The low intrinsic strength of cordierite can be compensated by the presence of mullite. Bodies with a high content of cordierite, accompanied in some cases with spinel and mullite, are commonly produced from mixes of talc, plastic clay and alumina. These matrixes

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PII: S0008-8846(01)00725-6

mixed with aggregates of different compositions and sizes can be pressed, rammed, cast, etc., producing after heating cordierite-based bodies. The service temperature is about 1300 °C.

In this study, a cement paste based on calcined alumina, silica fume, magnesia and orthophosphoric acid or monoaluminum phosphate was designed to obtain a cold-setting material that converts into cordierite–mullite by heating at high temperature. The formed phases and the generated thermal effects during the setting process, as well as the phase evolution on thermal treatment, were observed. Refractory concretes with this cement paste and a cordierite–mullite aggregate were prepared and their thermomechanical properties measured.

2. Experimental

2.1. Materials

The cold-setting refractory concretes were formulated with a fine fraction or matrix and a coarse fraction or aggregate. The fine fraction, named F, was prepared with calcined alumina, silica fume and magnesium oxide, in such proportions of forming cordierite by heating at high temperature.

The alumina used was a calcined type, S3G, from Alcan with a mean particle size of 5 μm, a specific surface (BET) of 1 $m^2 g^{-1}$ and 0.49% of Na_2O. The crystalline phases observed by X-ray diffraction (XRD) were Al_2O_3 (corundum) and impurities of β-$NaAl_{11}O_{17}$.

The SiO_2 employed was silica fume EMS 965 from Elkem Materials. By XRD, it was observed that the silica fume was amorphous at low temperatures and it contained SiC as impurity. At temperatures higher than 1000 °C, the silica crystallized in cristobalite and tridymite form.

The magnesium oxide was refractory grade with a particle size under 75 μm. The chemical analysis reported MgO: 93.28%, SiO_2: 2.95%, Al_2O_3: 0.19%, Fe_2O_3: 0.70%, CaO: 1.97%, Na_2O: 0.46%, TiO_2: 0.02%, $K_2O < 0.01\%$ and loss on ignition $< 0.01\%$. The MgO was calcined at 1000 °C for 1 h to decrease its reactivity and to eliminate the carbonates and superficial hydrates.

The coarse fraction or aggregate, named A, was cordierite–mullite grains from scrap refractory material with adequate grain size distribution from mesh 8 to 50 (ASTM).

The setting agents used for the formation of the bond were orthophosphoric acid: H_3PO_4 85%, density 1.70 g cm^{-3} (named P) and monoaluminum phosphate: $Al(H_2PO_4)_3$ 50%, density 1.48 g cm^{-3} (named M).

2.2. Cement paste preparation

Cement pastes were prepared by mixing (by spatulation) the fine fraction (F) with a solution of orthophosphoric acid (P) or monoaluminum phosphate (M) [23]. The obtained pastes were named FP and FM, respectively. In both pastes, the MgO/P_2O_5 molar ratio was 4.8. Another portion of F fine fraction was mixed with water and it was named FW. These pastes were allowed to harden in air at room temperature (20 °C) and then they were submitted to thermal treatment: 24 h at 110 °C and 2 h at 600, 1100 and 1350 °C in electric furnace in air atmosphere.

2.3. Concrete preparation

The refractory concretes were constituted with 60% of aggregates (A) and 40% of fine fraction (F). These solids were mixed (in a Hobart type mixer) with orthophosphoric acid (P) or monoaluminum phosphate (M) and water until forming a workable paste. These concretes were named AFP and AFM, respectively. The MgO/P_2O_5 molar ratio for these concretes was the same as that for the FP and FM cement pastes. The mixtures obtained were poured in metallic molds $25 \times 25 \times 150$ mm^3, and vibrated for about 1 min [24]. The setting of the concretes began after approximately 20 min and finished within 5 h. The concretes were removed from the mold after 24 h at room temperature and put aside at room temperature for 20 days. Then, they were dried for 24 h at 110 °C and calcined for 2 h at 600, 1100 and 1350 °C in electric furnace in air atmosphere.

2.4. Analysis and testing techniques

Crystalline phases of the materials prepared were analyzed by XRD with a Philips PW 3710 equipment, using Cu–Kα radiation ($\lambda = 0.154$ nm).

Differential thermal analysis (DTA) and thermogravimetry (TG) were recorded using a Netzsch STA 409 apparatus with a heating rate of 5 °C min^{-1} in a static air atmosphere. In these tests, 200 mg of sample mass was employed with α-alumina as reference material.

Micrographs were obtained with a Philips 505 scanning electron microscope (SEM).

The thermal expansion coefficient of the concretes was determined with a Netzsch dilatometer. The flexural strength was measured using a T22K equipment from J.J. Instruments Limited (U.K.). The open porosity was determined by the immersion method in water (ASTM C-20).

The thermal effects of the cement pastes during the setting process were measured in a differential comparative calorimeter built in the laboratory, which consisted of two Dewar flasks thermally isolated, a differential thermocouple, a temperature measuring device and a recorder. In one of the flasks, a recipient was placed containing a sample of 4 g of fine fraction mixed with 2.6 g of a solution 25% of orthophosphoric acid (85%) or 45.6% of monoaluminum phosphate (50%) to give, in both cases, a MgO/P_2O_5 molar ratio of 4.8. In the other flask, a paste prepared with 4 g of mullite and 2.6 g of water was placed as reference. The differential thermocouple used was a chromel–alumel (type K) and it was embedded in the pastes.

3. Results and discussion

3.1. Cement pastes

3.1.1. Phase development during setting process

The F fine fraction of the refractory materials (alumina, silica and magnesia) treated with phosphates converted into cordierite–mullite during heating at high temperature. At room temperature, the phosphate anions react with the particles of magnesia, producing magnesium phosphates that form hydrated compounds which set as a hydraulic cement. The reaction between magnesia and phosphoric acid is rather violent, and if the conditions of the reaction are not controlled, the material will not harden (not set) and a porous friable structure will be obtained. The magnesia type and the magnesia/phosphate ratio are important aspects to keep in mind. Water-soluble $Mg(H_2PO_4)_2$ series compounds are produced with low magnesia/phosphate ratios. The setting rate also depends on the room temperature: the higher the temperature, the higher the reaction rate. At low temperatures, the alumina used practically did not react with the orthophosphoric acid due to the type of alumina (calcined, > 99% α-Al_2O_3) and the Al_2O_3/P_2O_5 ratio used [25]. At high temperatures, aluminum phosphates were formed, which acted as a good thermal-setting bond agent. At temperatures around 1250 °C, the constituents of the cement paste converted into cordierite ($2MgO\cdot 2Al_2O_3\cdot 5SiO_2$) and mullite ($3Al_2O_3\cdot 2SiO_2$) compounds.

Fig. 1 shows the X-ray diffractograms of the F fine fraction, and the FW and FP pastes after being at room temperature for 20 days. F and FW samples presented Al_2O_3 (corundum) and MgO (periclase) as main crystalline phases, β-$NaAl_{11}O_{17}$ and SiC as impurities. A higher background, about 22° 2θ, was also observed, indicating the presence of amorphous silica. The fine fraction treated with orthophosphoric acid (FP) and set at room temperature showed the same phases as F and FW, but the intensity of the MgO reflections was considerably lower. After 24 h from the FP paste preparation, a crystalline unidentified compound was observed, probably a hydrated phosphate. After 48 h, this unknown compound disappeared and small quantities of $MgHPO_4\cdot 3H_2O$ (newberyite) appeared, whose proportion increased slightly in the subsequent days. After 20 days, the quantity of newberyite was considered constant. The rest of the reacted magnesia was believed to form amorphous phosphates. Finch and Sharp [21] suggested the presence of amorphous phases containing magnesium to justify the "missing" magnesium. Furthermore, in this work, it was observed that the newberyite present in the set cement at room temperature converted into amorphous state at 110 °C by both systems, with orthophosphoric acid and with monoaluminum phosphate. The exact amount of magnesium, which appears in the form of newberyite, magnesia or in the amorphous phase, depends on a number of factors, such as the MgO/P_2O_5 molar ratio, the particle size and reactivity of the starting materials, the intimacy and the mixing time [21].

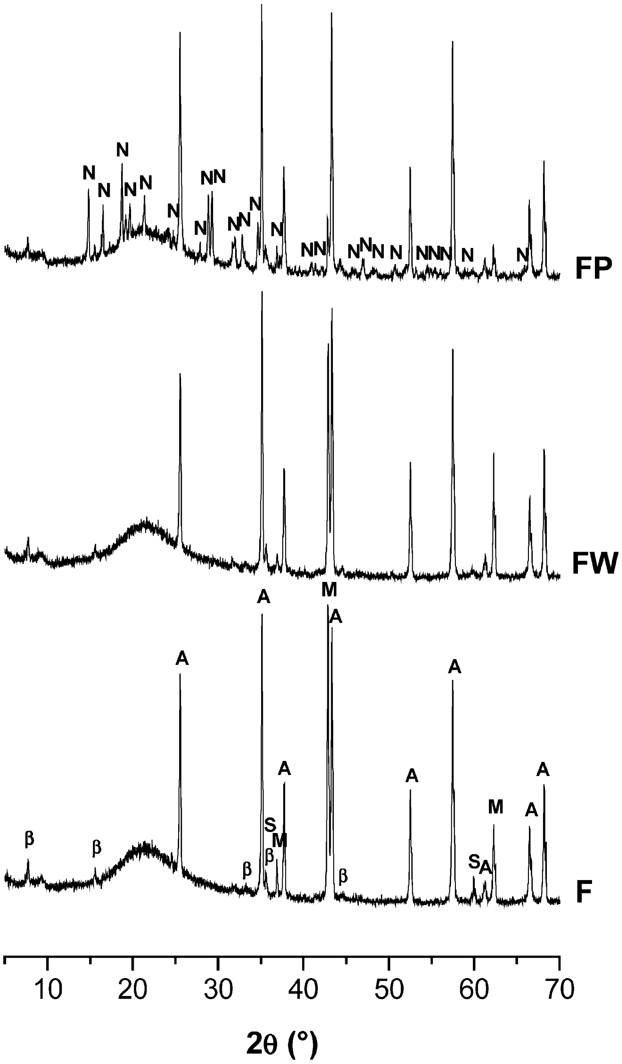

Fig. 1. XRD pattern of the fine fraction (F), the fine fraction mixed with water (FW) and with orthophosphoric acid solution (FP) at room temperature after 20 days of being prepared (A = Al_2O_3; M = MgO; N = $MgHPO_4\cdot 3H_2O$; β = β-$NaAl_{11}O_{17}$ and S= SiC).

The crystalline phases observed for the fine fraction treated with monoaluminum phosphate (FM) and set at room temperature were the same as those observed in the FP paste, although they were not so developed (intensity of XRD peaks). The aluminum introduced by means of monoaluminum phosphate was not present in the crystalline reaction products, suggesting the formation of an amorphous aluminum phosphate hydrate, being added to the amorphous magnesium phosphate hydrate and the amorphous silica.

Fig. 2a and b shows the SEM micrographs of the fine fraction with water (FW) and with orthophosphoric acid (FP), respectively, after being at room temperature for 20 days. The fine fraction treated with water (FW) showed that the fine particles were not "consolidated," forming a cementitious matrix. A homogeneous porosity distribution between particles was observed. On the other hand, the fine

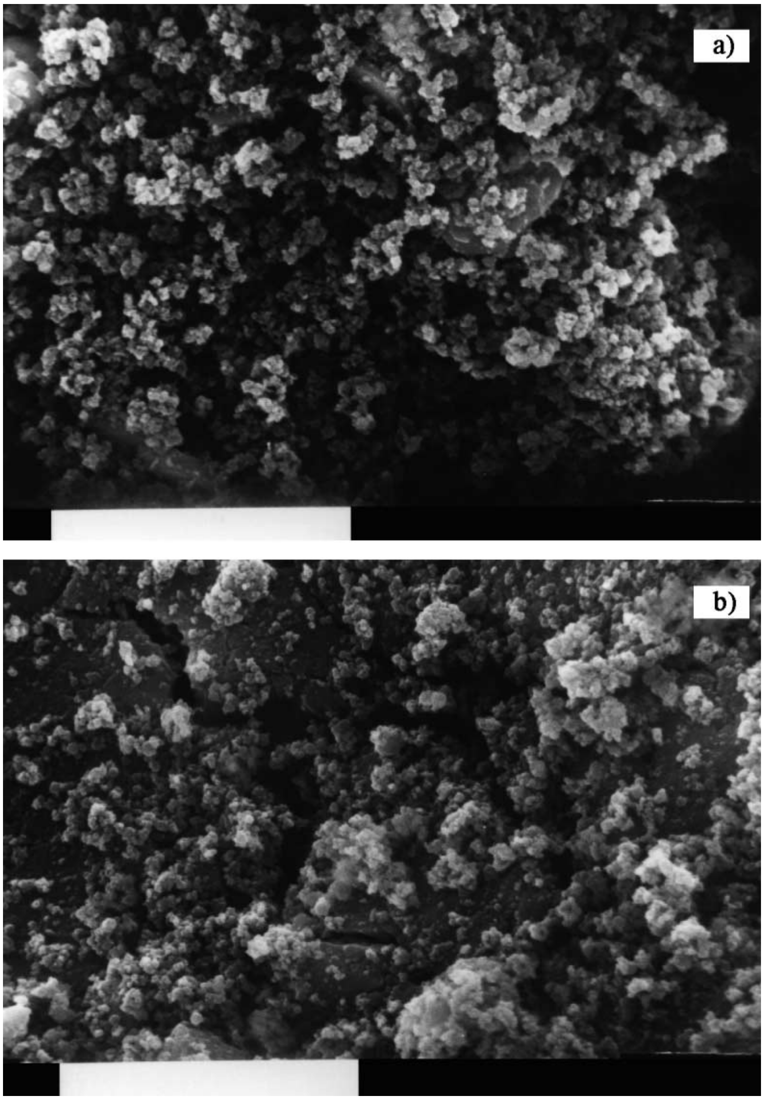

Fig. 2. SEM micrographs of (a) the fine fraction with water (FW) and (b) the fine fraction with orthophosphoric acid (FP) at room temperature (scale bar: 10 μm), after 20 days of being prepared.

fraction treated with orthophosphoric acid (FP) showed a monolithic structure, with a glassy aspect formed by the hydrated phosphate compounds. The newberyite crystals were not observed. The cracks were due to the stress during the shrinkage of this compact.

3.1.2. Calorimetry

A differential comparative calorimeter was used to study the formation of the bond during the setting process through the reaction between the fine fraction and the orthophosphoric acid. The phosphate and the magnesium ion concentrations were very important in the formation of this type of cold-setting compounds. In these tests, a portion of fine fraction was mixed with orthophosphoric acid to form the FP cement paste and two exothermic effects were observed: (1) the acid–base reaction of the magnesia dissolution by the orthophosphoric acid, which occurred immediately after the reagents were put in contact. This reaction was very exothermic and rapid unless the magnesia reactivity was controlled; (2) the formation of crystalline and noncrystalline hydrated magnesium phosphates, responsible for the setting. This second effect was less exothermic than the first one and its intensity and time appearance were variable. In Fig. 3, these thermal effects are schematically represented (medium values). The maximum of the second effect occurred at times between 1.5 and 4 h for most of the tests performed (curve *a*). In some cases, this effect did not appear within 48 h, the material had not set and crystalline phosphates were not observed by XRD. In this case, the newberyite appeared after allowing the material to dry for several days in the air at room temperature.

The same procedure, except for the addition of 1% of nuclei to the FP paste, was carried out. Two different classes of nuclei were used: hydrated FP paste (set and milled) and cordierite–mullite grains. In all these cases, the pastes set and the second thermal effect was more intense and at

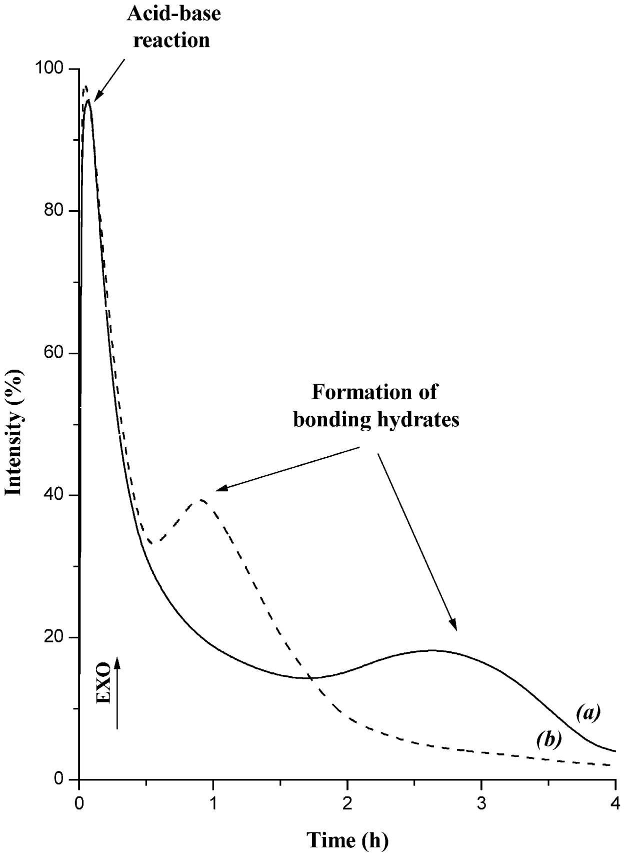

Fig. 3. Thermal effects during setting process of the fine fraction treated with orthophosphoric acid solution (FP) (a) without nuclei and (b) with nuclei of FP paste set and milled.

shorter times than the one observed in the pastes without nuclei. The maximum of the second effect, from the moment the reagents were put in contact, occurred at 0.9 h for nuclei of FP paste (Fig. 3; curve *b*) and at 1.8 h for cordierite nuclei (not shown).

In experiments carried out with an excess of water, 5%, 10% and 20% to favor the ionic mobility of the paste, the material set, but variations in the intensity and in the time of appearance of the second effect were observed again. When these pastes were seeded with nuclei, the intensities and the times were the same for all the added percentages of water. Therefore, it could be inferred that the setting reaction between the fine fraction and the orthophosphoric acid was controlled by a nucleation mechanism. The concretes always set due to the presence of the aggregates that act as nuclei for these reactives.

The substitution of orthophosphoric acid for monoaluminum phosphate in the reaction with the fine fraction (FM paste) produced the same exothermic effects, except for a marked decrease in the intensity of the first effect corresponding to the acid–base reaction. This fact is a consequence of lower acidity of the $H_2PO_4^-$ ions of the monoaluminum phosphate compared with the PO_4^{3-} ions of the orthophosphoric acid.

3.1.3. Thermal analysis and phase evolution on heat treatment

Table 1 shows the crystalline phase evolution on heat treatment for the fine fraction (F), the fine fraction mixed with water (FW) and with orthophosphoric acid solution (FP). The F and FW samples did not suffer phase transformations up to 1250 °C, except for the transformation of the amorphous silica into the cristobalite form (C-SiO_2) at temperatures higher than 1000 °C. At 1350 °C, cordierite was formed but alumina, magnesia and silica remained in excess. Small quantities of mullite and spinel ($MgAl_2O_4$) were also present.

Alumina, amorphous silica and magnesia were observed in the FP paste set at room temperature and put aside for 20 days. MgO was present in smaller proportion than in F, indicating the amorphous magnesium phosphate formation. The presence of $MgHPO_4{\cdot}3H_2O$ (newberyite) was also

Table 1
Phases observed by XRD of the dry fine fraction (F), the fine fraction with water (FW) and the fine fraction with orthophosphoric acid (FP) at different temperatures

	F	FW	FP
20 °C (20 days)	Al_2O_3[a] MgO[a] SiO_2 amorphous β-$NaAl_{11}O_{17}$[c] SiC[c]	Al_2O_3[a] MgO[a] SiO_2 amorphous β-$NaAl_{11}O_{17}$[c]	Al_2O_3[a] MgO[b] SiO_2 amorphous β-$NaAl_{11}O_{17}$[c] $MgHPO_4{\cdot}3H_2O$[b]
110 °C (24 h)		Al_2O_3[a] MgO[a] SiO_2 amorphous β-$NaAl_{11}O_{17}$[c]	Al_2O_3[a] MgO[b] SiO_2 amorphous β-$NaAl_{11}O_{17}$[c]
600 °C (2 h)		Al_2O_3[a] MgO[a] SiO_2 amorphous β-$NaAl_{11}O_{17}$[c]	Al_2O_3[a] MgO[b] SiO_2 amorphous β-$NaAl_{11}O_{17}$[c]
1100 °C (2 h)	Al_2O_3[a] MgO[a] SiO_2 amorphous C-SiO_2[c] SiC[c]		Al_2O_3[b] MgO[c] C-$AlPO_4$/C-SiO_2[a] $Mg_3(PO_4)_2$[b]
1250 °C (0 h)	Al_2O_3[a] MgO[a] SiO_2 amorphous C-SiO_2[c] SiC[c]	Al_2O_3[a] MgO[a] SiO_2 amorphous C-SiO_2[b]	Al_2O_3[b] MgO[c] C-$AlPO_4$/C-SiO_2[a] $Mg_3(PO_4)_2$[c] Cordierite[c]
1350 °C (2 h)	Cordierite[a] Mullite[c] $MgAl_2O_4$[c] Al_2O_3[b] MgO[b] C-SiO_2[b] SiC[c]	Cordierite[a] Mullite[c] $MgAl_2O_4$[c] Al_2O_3[b] MgO[b] C-SiO_2[b]	Cordierite[a] Mullite[b] MgO[c] C-$AlPO_4$/C-SiO_2[c] $Mg_3(PO_4)_2$[c]

[a] Intensity: high.
[b] Intensity: low.
[c] Intensity: very low.

observed. This magnesium hydrogen phosphate hydrate disappeared after drying the paste at 110 °C, converting the phosphates into an amorphous state. At 600 °C, the crystalline phases were the same as those formed at 110 °C. Traces of B-$AlPO_4$ (berlinite) were detected at low temperatures. At 1100 °C, a very intense reflection was observed in the 21.8° 2θ zone, mainly corresponding to the cristobalite form of the aluminum orthophosphate (C-$AlPO_4$), and, to a lesser degree, to the cristobalite form of the silica (C-SiO_2), coming from the transformation of the amorphous silica of the fine fraction at that temperature. Aluminum orthophosphate has practically the same polymorphic transformations as silica [26,27]. A decrease in the Al_2O_3 and MgO contents was also observed, compared with those at 600 °C, due to the formation of $AlPO_4$ and $Mg_3(PO_4)_2$ (farringtonite), respectively. At 1250 °C (without any dwell time at this temperature), the transformation of the fine fraction into cordierite was observed. At 1350 °C, the two main crystalline phases present were cordierite and mullite.

The phases evolution of the fine fraction during heating, treated with monoaluminum phosphate, was very similar to that observed with the orthophosphoric acid, except for a higher content of mullite at 1350 °C.

The fine fraction without phosphates converted partially into cordierite at high temperatures; therefore, cordierite formation in the presence of phosphates during the heating is favored by the presence of liquid phosphate phases of low melting point.

Fig. 4a and b shows the TG and DTA of the fine fraction (F) and of the fine fraction treated with orthophosphoric acid (FP), respectively, after being at room temperature for 20 days. The TG of the F fine fraction indicated a continuous weight loss of 1.5% (total). On the other hand, the FP paste showed 9.5% of total weight loss with an important weight decrease at low temperature (100–300 °C), due to the dehydration of the magnesium phosphate hydrates. In agreement with this, the DTA of the FP paste presented a great endothermic peak at 168 °C, attributable to the decomposition of $MgHPO_4 \cdot 3H_2O$ (newberyite) and to the amorphous phases [5,21]. The exothermic effects between 450 and 800 °C could be related to the crystallization of the amorphous aluminum phosphate phases [28]. The cordierite starts forming at around 1000 °C, but the reaction is too slow to be detected by DTA; then, when increasing the temperature, the reaction occurs more quickly.

When the orthophosphoric acid was replaced by monoaluminum phosphate, a similar behavior was observed: the same DTA peaks and the same type of TG curve, with a total weight loss of 10.3%.

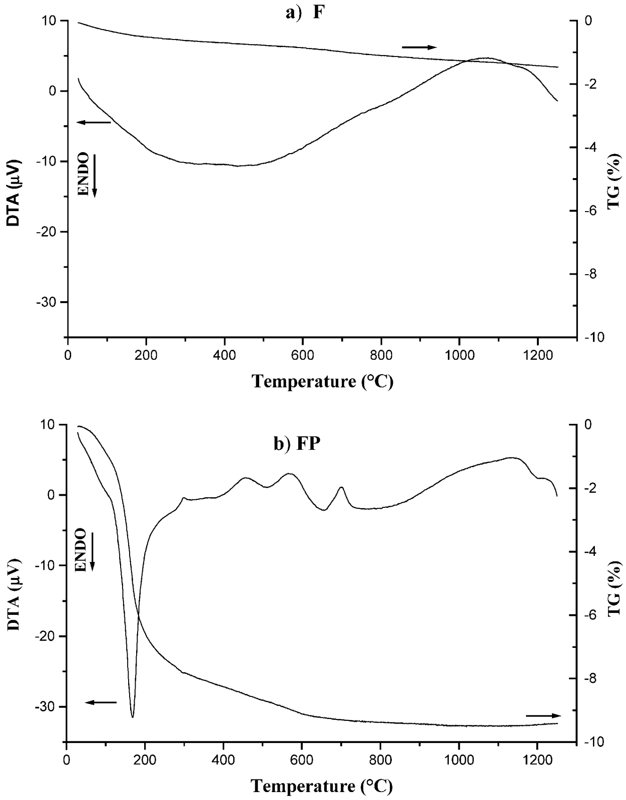

Fig. 4. DTA and TG of (a) the fine fraction (F) and (b) the fine fraction treated with orthophosphoric acid (FP), after 20 days of being prepared.

3.2. Concretes

3.2.1. Phase formation and evolution during heating

The AFP and AFM cold-setting concretes were designed with a cordierite–mullite aggregate and a cement paste constituted by alumina, silica fume, magnesia and orthophosphoric acid or monoaluminum phosphate solution, respectively. Table 2 shows the main crystalline phases observed by XRD in the aggregate and in the AFP concrete, set at room temperature, put aside for 20 days and thermally treated at different temperatures. The A aggregate contained cordierite as the main crystalline phase, mullite in smaller proportion and alumina, magnesia and spinel as minor phases. The AFP concrete, set at room temperature and analyzed 20 days later, showed the aggregate characteristic reflections (cordierite–mullite), the fine fraction (Al_2O_3, MgO and amorphous silica) and $MgHPO_4 \cdot 3H_2O$ (newberyite) coming from the reaction between the MgO and the H_3PO_4–H_2O. At 110 °C (24 h), the magnesium hydrogen phosphate was not observed, as it happened in the FP cement paste. At 600 °C (2 h), there was no change in the phases observed comparing with those at 110 °C. At 1100 °C (2 h), very intense reflections of the aluminum orthophosphate and of the silica, both in cristobalite form, were observed as well as the formation of small amounts of magnesium orthophosphate, $Mg_3(PO_4)_2$ (farringtonite). At 1350 °C (2 h), the fine fraction converted into cordierite–mullite. At this temperature, the alumina was totally consumed and small amounts of $Mg_3(PO_4)_2$, MgO and C-$AlPO_4$/C-SiO_2 were detected.

The concretes bonded with monoaluminum phosphate, AFM, presented practically the same crystalline phases as the concretes bonded with orthophosphoric acid, AFP.

3.2.2. Thermomechanical properties

In the dilatometric test of the AFP concrete, dried at 110 °C, no linear changes were observed up to 1100 °C. From this temperature, a contraction began reaching 0.35% at 1200 °C and 2.8% at 1350 °C. At these temperatures, liquid phases were generated, probably magnesium metaphosphate with a melting point of 1165 °C and compounds of the $SiO_2-P_2O_5$ system. At ordinary temperatures, the silica does not react with the orthophosphoric acid and it does not produce phosphorus compounds with bonding properties. At temperatures between 1100 and 1300 °C, liquid phases ($SiO_2 \cdot P_2O_5$ and $2SiO_2 \cdot P_2O_5$) are formed, not desirable for refractory materials.

Table 3 shows the flexural strengths (MOR) of the AFP concrete submitted to thermal treatment. At 110 °C, a decrease of the MOR was observed compared with the material at room temperature. This fact is related to the disappearance of the hydrated phosphate compounds responsible for the chemical setting that contributes significantly with the resistance at room temperature. An increase of the MOR values, with an increase in the temperature, was observed, in a similar way as it occurs in commercial heat-setting refractories, in which stable phosphate compounds, mainly $AlPO_4$, are formed.

Table 2
Phases observed by XRD of aggregate (A) and concrete (AFP) after setting at room temperature and thermal-treated

A	Cordierite[a] Mullite[b] Al_2O_3[c] MgO[c] $MgAl_2O_4$[c]
AFP 20 °C (20 days)	Cordierite[a] Mullite[b] Al_2O_3[d] MgO[b] SiO_2 amorphous $MgHPO_4 \cdot 3H_2O$[c]
AFP 110 °C (24 h)	Cordierite[a] Mullite[b] Al_2O_3[d] MgO[b] SiO_2 amorphous
AFP 600 °C (2 h)	Cordierite[a] Mullite[b] Al_2O_3[d] MgO[b] SiO_2 amorphous
AFP 1100 °C (2 h)	Cordierite[d] Mullite[b] Al_2O_3[b] MgO[c] C-$AlPO_4$/C-SiO_2[a] $Mg_3(PO_4)_2$[c]
AFP 1350 °C (2 h)	Cordierite[a] Mullite[b] MgO[c] C-$AlPO_4$/C-SiO_2[c] $Mg_3(PO_4)_2$[c]

[a] Intensity: high.
[b] Intensity: low.
[c] Intensity: very low.
[d] Intensity: medium.

Table 3
Flexural strength (MOR) of AFP concretes after setting at room temperature and thermal-treated

AFP (°C)	MOR (MPa)
20	2.5
110	1.2
600	1.3
1100	3.2
1350	10.4

The AFP concretes calcined at 1350 °C for 2 h presented an apparent density of 1.74 g cm^{-3}, an open porosity of 29.4% and a thermal expansion coefficient in the range of 25–1000 °C of 0.90×10^{-6} $°C^{-1}$, which indicated that the material behaved as pure cordierite instead of as a cordierite–mullite compound.

For concretes with monoaluminum phosphate (AFM), the MOR values were slightly lower than those obtained for concretes with orthophosphoric acid (AFP), except for the concretes set at room temperature, where the values were slightly higher due to the lower intensity in the reaction of the monoaluminum phosphate with the magnesia. The values of apparent density, open porosity and thermal expansion coefficient were practically equal to those obtained with orthophosphoric acid.

4. Conclusions

Cold-setting cordierite-based refractories were developed by employing the reaction between orthophosphoric acid or monoaluminum phosphate with magnesia. The phases responsible for the chemical setting were mainly magnesium phosphate hydrates.

The cement paste prepared with alumina, silica fume, magnesia and orthophosphoric acid or monoaluminum phosphate formed cordierite–mullite during thermal treatment.

The cement paste set at room temperature and the reaction rate was controlled by means of the type of magnesia, phosphate concentration and magnesia/phosphate ratio. After setting, $MgHPO_4 \cdot 3H_2O$ (newberyite) was observed, but amorphous phases were predominant.

Two exothermic effects were observed during the setting process of the cement paste due to the acid–base reaction and to the formation of hydrated magnesium acid phosphates. The setting reaction of this system had a nucleation mechanism.

The cordierite-based refractories constituted by the cement paste and the cordierite–mullite aggregate, calcined at 1350 °C for 2 h, exhibit a thermal expansion coefficient of 0.9×10^{-6} °C^{-1} and flexural strength of 10 MPa.

No significant differences in the mechanical and thermal properties were observed among materials formed using orthophosphoric acid or monoaluminum phosphate.

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