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Thermal study of chromium–phosphorus-doped tricalcium aluminate

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Abstract

The evolution with the temperature of the composition of some mixtures of $CaCO_3$, Al_2O_3, Cr_2O_3 and P_2O_5 has been investigated. The influence of chromium and phosphorus additions on the thermal decomposition of $CaCO_3$ and the formation of the tricalcium aluminate have been observed. The synthesized solid solutions have been characterized through X-ray diffraction (XRD). The free lime content has been determined by chemical analysis. The formation of the cubic polymorph of C_3A with Cr and P additions less than 4.24 wt.% Cr_2O_3 and 3.97 wt.% P_2O_5 was shown. The temperatures of the decarbonation and the enthalpy variations during the raw firing have been studied. The results showed that the presence of the Cr_2O_3 and P_2O_5 oxides lowered the decomposition of $CaCO_3$. The enthalpy of decarbonation and the enthalpy of the formation of the solid solutions based on tricalcium aluminate formation decreased when the concentrations of additives increased.

Keywords: $Ca_3Al_2O_6$; Chromium; Phosphorus; Thermal analysis; Calorimetry; X-ray diffraction

1. Introduction

Tricalcium aluminate ($Ca_3Al_2O_6$) is one of the main phases in the cement chemistry. The ionic substitutions in this phase can induce some modifications in the structure and thermal behaviour. Some elements have beneficial effects at low concentrations. They reduce the temperature at which the reaction of formation begins. In the literature, few works have paid attention to the energy of the formation of the C_3A solid solution with some specific elements like chromium and phosphorus.

Portland cement clinker manufacture requires higher energy consumption, about 1800 kJ/kg of clinker [1]. The thermal energy for the decomposition of the calcium carbonate of raw meal takes the main part of the total energy.

Several efforts are being made to reduce the enthalpy of $CaCO_3$ decomposition. The effect of various dopants on the decarbonation temperature and on the formation of clinker phases has been reported [2–9]. Caurtault [10] has shown that the presence of CaF_2 in the $CaCO_3$–Al_2O_3 system at the 3:1 molar ratio leads to the formation of a liquid phase in the $CaCO_3$–CaF_2 system. It enhances the crystallisation reaction of the calcium aluminates. Tricalcium aluminate C_3A is one of the main components of ordinary Portland cement. It forms solid solutions with various metal oxides such as Fe_2O_3, MgO, Na_2O and K_2O [11].

Several authors have studied the influence of Cr_2O_3 additions in Portland cement clinker manufacture and strength development of the cement paste [12–15]. They reported that the chromium causes an improvement in the burnability of cement raw meal and increases the early strength development. Hornain [14] found that in the clinker, the maximum chromium content in tricalcium aluminate is 0.04 wt.%. Recently, Murat and Sorrentino [16] showed that calcium aluminate cement could trap a large amount of chromium that is probably concentrated in the calcium aluminate phase.

The influence of the phosphorus element on clinker reactions was also investigated. Halicz and Nathan [17] have shown that P_2O_5, like Al_2O_3, lowers the melting point of the raw meal. Page et al. [18] noticed a possible phosphorus incorporation in tricalcium aluminate $CaAl_2O_3$ in industrial clinker.

In this paper, we investigate the simultaneous effect of chromium and phosphorus additions on the thermal decom-

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Table 1
Chemical compositions (wt.% oxide) and specific temperature of the decarbonation step (reported from DTA curves) of A(CrP)*x* starting samples

A(CrP)*x* samples	CaO	Al_2O_3	Cr_2O_3	P_2O_5	Onset temperature	Maximum temperature peak	Final temperature
A(CrP)0	62.26	37.73	0.00	0.00	646	865	874
A(CrP)0.02	61.90	37.01	0.56	0.52	631	848	861
A(CrP)0.05	61.35	35.92	1.41	1.31	612	840	854
A(CrP)0.10	60.44	34.10	2.82	2.64	627	850	864
A(CrP)0.15	59.52	32.27	4.24	3.97	690	866	887

position of $CaCO_3$ and on the formation of C_3A in a $CaCO_3$–Al_2O_3 system, at the 3:1 molar ratio. The synthesized samples were analyzed by X-ray diffraction (XRD) and the concentration of free lime was chemically determined. The temperatures of decarbonation were determined by means of a differential thermal analysis (DTA). Enthalpimetry has been used to evaluate the energy consumption during the formation of the C_3A solid solutions.

2. Experimental

The investigated compositions are synthesized from $CaCO_3$ (UCB Brussels, Belgium), Al_2O_3, Cr_2O_3 and $NH_4H_2PO_4$ (Merck Darmstadt, Germany; purity > 99%). Stoichiometric mixtures are ground in an agate mortar for several x values ($0 \leq x \leq 0.15$) following the reaction:

$$(3-x)CaCO_3 + x/2Cr_2O_3 + (2-2x)Al_2O_3 + xNH_4H_2PO_4 \rightarrow (Ca_{3-x}Cr_x)(Al_{2-2x}P_x\square_x)O_6 + (3-x)CO_2\nearrow + xNH_3\nearrow + 2xH_2O\nearrow.$$

The products $(Ca_{3-x}Cr_x)(Al_{2-2x}P_x\square_x)O_6$ will be quoted A(CrP)*x*. Table 1 gives the corresponding chemical compositions (wt.% oxide). One part of these samples was assigned to DTA and to the determination of enthalpy variations. The other part was heated slowly from 300°C to 1000°C with an intermediate grinding and compacted in pellets. The pellets were heated at 1100°C and 1250°C for 24 h and finally cooled rapidly under air atmosphere. The identification of the crystalline phases in the products was made by XRD using a Siemens D 5000 diffractometer with Cu K_α radiation. The free lime content was determined by the ammonium acetate method [19].

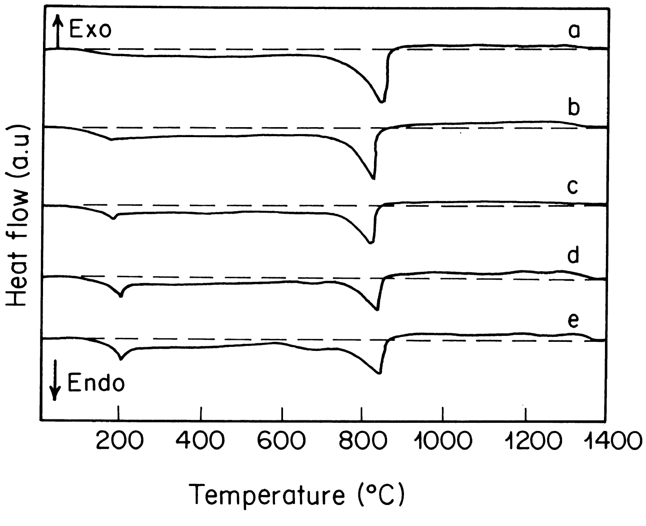

Fig. 1. DTA thermograms of starting samples: (a) A(CrP)0, (b) A(CrP)0.02, (c) A(CrP)0.05, (d) A(CrP)0.10, (e) A(CrP)0.15.

The temperatures of decarbonation were measured by a DTA using a heating rate of about 5°C min^{-1} (samples of 300–400 mg). The temperature was measured with a Pt/Pt – Rh (10 wt.%) thermocouple.

In order to determine the enthalpy variations, an isothermal calorimetric study was carried out using a high-temperature TIAN CALVET calorimeter ($T \leq 1100$°C). The thermal effect was measured by Pt/Pt – Rh (13 wt.%) thermopiles [20]. The atmosphere was pure argon in order to prevent the oxidation of Cr^{3+} ions. The standardization of the calorimeter was made with α alumina of the US-NBS laboratory [21]. The calorimeter was set at constant chosen temperature. The sample initially at room temperature was drooped into the measurement cell at higher temperature. The enthalpy increment of the sample to reach the fixed temperature was measured.

3. Results

3.1. DTA

The thermograms of pure and doped samples are given in Fig. 1. The specific temperatures of decarbonation are presented in Table 1.

A little endothermic peak located at 190°C has been identified only in the doped compositions. It is due to two

Table 2
Enthalpy variations (J/g) of A(CrP)*x* starting mixtures as a function of temperature

	Temperature (°C)			
A(CrP)*x* samples	605	656.6	842	938
A(CrP)0	613.46	682.12	2472.45	3127.73
A(CrP)0.02	637.24	690.38	2343.28	3069.90
A(CrP)0.05	648.1	733.57	2322.03	2972.12
A(CrP)0.10	723.15	793.49	2420.74	3126.59

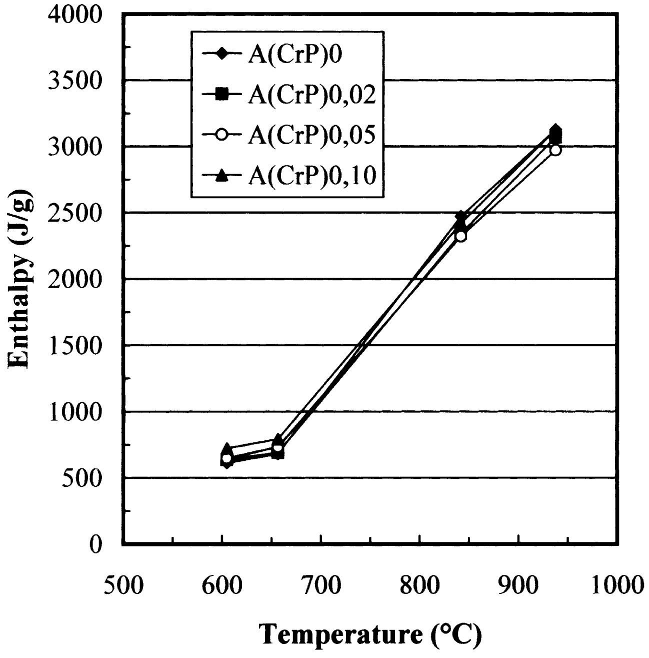

Fig. 2. Enthalpy variations as a function of temperature of the A(CrP)x as starting mixtures ($600 < T < 938°$).

effects that overlap: the melting and the onset decomposition of $NH_4H_2PO_4$ [22]. The DTA thermogram of pure $NH_4H_2PO_4$ confirms this explanation.

The main endothermic effect due to the decarbonation begins beyond 600°C. It appears that the temperature onset of the $CaCO_3$ decomposition decreases when the concentrations of Cr_2O_3–P_2O_5 increase from 0.56–0.52 to 1.41–1.31 wt.%, respectively. Beyond those values, an increase of the temperature of the onset of the decarbonation was observed.

A critical composition of the dopants (Cr_2O_3 1.41 wt.%–P_2O_5 1.31 wt.%), which corresponds to a minimal temperature (612°C) of the decarbonation onset, can be determined. Also, an exothermic effect was observed by DTA behind the end of the decarbonation and which went up to 1300°C.

3.2. Enthalpimetry

The enthalpy variations of all the mixtures, between 600°C and 938°C, are reported in Table 2 and plotted in Fig. 2. The results showed that the reaction of the decarbonation started at about 650°C and went up to 938°C. At about 840°C, a decrease of the enthalpy variation was observed when the concentrations of Cr_2O_3–P_2O_5 increased from 0.56–0.52 to 1.41–1.31 wt.%, respectively. For samples at higher concentrations, the enthalpy increments increased. The same evolution at 938°C was observed.

Powders obtained after the heating of the A(CrP)x samples in the calorimeter at 938°C were examined using XRD. The corresponding patterns are presented in Fig. 3. An increase in the concentrations of CaO and Al_2O_3 was observed for the pure samples. Moreover, a very weak peak attributed to the CA phase appeared. A decrease of the CaO and Al_2O_3 content was observed with an increase of the concentration of Cr_2O_3 and P_2O_5. The A(CrP)0.05 sample gave only a little amount of CA phase. A weak X-ray peak corresponding to $CaCr_2O_4$ compound also appeared in the pattern. The 2.82–2.64 wt.% of A(CrP)0.10 sample showed the onset of formation of a small quantity of C_3A, $C_{12}A_7$ along with $Ca_2P_2O_7$. The formation of the hydroxide $Ca(OH)_2$ was due to the reaction of CaO with the absorbed water from the air atmosphere.

3.3. XRD

The pattern of the crystalline phases present in the samples heated at 1100°C and 1250°C is given in Fig. 4. The expanded portions around 33.3°, 47.7° and 59.4° of the XRD pattern of the synthesized samples ($x = 0.05$) at 1250°C are shown in Fig. 5. At 1100°C, the samples showed the same mineralogical composition, constituted essentially with $C_{12}A_7$ and C_3A. Thus, as the concentration of dopants increases, the crystalline phase $C_{12}A_7$ becomes more abundant. The mineralogical analysis

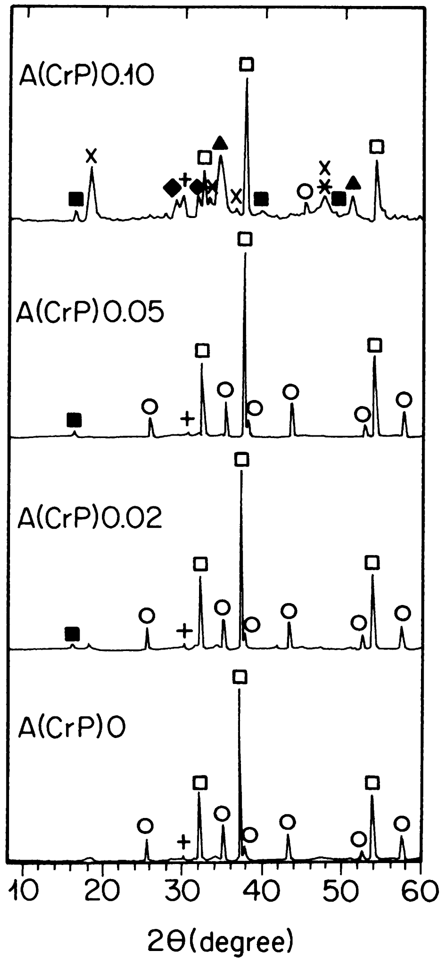

Fig. 3. XRD patterns of A(CrP)x as starting materials heated in the calorimeter at 938°C: (✱) C_3A, (×) $C_{12}A_7$, (+) CA, (■) $CaCr_2O_4$, (◆) C_2P, (□) CaO, (○) Al_2O_3, (▲) $Ca(OH)_2$.

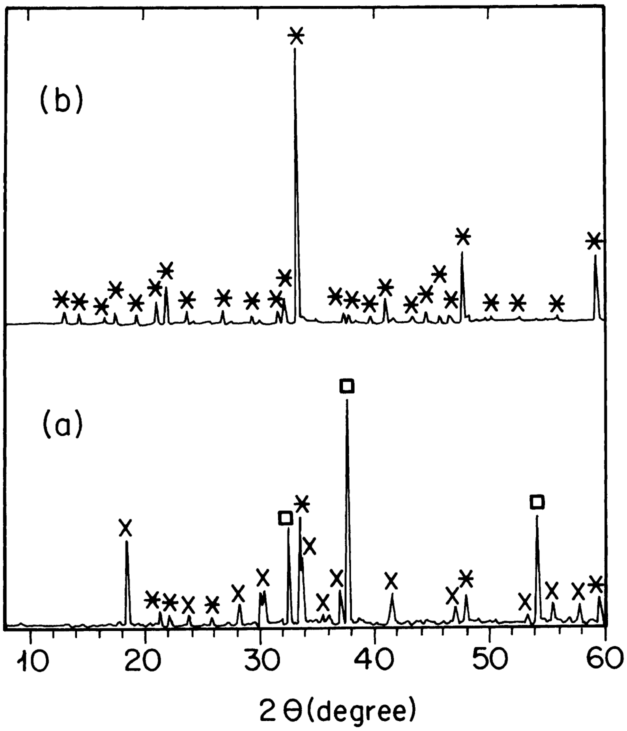

Fig. 4. XRD patterns of A(CrP)*x* synthesized samples at: (a) 1100°C, (b) 1250°C. Symbols: (✻) C_3A, (×) $C_{12}A_7$, (□) CaO.

showed also that all the A(CrP)*x* samples present the same diffraction patterns, whereas the only crystalline phase present at 1250°C is the tricalcium aluminate in the cubic form. This phase is indicated by the characteristic diffraction peak at $d = 2.70$ Å, $d = 1.91$ Å and $d = 1.56$ Å corresponding to the main reflection, respectively, (440), (008) and (844) [23,24].

3.4. Free lime analysis

The free lime concentration in the final products obtained by the treatment for 24 h at 1250°C was of 0.27 wt.% in the pure sample, while it is not present in any composition with added chromium and phosphorus.

4. Discussion

The X-ray analysis of the A(CrP)*x* samples heated at 1100°C indicates that the amount of the crystalline phase $C_{12}A_7$ is higher when the concentrations of additives increase. That is probably due to the mineralizing effect of P_2O_5, which had formed a solid solution with $C_{12}A_7$ in the rich lime region of the ternary system $CaO-Al_2O_3-P_2O_5$ [25,26].

The mineralogical evolution at 1250°C reveals that the tricalcium aluminate is formed with Cr and P oxides inclusions, less than 4.24 wt.% Cr_2O_3 and 3.97 wt.% P_2O_5, respectively.

From our observation, we suggest that Cr_2O_3 and P_2O_5 are entering the C_3A crystal lattice without modification in the symmetry. In the XRD pattern, the peaks of synthesis-doped tricalcium aluminate occur at higher 2θ values than pure C_3A, which agrees with the results obtained by Takéuchi et al. [27]. They found that the lattice parameters of doped C_3A were smaller than those for pure C_3A.

Therefore, the chromium ions can exist in the structure of C_3A as Cr^{3+}, Cr^{4+} and/or Cr^{5+}, where Cr^{3+} could be located in octahedral sites of calcium ions and Cr^{4+} and Cr^{5+} in aluminium tetrahedral positions of the lattice [28]. The ionic radius of Cr^{3+} (0.615 Å) is larger than that of Al^{3+} (0.39 Å) [29]. According to the work of Boikova [30], the phosphorus as PO_4 entities can take the place of AlO_4 groups in tricalcium aluminate structure.

The absence of free lime in the C_3A synthesized solid solutions was due to the high burnability with the addition of Cr_2O_3 and P_2O_5. The DTA test showed the decrease of the decarbonation temperature with an increase in composition from $x = 0.02$ to 0.05. Beyond this value, an increase in the temperature of decomposition of $CaCO_3$ was observed. Ahluwalia and Mathur [31] made the same conclusion. They noticed a decrease of the decarbonation temperature with an increase of Cr_2O_3 content up to 1 wt.%.

The decarbonation onset temperature decreases from 646°C to 612°C, respectively, for Cr_2O_3/P_2O_5 (wt.%) compositions ranging between 0.56/0.52 and 1.41/1.31 in the $CaO/Al_2O_3 \approx 3$ (molar ratio) mixtures. This phenomenon corresponds to the reduction in the decarbonation temperature of about 34°C. Above these compositions, there was an increase in the temperature up to 627°C or 690°C for high dopant contents. The study carried out by Agarwal et al. [2] on the thermal decomposition of $CaCO_3$ with $CaCl_2$ addition lead to the conclusion that the addition of 6.6 wt.% induces a minimum of about 35°C for the decarbonation temperature.

The exothermic effect observed after the end of the A(CrP)*x* samples decarbonation is mainly attributed to the crystallisation of the CA, $C_{12}A_7$ and C_3A phases [32]. In the $CaO-Al_2O_3$ system at the 3:1 molar ratio, Cüneyt Tas [33] have shown that the powders heated in the temperature of

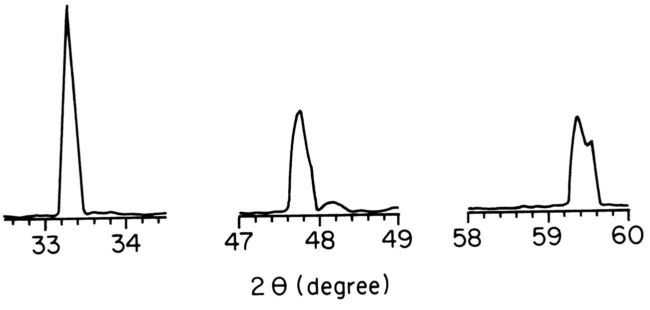

Fig. 5. An example of expanded portions of the XRD patterns of A(CrP)*x* synthesized samples ($x = 0.05$) at 1250°C.

950°C exhibited a phase mixture of CA, $C_{12}A_7$ and C_3A. Single phase of C_3A powders could be obtained by thermal treatment over 1050°C.

The formation of C_3A between 980°C and 1370°C results from a reaction between the intermediate phases CA, $C_{12}A_7$ and CaO. CA and $C_{12}A_7$ phases are often observed as intermediate products in laboratory experiments using pure chemical raw meals. C_3A is usually a final product [34,35].

Enthalpimetry data obtained from the mixtures with the $CaO/Al_2O_3 \approx 3$ molar ratio give a decrease of enthalpy around 840°C and 940°C. The enthalpy maximum reduction is observed with 1.41 wt.% Cr_2O_3 and 1.31 wt.% P_2O_5 concentrations. This result is in agreement with our DTA measurements.

The total enthalpy increment up to 938°C of the mixture without additives is 3128 J/g, while the A(CrP)0.02 and A(CrP)0.05 mixtures required 3069 and 2972 J/g, respectively. Thus, the energy consumption with compositions ranging between $x = 0.02$ and 0.05 is reduced comparatively to that of the dopants free mixtures.

The addition of Cr_2O_3 and P_2O_5 in A(CrP)x samples fired at 938°C promotes the exothermic formations of C_3A, $C_{12}A_7$ and some new compounds such as $CaCr_2O_4$ and C_2P which induce the decrease of enthalpy. On the other hand, it is well known [36] that the crystallisation of the tricalcium aluminate phase occurs by the diffusion of CaO in $C_{12}A_7$. The present work confirms this diffusion, which is favoured at 938°C with the mineralizing effect of chromium and phosphorus.

5. Conclusion

The simultaneous additions of chromium and phosphorus oxides up to 1.41 and 1.31 wt.%, respectively, lower the temperature decomposition of $CaCO_3$ and improve the burnability of the synthesized doped tricalcium aluminate. The corresponding reduction of temperature decarbonation was about 34°C. The energy consumption during the decarbonation and the formation of the tricalcium aluminate decreased also with an increase of the concentration of the chromium and the phosphorus oxides.

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