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The effect of Cr_2O_3 and P_2O_5 additions on the phase transformations during the formation of calcium sulfoaluminate $C_4A_3\bar{S}$

My.Y. Benarchid, J. Rogez *

Laboratoire TECSEN, UMR 6122, CNRS-FST de Saint Jérôme, Case 251, Avenue Escadrille Normandie Niemen, 13397 Marseille Cedex 20, France

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Abstract

The study describes the influence of chromium and phosphorus additions on the phase transformations during the formation of the calcium sulfoaluminate $Ca_4Al_6SO_{16}$ from $CaCO_3-Al_2O_3-CaSO_4$ mixtures. The temperatures of decarbonation reaction were measured by means of differential thermal analysis. The enthalpy variations at different heating temperatures were determined by isothermal calorimetry. The results show that the Cr_2O_3 and P_2O_5 additions lower the onset temperature of decarbonation. The energy requirement at high temperature of the doped mixtures is less, compared to that of mixtures without dopants. The formation of solid solutions is followed by X-ray diffraction. The higher concentrations of additives hinder the formation of the $C_4A_3\bar{S}$ phase.

Keywords: Calorimetry; Thermal analysis; $CaCO_3$; Sulfoaluminate; Mineralizers

1. Introduction

The manufacture of Portland clinker requires a high thermal and mechanical energy. The major part of this energy is consumed during the endothermic process of calcium carbonate decomposition in raw meal and during the formation of the Ca_3SiO_5 (C_3S) phase. One of the main aims of the cement industry is to reduce this energy consumption. Several authors have already studied the influence of minor elements present in or added to the raw meal, on the $CaCO_3$ decomposition and on the formation of the clinker phases [1–9]. The use of fluxes and mineralizers, which can reduce the clinkerization temperature and accelerate the formation rate of clinker phases, is one of the processes that is more studied and may be used to decrease the enthalpy of clinker formation and thus to obtain low energy cements [10–17].

Recently, many researchers were interested in the use of mineralizer elements, not only for reducing the energy cost of cement production, but also for increasing the mechanical strengths. Beside the formation of the active belite, these researchers suggested that the role generally attributed to the alite C_3S in the increase of early strengths could be played by other phases elaborated at low temperature [18]. One of the most promising is the calcium sulfoaluminate $Ca_4Al_6SO_{16}$ ($C_4A_3\bar{S}$) that can be easily formed above 1200 °C in the industrial raw containing calcium sulfate $CaSO_4$ and is stable up to 1400 °C. The clinkerization temperature of this type of raw meal is low (1200–1250 °C) compared to the one of the ordinary Portland cement (1400–1450 °C). The obtained final product contains a high proportion of the calcium sulfoaluminate phase $C_4A_3\bar{S}$ which can replace tricalcium silicate C_3S, the main component of the common ordinary cement clinker, in the development of early strengths [13,19]. This type of cement exhibits a 25% energy saving and can give high early strengths as 35 and 60 MPa, respectively, after 1 and 28 days. It can also develop a good durability, especially in a sulfate environment [20,21].

Ragozina has described the formation of a ternary compound in the $CaO-Al_2O_3-SO_3$ system by the reaction of calcium sulfate with aluminates at 1200 °C [22].

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* Corresponding author. Tel.: +33 4 91 28 28 87; fax: +33 4 91 28 28 86.
E-mail address: j.rogez@univ.u-3mrs.fr (J. Rogez).

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Halstead and Moore have confirmed the formula of the ternary phase as $3CaO{\cdot}3Al_2O_3{\cdot}CaSO_4$ ($C_4A_3\bar{S}$) and reported that $C_4A_3\bar{S}$ exhibited a body-centered cubic structure with $a = 18.39$ Å [23]. Valenti et al. have studied the high temperature synthesis of calcium sulfoaluminate $C_4A_3\bar{S}$, indicating a considerable reduction in the temperature and time required for completion of the $C_4A_3\bar{S}$ synthesis, owing to the fluxing and mineralizing properties of phosphogypsum impurities compared to pure gypsum [24]. Several authors have studied the role of chromium in promoting the formation and the strength development of Portland cement clinker [25–28]. They have shown that the chromium enhances the burnability of the cement raw meal and increases the early strength of cement pastes. The effect of Cr_2O_3 on the $CaO{-}Al_2O_3{-}SO_3$ system was investigated by Ivashchenko [29], indicating that the solubility limit of chromium in the calcium sulfoaluminate is 5 wt.%, and the mineral formation reactions of $C_4A_3\bar{S}$ are intensified and the thermal stability at high temperature is raised. The hydration study of the modified calcium sulfoaluminate with chromium indicated an improvement of the strength properties compared to that of the chromium-free $C_4A_3\bar{S}$. The effect of phosphorus on the phase transformations during the formation of cement clinker was also investigated. Halicz et al. [30] have reported that P_2O_5 like Al_2O_3 decreases the melting point of the raw meal. Chae et al. [31] have studied the formation of the calcium sulfoaluminate by adding calcium phosphate as $CaHPO_4{\cdot}2H_2O$ (3 wt.%). They have noticed that phosphorus hinders the $C_4A_3\bar{S}$ formation. The P_2O_5 oxide amount incorporated in the calcium sulfoaluminate phase was only of 0.20 wt.%. The solubility limit is probably higher.

In the literature, few systematic studies are devoted to the heat of formation of calcium sulfoaluminate from initial mixtures in the presence of foreign elements [32]. The aim of this work is to study the effect of simultaneous additions of chromium and phosphorus on the phase transformations during the formation of the calcium sulfoaluminate $C_4A_3\bar{S}$ phase from a mixture $CaCO_3{-}Al_2O_3{-}CaSO_4$ at the (3 : 1 : 1) molar ratio. The temperatures of decarbonation reaction are determined by means of differential thermal analysis. The enthalpy variations of the reaction at various temperatures are measured through isothermal calorimetry. The synthesized solid solutions are analyzed by X-ray diffraction.

2. Experimental

Starting materials are synthesized from stoichiometric amounts of reagent grade $CaCO_3$, Al_2O_3, $CaSO_4$, Cr_2O_3 and $(NH_4)_2HPO_4$ provided by Merck (Darmstadt, Germany) with >99% purity. The mixtures are ground in an agate mortar with ethanol as dispersive and homogeneity medium. The chemical reaction adopted is as follows:

$$\begin{aligned}&(3-x)CaCO_3 + x/2Cr_2O_3 + (3-x/2)Al_2O_3\\&\quad + (1-x)CaSO_4 + 2x(NH_4)_2HPO_4 \rightarrow (Ca_{4-2x}Cr_x)\\&\quad \times (Al_{6-x}S_{1-x}P_{2x})O_{16} + (3-x)CO_2^{\nearrow} + 4xNH_3^{\nearrow}\\&\quad + 3xH_2O^{\nearrow}\end{aligned}$$

In that reaction, only one Cr substitutes two Ca. The resulting missing charge is compensated by the phosphorus addition. The mixtures for $0 \le x \le 0.075$ are quoted S(CrP)x and the corresponding chemical compositions (wt.% oxide) are reported in Table 1. One part of the mixtures is devoted to differential thermal analysis and the enthalpy measurements. The other part is thermally treated in laboratory furnace between 300 and 1000 °C by steps of 200 °C, with an intermediate grinding in order to increase the homogeneity, and pelletized. The pellets are heated at 1100 and 1250 °C during 12 h and finally rapidly quenched in air.

The reactions of decarbonation and calcium sulfoaluminate formation are observed by differential thermal analysis (DTA) from room temperature to 1500 °C at constant heating rate of about 5 °C min^{-1} (samples of 200–300 mg) with pure gold as reference material. The enthalpy variations are measured by isothermal calorimetry using a high temperature Tian–Calvet calorimeter. The sensors consist in two thermopiles constituted by hundreds of thermocouples Pt/Pt-Rh 13% [33]. Samples of about 30 mg are dropped at room temperature into the calorimetric cell, which is brought at various successive temperatures. At each temperature, the enthalpy variation is determined by time integration of the instantaneous heat flux over the whole duration of the occurring phenomenon. The atmosphere is argon. The calorimeter is standardized by drops of α alumina provided by US-NBS laboratory [34], the enthalpy variations of which between ambient and experimental temperatures are well known. Identification of the crystalline phases in the synthesized solid solutions at 1100 and 1250 °C is performed by X-ray diffraction using a Siemens D-5000 diffractometer with Cu K_α radiation.

Table 1
Chemical compositions (wt.%) and specific temperatures of the decarbonation step (reported from DTA thermograms) of S(CrP)x starting mixtures

S(CrP)x samples	CaO	Al_2O_3	$CaSO_4$	Cr_2O_3	P_2O_5	Onset temperature	Maximum temperature peak	Final temperature
S(CrP)0	27.56	50.12	22.31	0.00	0.00	639	915	938
S(CrP)0.01	27.49	50.06	22.09	0.12	0.23	610	906	929
S(CrP)0.025	27.36	49.97	21.77	0.31	0.58	603	905	926
S(CrP)0.05	27.16	49.81	21.23	0.62	1.17	649	905	923
S(CrP)0.075	26.96	49.65	20.69	0.94	1.75	654	903	930

3. Results

3.1. Differential thermal analysis

The thermograms of the mixtures $CaCO_3$–Al_2O_3–$CaSO_4$ (3 : 3 : 1) without and with addition of Cr_2O_3 and P_2O_5 ($x = 0.01$) are shown in Fig. 1. The endothermic peak observed at 190 °C, is relative to the dehydration of hemihydrate $CaSO_4 \cdot 1/2H_2O$ formed by reaction of anhydrite $CaSO_4$ with air atmosphere. A weak endothermic peak located at 300 °C is due to the $CaSO_4$ (III)→$CaSO_4$ (II) transition.

The expanded portions around 500 to 1000 °C of the DTA thermograms of the S(CrP)*x* starting samples are shown in Fig. 2. The specific temperatures of decarbonation step are given in Table 1 and are represented in Fig. 3. The major endothermic effect associated to the decarbonation reaction starts beyond 600 °C. The onset temperature of calcium carbonate decomposition lowers with the increase of concentration of the additives (Cr_2O_3–P_2O_5) ranging (0.12–0.23) to (0.31–0.58) wt.%. A weak endothermic effect occurs below the onset decarbonation reaction and is in particular observable for the $x = 0.05$ and $x = 0.075$ compositions. This effect increases with the value of *x*, due to the formation of a liquid phase in the rich chromium–phosphorus mixtures under the flux effect of Cr_2O_3 and P_2O_5 oxides [25,30]. This phenomenon increases the apparent onset temperature of the endothermic reaction of $CaCO_3$ decomposition.

The thermal effect corresponding to the melting point of gold, used as temperature reference, is observed at 1064 °C [35]. The endothermic effect located at 1215–1230 °C is due to the $CaSO_4$ (II)→$CaSO_4$ (I) transition. An exothermic peak observed around 1300–1325 °C is associated mainly to the formation of calcium sulfoaluminate $Ca_4Al_6SO_{16}$ ($C_4A_3\bar{S}$) by the chemical reaction (3 CA + $CaSO_4$ → $C_4A_3\bar{S}$) at high temperature. An endothermic effect occurs at around 1390 °C is attributed to the melting of calcium aluminates in the CaO–Al_2O_3 system.

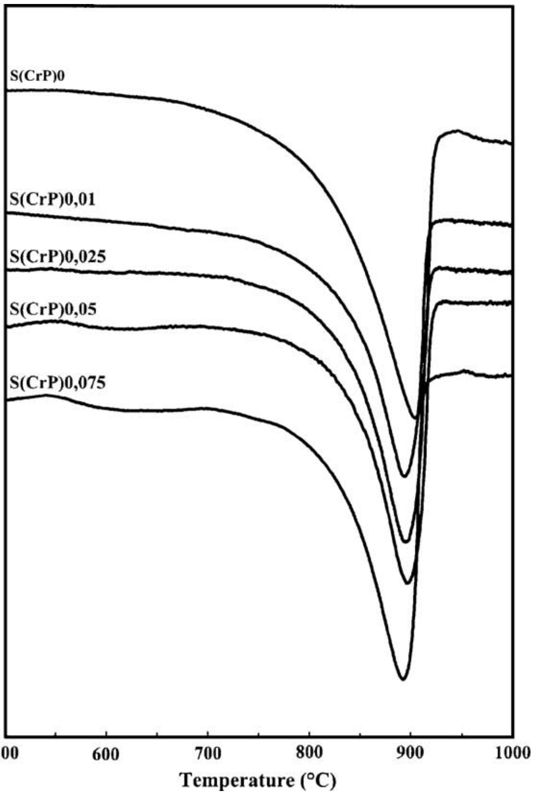

Fig. 2. Expanded portion of the DTA thermograms of S(CrP)*x* starting mixtures.

3.2. Enthalpimetry

The enthalpy variations at the temperature ranging 700–1075 °C of the S(CrP)*x* starting mixtures are reported

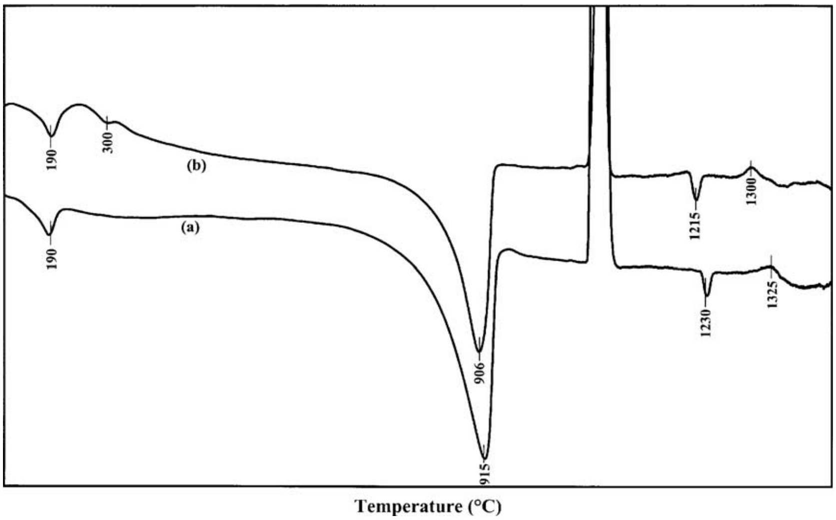

Fig. 1. DTA thermograms of starting samples: a) S(CrP)0, b) SCrP)0.01.

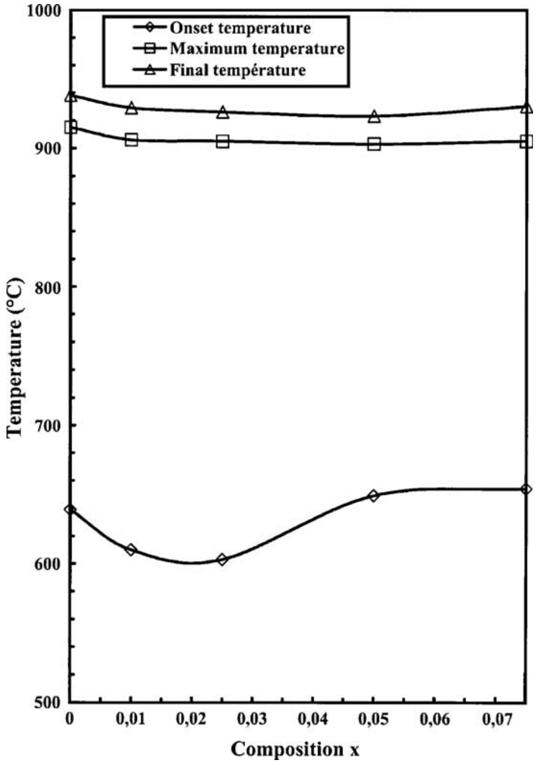

Fig. 3. Specific temperatures of decarbonation step as a function of the composition *x* of the S(CrP)*x* starting mixtures.

in Table 2 and are illustrated in Fig. 4. The results show that at 700 °C, the value of the enthalpy variation increases slightly as the phosphorus and chromium content increases. This is due to the endothermic reaction of $(NH_4)_2HPO_4$ decomposition, the concentration of which increases while passing from the mixture without addition S(CrP)0 to the doped mixture S(CrP)0.075. Around 843 °C, the enthalpy increases significantly from 812 to 1465 J/g for the S(CrP)0 sample and from 967 to 1580 J/g for S(CrP)0.075. This phenomenon is attributed to the decarbonation reaction, which starts at lower temperature and the maximum temperature peak is near 843 °C, according to the DTA observation. At 953 °C, the enthalpy decreases with the increase of the Cr_2O_3 and P_2O_5 concentrations from (0.12–0.23) to (0.62–1.17) wt.%. The optimal measured value of enthalpy is 1594 J/g. For the rich chromium and phosphorus composition S(CrP)0.075, the enthalpy increases. The same evolution is observed at 1075 °C.

Table 2
Enthalpy variations (J/g) of S(CrP)*x* starting mixtures versus temperature

	Temperature (°C)			
S(CrP)*x* samples	700	843	950	1075
S(CrP)0	812	1465	1677	1921
S(CrP)0.01	883	1491	1624	1789
S(CrP)0.025	908	1535	1609	1745
S(CrP)0.05	926	1554	1594	1734
S(CrP)0.075	967	1580	1651	1822

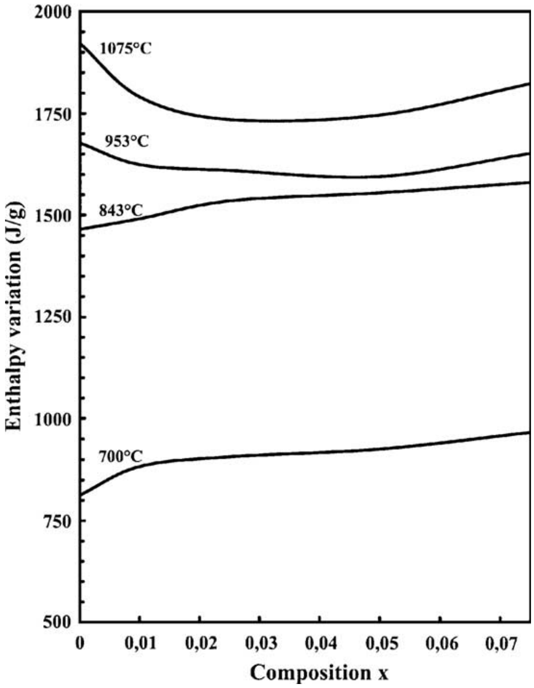

Fig. 4. Enthalpy variations versus the composition *x* of the S(CrP)*x* starting mixtures.

3.3. High temperature mineralogy

At 1100 °C, the S(CrP)0 pure sample and the S(CrP)0.01–S(CrP)0.075 doped samples show the same mineralogical composition with the predominance of $C_4A_3\bar{S}$ phase and a small quantity of CA phase along with anhydrite $CaSO_4$ is also detected. A decrease of the CA and $CaSO_4$ amount was observed with an increase of the concentration of Cr_2O_3 and P_2O_5 oxides. The mineralogical analysis of the samples heated at 1250 °C indicates that the compositions ranging up to 0.05 are only constituted by the crystalline phase $C_4A_3\bar{S}$ (Fig. 5A). This phase is identified by XRD peak at $d=3.74$ Å, $d=2.65$ Å and $d=2.17$ Å [36]. The sample S(CrP)0.075 shows that complete formation of calcium sulfoaluminate phase is not achieved and small amount of the CA phase is identified (Fig. 5B).

4. Discussion

The DTA test carried out on S(CrP)*x* starting mixtures of $CaCO_3$–Al_2O_3–$CaSO_4$ system with added Cr_2O_3 and P_2O_5 oxides, shows a decrease of the onset temperature of $CaCO_3$ decomposition with the increase of the dopant concentrations. It lowers from 639 °C for the mixture without addition to 603 °C for the optimal composition of the dopants (Cr_2O_3 0.31 wt.%–P_2O_5 0.58 wt.%), inducing a reduction of the onset decarbonation temperature of about 36 °C. Above these concentrations, an increase of the temperature is observed up to 649 °C or 654 °C. The study carried out by Agarwal et al. [37] on the thermal decomposition of $CaCO_3$ with $CaCl_2$

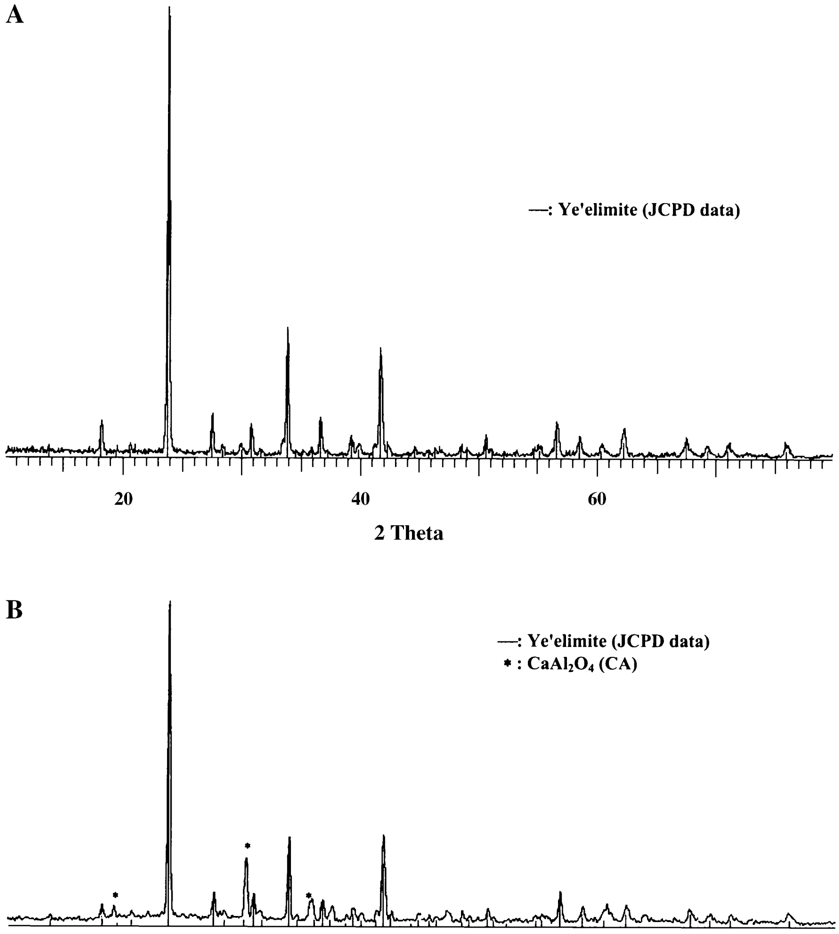

Fig. 5. X-ray diffraction patterns of S(CrP)*x* synthesized samples at 1250 °C. A) S(CrP)0–S(CrP)0.05, B) S(CrP)0.075.

addition; shows that the content of 6.6 wt.% leads to a decrease of about 35 °C for the decarbonation temperature. Several researchers have studied the effect of various additives on the kinetic of $CaCO_3$ decomposition [9,38–41]. Ahluwalia and Mathur [8] have reported that the addition of chromium as Cr_2O_3 lowers the onset temperature of decarbonation when the concentration increases from 0.1 to 1 wt.%. Then, the decrease of the onset temperature seems to be much bigger in the simultaneous addition of the two oxides than when only Cr_2O_3 is added. According the DTA results, the formation of calcium sulfoaluminate $C_4A_3\bar{S}$ by the exothermic reaction of calcium sulfate $CaSO_4$ with aluminate CA, takes place around 1300 °C. This formation occurs in solid state by direct diffusion reactions between the constituent oxides as well as through the layer formed by intermediate calcium aluminates of the $CaO–Al_2O_3$ reaction.

In the doped raw mixtures, the endothermic reaction of calcium carbonate decomposition starts at lower temperature than that of the pure mixture. That is in agreement with the enthalpimetry measurements that show an increase of the enthalpy variations at 843 °C. At high temperature, the enthalpy variations exhibit a decrease as the chromium and phosphorus contents increase. The minimal value is observed for the composition $x = 0.05$ of the doped mixtures. That is due to the effect of Cr_2O_3 and P_2O_5 oxides, which can promote the exothermic reaction of the crystallization of the intermediate phase CA resulting from a reaction in solid state between the CaO produced from the decarbonation of $CaCO_3$ and Al_2O_3. This crystallization leads to the decrease of the energy exchange during the burning in the calorimeter of the doped raw mixtures. For the composition behind $x = 0.05$, an increase of the enthalpy variations is observed, due to the partial melting of the starting mixtures through the effect of chromium and phosphorus. The enthalpy necessary to heat the starting mixture without additives S(CrP)0 from room temperature to 1075 °C is 1921 J/g; whereas the S(CrP)0.01, S(CrP)0.025 and S(CrP)0.05 mixtures require respectively only 1789, 1745, and 1734 J/g. Consequently, the energy consumption of the compositions ranging between $x = 0.01$ and 0.05, are less compared to that of the composition without dopants, corresponding to a reduction of the enthalpy of about 5%–7%.

The X-ray analysis of S(CrP)*x* samples synthesized at 1250 °C, shows the formation of the cubic polymorph of calcium sulfoaluminate at Cr_2O_3 and P_2O_5 inclusions respectively less than 0.62 and 1.17 wt.%. Beyond these concentrations, the formation of the $C_4A_3\bar{S}$ phase is delayed, and the solid solutions of the CA phase persist. This phenomenon is due mainly to the presence of the phosphorus that hinders the chemical transformation 3 $CA + CaSO_4 \rightarrow C_4A_3\bar{S}$ at high temperature. Through the formation of solid solutions, the phosphorus enlarges the stability field of the CA phase at the expense of the $C_4A_3\bar{S}$ field. This process can be compared to that shown by Chae et al. [31]. They have noticed that additives like calcium phosphate hinder calcium sulfoaluminate crystallization at 1250 °C. On the other hand, in solid solutions of doped $C_4A_3\bar{S}$ at higher amount of additive, the presence of chromium does not influence the effect of phosphorus. In the XRD pattern, the peaks of synthesized cubic chromium–phosphorus doped calcium sulfoaluminate occur at lower 2θ values compared with the pure $C_4A_3\bar{S}$. Thus, in the structure of $C_4A_3\bar{S}$, the chromium ions as Cr^{6+} (ion radius = 0.26 Å) can be located in the tetrahedral sites of aluminum ions as Al^{3+} (ion radius = 0.39 Å) [29]. The phosphorus as PO_4 can replace the AlO_4 and SO_4 groups. The lattice of the doped $C_4A_3\bar{S}$ exhibits an expansion inasmuch as the ionic radius of P^{5+} (0.17Å) is larger than that of S^{6+} (0.12 Å). The intensities of the diffraction peaks of doped $C_4A_3\bar{S}$ phase are higher than in the additives-free sample. In the samples fired at 1100 °C, a decrease of the calcium aluminate CA and anhydrite $CaSO_4$ amount was observed with an increase of the concentration of chromium and phosphorus. Thus, the crystalline phase $C_4A_3\bar{S}$ in the doped samples became more abundant compared to the pure sample, indicating that Cr_2O_3 and P_2O_5 oxides promote formation of the calcium sulfoaluminate mineral at 1100–1250 °C.

5. Conclusion

The main conclusions to be drawn from the obtained results can be summarized as follows:

(a) The temperature of decarbonation reaction in a $CaCO_3–Al_2O_3–CaSO_4$ system decrease with the increase of Cr_2O_3 and P_2O_5 addition, respectively, up to 0.31 and 0.58 wt.%.
(b) The energy requirement for the reactions at high temperature of doped starting mixtures is less than that of starting mixtures without additions. The corresponding reduction of energy is about 5%–7%.
(c) The formation of solid solutions based on $C_4A_3\bar{S}$ is hindered for rich concentrations of additives, mainly due to the phosphorus effect that enlarges the stability field of the CA phase at the expense of the calcium sulfoaluminate field.

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