Available online at www.sciencedirect.com

ScienceDirect

Journal of the European Ceramic Society 27 (2007) 1781–1784

www.elsevier.com/locate/jeurceramsoc

Chemical synthesis of hydraulic calcium aluminate compounds using the Pechini technique

A. Gaki, R. Chrysafi, G. Kakali *

National Technical University of Athens, Chemical Engineering Department, Labs of Inorganic and Analytical Chemistry,
9 Heroon Polytechniou Street, 15773 Athens, Greece

Abstract

$3CaO{\cdot}Al_2O_3$ and $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$ are two of the main compounds in portland cement and are conventionally prepared by sintering the solid oxide mixture above 1350 °C for many hours. The Pechini technique is a polymeric precursor route for the synthesis of ceramics. In this work, an equimolar mixture of C_3A and C_4AF was prepared by the Pechini technique. The preparation of the precursor mixture and the formation of the ceramic product were monitored using TG/DTA, XRD, FTIR and SEM. The combination of these techniques led to the recording of all the transformations occurring during the processing of the precursors and the formation of the final products. As it was concluded, the Pechini technique can be successfully applied for the preparation of $3CaO{\cdot}Al_2O_3$ and $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$ mixtures. The final products consists of fine and well-formed grains of $3CaO{\cdot}Al_2O_3$ and $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$. Their formation requires a 3-h sintering at 1000 °C.

Keywords: Calcium aluminates; Powders-chemical preparation

1. Introduction

Portland cement is the main construction material of our age with a world production of 2000×10^6 tonnes in 2004. Ordinary portland cement (OPC) consists of four main phases: $3CaO{\cdot}SiO_2$ (C_3S),[a] $2CaO{\cdot}SiO_2$ (C_2S), $3CaO{\cdot}Al_2O_3$ (C_3A) and $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$ (C_4AF). The silicate compounds are responsible for the development of mechanical strength, while the aluminate compounds are mainly responsible for the setting of cement. The formation and hydration chemistry of clinker and cement is complex due to the coexistence of multiple binary and ternary phases and the variety of impurities. For this reason, fundamental research on cement chemistry usually starts with pure compounds.

Conventionally, the synthesis of pure cement compounds is performed through solid-state reactions and involves the sintering of stoichiometric mixtures of oxides or carbonates at high temperatures for prolonged time. According to the literature, pure C_3A is produced by sintering $CaCO_3$ and Al_2O_3 once for 18 h and twice for 24 h at 1450 °C, while the formation of pure C_4AF requires sintering three times for 6 h at 1320 °C. In both cases, intermediate grinding is necessary.[1]

Instead of solid-state sintering, alternative low temperature techniques such as sol–gel,[2–4] polymeric precursor processes[5–9] and combustion[9–11] have also been applied for the synthesis of aluminate compounds. Among them, the Pechini technique is known to be simple, cost-effective and versatile. The Pechini synthesis comprises the mixing of nitrate solutions, the complexion of the cations with citric acid, the esterification of the citrate complexes with the addition of ethylene glycol, and the concentration of solution by heating under agitation. When the mixture is heated, polyesterification occurs. Afterwards, the excess solvent is removed and a solid resin is formed. This method allows the mixing of reactants at molecular level and the formation of polymerized macromolecular networks (resins) which withhold large amounts of solvents. The resins that are formed have high porosity, high surface energy and high free energy. As a result the final burning takes place at relatively lower temperatures than these required at solid-state conventional methods.

In this paper, an equimolar mixture of the two cement aluminate compounds ($3CaO{\cdot}Al_2O_3$ and $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$) is synthesized using the Pechini route. A combination of techniques (DTA/TG, XRD, FTIR, SEM) is applied for the characterization of the intermediate and final products. This work is part of a project aiming to the development of alternative low temper-

---

* Corresponding author. Tel.: +30 2107723270; fax: +30 2107723188.
E-mail address: kakali@central.ntua.gr (G. Kakali).

[a] Cement chemistry notation: C, CaO; S, SiO_2; A, Al_2O_3; F, Fe_2O_3.

0955-2219/$ – see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2006.05.002

ature techniques for the synthesis of hydraulic compounds and materials.

2. Experimental

Pure $Ca(NO_3)_2{\cdot}4H_2O$, $Al(NO_3)_3{\cdot}9H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$ were used as the cations' source. The $CaO:Al_2O_3:Fe_2O_3$ molar ratio in the starting mixture was kept to 7:2:1 in order to obtain a equimolar mixture of $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$ and $3CaO{\cdot}Al_2O_3$. The nitrate salts were dissolved in 75 ml of deionized water and citric acid (CA) was then added (molar ratio CA:total cations = 1). The mixture was magnetically stirred until a clear yellowish solution was obtained. Ethylene glycol (EG) was added in this solution in the molar ratio EG:CA = 2. The molar ratios of the reactants ensure the complete chelation of the cations and the complete esterification of citrates. The solution was continuously stirred at 80 °C in order to facilitate the evaporation of the excess water and accelerate the polyesterification reaction. During the polyesterification process no turbidity or precipitation was observed. The polyesterification reaction was monitored through the continuous recording of the conductivity of the solution. The procedure was stopped when the conductivity was diminished and a viscous gel was obtained. The gel was then heated at 150 °C in an oven for 24 h. The xerogel was ground and sintered at various temperatures for 3 h.

Thermogravimetric analysis (TG/DTG) was used in order to record the sintering reactions of the prepared resin. TG and DTG curves were obtained using a Mettler Toledo 851 instrument. The sample was heated from 20 to 1000 °C at a constant rate of 10 °C/min in an atmosphere of air.

XRD and FTIR were used in order to identify the products and check their crystallinity. X-ray powder diffraction patterns were obtained using a Siemens D5000 diffractometer, with Cu $K\alpha_1$ radiation ($\lambda = 1.5405$ Å), operating at 40 kV, 30 mA. The IR measurements were carried out using a Fourier transform IR (FTIR) spectrophotometer (Perkin-Elmer 880). The FTIR spectra in the wavenumber range from 400 to 4000 cm^{-1}, were obtained using the KBr pellet technique. The pellets were prepared by pressing a mixture of the sample and dried KBr (sample:KBr approximately 1:200) at 8 $tonnes/cm^2$.

The xerogel and the sintered sample were examined using a JEOL JSM-5600 Scanning Electron Microscope equipped with an OXFORD LINK ISIS 300 energy dispersive X-ray spectrometer (EDX).

3. Results and discussion

3.1. Gel preparation

Fig. 1 presents the conductivity of the starting solution in relation to time. The conductivity was recorded from the time of the nitrates' addition until the time of the complete gelation of the solution which took place approximately after 2.5 h. The curve in Fig. 1 indicates an abrupt increase of conductivity due to the addition of nitrate salts, while the addition of citric acid and ethylene glycol contributed to a further small increase of conductivity. A sudden raise of the solution's temperature was observed about half an hour after the addition of ethylene glycol. The temperature raise caused a significant raise of the conductivity and it was accompanied by the evolution of orange vapor. The temperature raise indicates that certain exothermic events took place in the solution. Such an event could be a redox reaction between ethylene glycol and nitric ions, which would result in NO_2 gas. This also explains the orange vapors observed. After gelation, the sample was heated at 150 °C for 24 h. During this treatment, dehydration, polyesterification and removal of volatile compounds took place. This results to the swelling of the material and the formation of a crisp aerated xerogel.

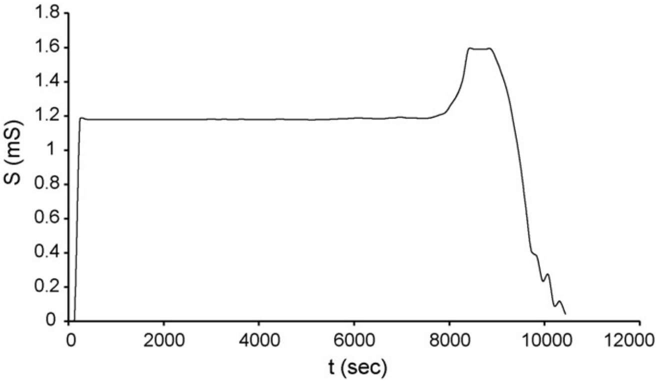

Fig. 1. Conductivity of the precursor solution in relation to time.

Fig. 2 presents the TG, DTG and DTA curves of the xerogel. The total weight loss of the sample is 77.56% (w/w). The 5.10% weight loss at 100 °C is attributed to the loss of moisture, absorbed after the thermal treatment of the gel at 150 °C. The major weight loss of the sample (60.75%) took place between 200 and 500 °C, in two stages, probably associated with the dissociation of the polymer's network and the burning of organic carbon. There is also a weak endothermic effect at 850 °C, involving a low weight loss, which may be due to the decomposition of calcium carbonate. Other researchers have also reported the formation of carbonates during the processing of Pechini precursors.[9] This is probably due to the reaction between calcium and CO_2 evolved during the burning of organic carbon. The formation reactions of $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$ and $3CaO{\cdot}Al_2O_3$ are not recorded due to their low heat content. The total ceramic yield, according to TG curve, is 22.42%.

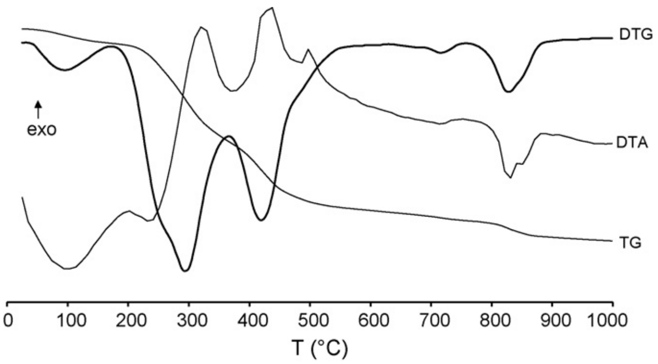

Fig. 2. TG/DTG/DTA curves of xerogel.

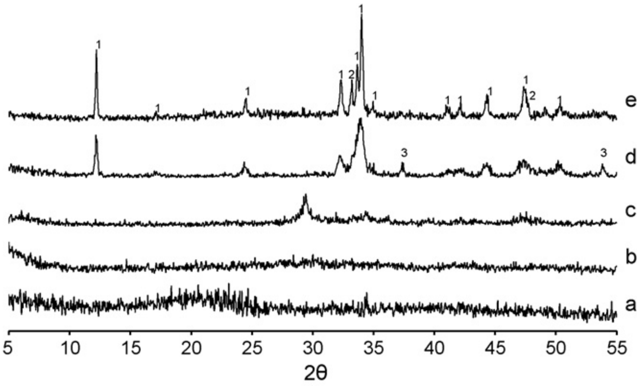

Fig. 3. X-ray diffraction patterns of dried gel and the sintered products: (a) xerogel; (b) 400 °C; (c) 600 °C; (d) 800 °C; (e) 1000 °C. (1) C_4AF; (2) C_3A; (3) CaO.

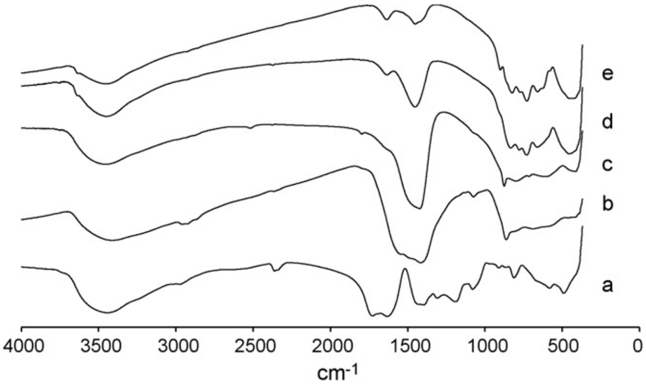

Fig. 4. IR spectra of the dried gel and the calcined products: (a) xerogel; (b) 400 °C; (c) 600 °C; (d) 800 °C; (e) 1000 °C.

3.2. Characterization of intermediate and final products

Fig. 3 presents the XRD patterns of the dried gel and the calcined products. As it is seen, the dried gel is completely amorphous. After sintering at 400 °C, the sample continues to be amorphous, while at 600 °C, the only crystalline compound is calcite. At 800 °C, calcite has been decomposed and $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$ has already been formed but not very well crystallized. The characteristic peak of $3CaO{\cdot}Al_2O_3$ (2θ: 31–32°) is very weak. At 1000 °C, the sample consists of $3CaO{\cdot}Al_2O_3$ and $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$. It must be noted that the sinterring of the xerogel directly at 1000 °C, improves the combinability of the oxides and eliminates the content of uncombined lime (below 1%, w/w). In the case of two-step sintering (first at 400 °C and then at 1000 °C) the product contains impurities of free lime (4.7%, w/w).

The crystal structures of $3CaO{\cdot}Al_2O_3$ and $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$ were refined using Rietveld profile analysis. The structural data resulting from the refinement are presented in Table 1. All these data are very close to those reported in literature for pure $3CaO{\cdot}Al_2O_3$ and $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$, indicating the satisfactory formation of these compounds.

Fig. 4 presents the FTIR spectra of the samples in relation to the curing temperature. The broad peak at 3400 cm^{-1} is typical of the O–H stretching vibration and can be assigned either to the hydroxyl ions of the organic compounds (at lower temperatures) or to the water absorbed on the surface of the highly reactive calcium aluminates. The bands observed in the spectrum of xerogel indicate the presence of esters (1075–1190 and 1700–1730 cm^{-1}) and citrate ions (1450 and 2960 cm^{-1}). The absence of the characteristic NO_3^- bands (about 1380, 1440 and 1630 cm^{-1}) confirms the removal of nitrates during the heating of the starting solution. After calcination at 400 °C, the peaks related to the citrate skeleton are still present, while the peaks assigned to the esters have been diminished. This fact indicates that the organic degradation has started from the carboxyl sites and is still proceeding. At 600 °C, all the peaks related to organic species have vanished. The strong band at 1450 cm^{-1} is associated with the carbonate ions, while the broad multiple band between 400 and 900 cm^{-1} is probably due to the first ill-formed AlO_4 and FeO_4 groups. The FTIR spectra at higher temperature indicate the decrease of carbonates and the further formation and development of Al and Fe tetrahedra. The characteristic multiple bands of aluminate and ferrite compounds (400–900 cm^{-1}) comprises the peaks of Al tetrahedra (720–780 and 430 cm^{-1}) and the peaks of Fe tetrahedra (610–660 cm^{-1}) which are formed through the isomorphous replacement of Al^{3+} by Fe^{3+}.

Table 1
Structural data resulting from Reitveld refinement of the final product

	C_3A Space group, *Pa*3	C_4AF Space group, *Ibm*2
Lattice parameters (Å)	$a = 15.2673349$	$a = 5.5351044$, $b = 14.5141932$, $c = 5.3247584$
Cell volume (Å^3)	3558.68622	427.77817

The results drawn from each one of the used monitoring techniques are in good accordance with each other. An attempt to summarize the stages involved in the Pechini synthesis of the mixture is presented below:

(i) starting solution (80 °C): chelation, removal of nitrates, esterification;
(ii) gel (150 °C): removal of solvents, polyesterification;
(iii) xerogel (400 °C): organic degradation at carboxyl sites;
(iv) xerogel (600 °C): total burning out of organics, formation of calcium carbonate, formation of ill-shaped AlO_4 and FeO_4 groups;
(v) xerogel (1000 °C): decomposition of carbonates, development of Al and Fe tetrahedra.

Fig. 5 presents the SEM photos of the xerogel and the sample sintered at 1000 °C for 3 h. The photos were selected to be representative as far as the size and texture of grains are concerned. As it is seen, the xerogel consists of small fragments in the range of 100–400 μm (Fig. 5a). The shape of these particles indicates an abrupt rupture of the material due, probably, to gas evolution. The microanalysis on the surface of selected particles (Fig. 5b) showed that the molar ratio of Ca, Al and Fe is very close to 7:2:1, which indicates a uniform distribution of the cations in the gel. The final product (Fig. 5c) consists of well formed, prismatic

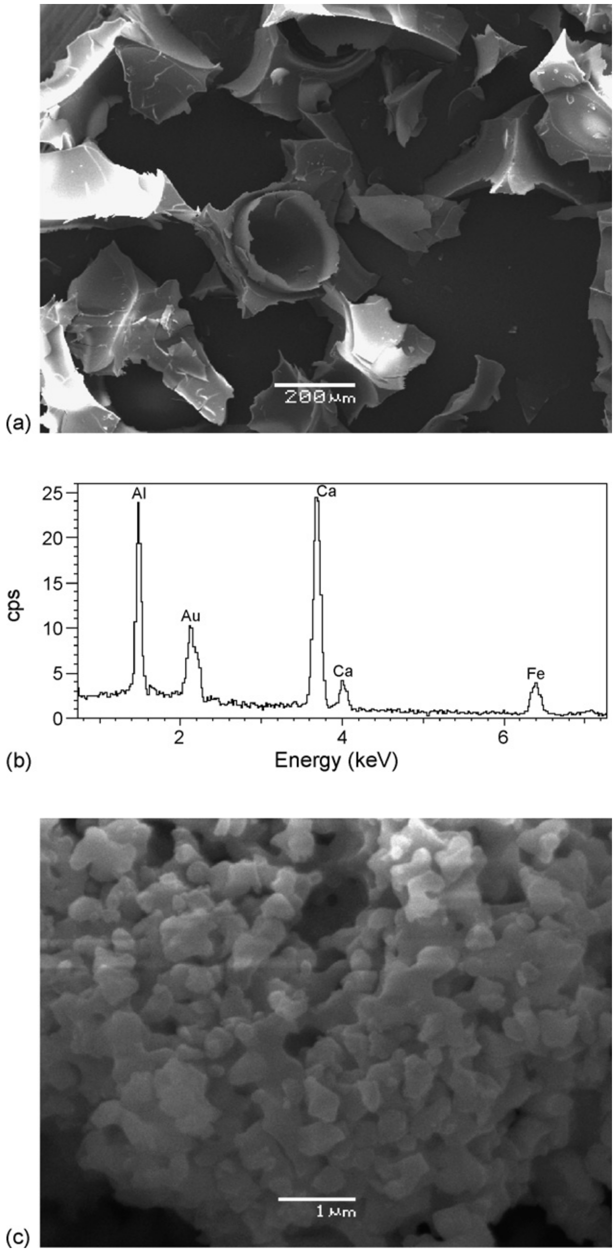

Fig. 5. SEM photos: (a) xerogel; (b) microanalysis on xerogel grain; (c) sintered product (1000 °C).

crystals in the range 0.2–1 μm. Crystals of both $3CaO{\cdot}Al_2O_3$ and $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$ have the same appearance and texture and cannot be distinguished.

4. Conclusions

This work led to the following conclusions:

- The Pechini technique can be successfully applied for the preparation of $3CaO{\cdot}Al_2O_3$ and $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$ mixtures.
- The final product consists of fine and well-formed grains of $3CaO{\cdot}Al_2O_3$ and $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$. Their formation requires a 3-h sintering at 1000 °C.
- The sintering of the xerogel directly at 1000 °C, improves the combinability of the oxides and eliminates the content of uncombined lime. In the case of step-by-step sintering the product contains impurities of free lime.
- The combination of TG/DTA, XRD and FTIR leads to the recording of all the transformations occurring during the processing of the precursors and the formation of the final products.

Acknowledgements

The authors acknowledge the financial support of this research under program Grant no. Heraklitos 68/647. The project is co-funded by the European Social Fund (75%) and National Resources (25%).

References

1. Stephan, D., Maleki, H., Knofel, D., Eber, B. and Hardtl, R., Influence of Cr, Ni and Zn on the properties of pure clinker phases. Part II. C_3A and C_4AF. *Cem. Conc. Res.*, 1999, **29**, 651–657.
2. Escribano, P., Marchal, M., Sanjuan, M., Alonso-Gutierrez, P., Julian, B. and Cordoncillo, E., Low-temperature synthesis of $SrAl_2O_4$ by a modified sol–gel route: XRD and Raman characterization. *Solid State Chem.*, 2005, **178**, 1978–1987.
3. Stephan, D. and Wilhelm, P., Synthesis of pure cementitious phases by sol–gel process as precursor. *Z. Anorg. Allg. Chem.*, 2004, **630**, 1477–1483.
4. Narayanan, R. and Laine, R., Synthesis and characterization of precursors for Group II metal aluminates. *Appl. Org. Chem.*, 1997, **11**, 919–927.
5. Kwon, S. W., Park, S. B., Seo, G. and Hwang, S. T., Preparation of lithium aluminate via polymeric precursor routes. *J. Nucl. Mater.*, 1998, **257**, 172–179.
6. Hernadez, M. T. and Gonzalez, M., Synthesis of alpha alumina precursors by the Pechini method using microwave and infrared heating. *J. Eur. Ceram. Soc.*, 2002, **22**, 2861–2868.
7. Cicillini, S. A., Pires, A. M. and Serra, O. A., Luminescent and morphological studies of Tm-doped $Lu_3Al_5O_{12}$ and $Y_3Al_5O_{12}$ fine powders for scintillator detector application. *J. Alloys Compd.*, 2004, **374**, 169–172.
8. Gulgun, M., Popoola, O. and Kriven, W., Chemical synthesis and characterization of calcium aluminate powders. *J. Am. Ceram. Soc.*, 1994, **77**, 531–539.
9. Aitasalo, T., Holsa, J., Jungner, H., Lastusaari, M., Niittykoski, J., Parkkinen, M. *et al.*, Eu^{2+} doped calcium aluminates prepared by alternative low temperature routes. *Opt. Mater.*, 2004, **26**, 113–116.
10. Fumo, D. A., Morelli, M. R. and Segadaes, A. M., Combustion synthesis of calcium aluminates. *Mater. Res. Bull.*, 1996, **31/10**, 1243–1255.
11. Tas, A. C., Chemical preparation of the binary compounds in the calcia-alumina system by self-propagating combustion synthesis. *J. Am. Ceram. Soc.*, 1998, **81/11**, 2853–2863.