

# Wet chemical synthesis of hydraulic compounds and materials

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## ABSTRACT

Conventionally, pure cement phases are prepared through long lasting sintering of solid oxide mixtures, at temperatures exceeding 1400 °C. The Pechini process is an alternative, low temperature polymeric precursor route for the synthesis of high purity oxides. In the present work, a modified Pechini technique is applied for the synthesis of the main hydraulic compounds ( $C_3S$ ,  $C_2S$ ,  $C_3A$  and  $C_4AF$ ). The synthesis of calcium aluminate cements is also examined. The preparation of the gel is monitored through constant conductivity measurements, and the intermediate and final products are fully characterized through XRD, TG-DTG, FTIR and SEM experiments.

As it is concluded, the Pechini technique can be successfully applied for the synthesis of hydraulic compounds, at much lower temperature than in the conventional synthesis. The final products consist of fine and well-formed grains without any impurities of reactants or secondary phases.  $\beta$ - $2CaO \cdot SiO_2$  is obtained without the need of sudden cooling or chemical stabilizers.

## 1. Introduction

Cement systems are quite complex, due to the appearance of a mixture of multiple binary and ternary compounds. Therefore, the use of pure doped or undoped clinker phases can be of great interest in fundamental research on cement materials, as the investigation of the hydration process or the influence of minor elements on the reactivity of cement. 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]. However, powders prepared by this

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method are usually agglomerated, have irregular size and shape and poor sinterability, while the final product may still contain secondary phases.

Instead of solid state sintering, alternative low temperature techniques such as sol-gel [2-7], polymeric precursor processes [8-10] and combustion [11,12] have also been applied for the synthesis of calcium aluminate and calcium silicate compounds. Among the above techniques, the Pechini-type polymerized complex method is known to be simple, cost-effective and versatile. This technique involves the formation of stable metal-chelate complexes with certain alpha-hydroxycarboxyl acids, such as citric acid (CA), and the polyesterification in the presence of a polyhydroxy alcohol, such as ethylene glycol (EG), to form a polymeric resin. The metal cations are homogeneously distributed in the polymeric resin which is then sintered to yield the desired oxides. The method is suitable for the preparation of multi component oxides of high purity at low temperatures [13,14].

In this paper the Pechini-type polymerized complex method is applied for the synthesis of the main hydraulic compounds ( $C_3S$ ,  $C_2S$ ,  $C_3A$  and  $C_4AF$ ) and calcium aluminate clinkers.

## **2. Experimental**

### **2.1. Synthesis**

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 source material for  $CaO$ ,  $Al_2O_3$  and  $Fe_2O_3$ .  $CaCO_3$  can also be used because it is easily dissolved in citric acid.  $SiO_2$  was introduced as aqueous silica sol. All samples were prepared according to the following procedure. First, the amount of citric acid (CA) was dissolved in approximately 50ml deionised water (molar ratio CA:total cations=1). Suitable amounts of the cation sources were added and the solution was stirred on a hot-stirring plate at 60 °C, until complete dissolution occurred. In each sample the cations' molar ratio was indicated by the stoichiometry of the final products. Ethylene glycol (EG) was then added and the solution was continuously stirred at 80 °C in order to achieve evaporation of excess water and acceleration of the polyesterification reaction, which was monitored through continuous conductivity measurements (molar ratio EG:CA=2). The procedure was stopped when the conductivity was diminished and viscous gels were obtained. The gels were then dried at 150 °C for at least 20 h to complete the polyesterification reaction. The resins were ground to powders, formed into pellets and then sintered.

Two type of calcium aluminate clinkers were also synthesized using the Pechini-type polymerized complex method. The first one was a standard

low alumina clinker (SLA) and the second one was a medium alumina clinker (MA). The oxide composition of the clinkers is shown in Table 1.

Table 1. Oxide composition of calcium aluminate clinkers (%w/w)

	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>
SLA	40	40	15	5
MA	55	38	2	5

## 2.2. Characterization Methods

Thermogravimetric analysis (TG/DTG) was applied in order to record the sintering reactions on the powder precursors. A Mettler Toledo 851 instrument was used. The samples were heated at a temperature range from 20 °C to 1000 °C with a constant rate of 10 °C/min in an atmosphere of air.

The phase distribution of the powders was investigated by X-Ray Diffraction, on a Siemens D-5000 Diffractometer with CuKα<sub>1</sub> radiation (λ=1.5405 Å), operating at 40 kV, 30 mA.

FTIR measurements were carried out using a Fourier Transform IR spectrophotometer (Perkin Elmer 880). The FTIR spectra in the wave number range from 400 cm<sup>-1</sup> to 4000 cm<sup>-1</sup>, 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 tons/cm<sup>2</sup>. The dried gels and the final samples were examined using a JEOL JSM-5600 Scanning Electron Microscope equipped with an OXFORD LINK ISIS 300 Energy Dispersive X-Ray Spectrometer (EDX).

Finally, the ethylene glycol method was used to measure the free CaO content in the sintered products.

## 3. Results and Discussion

### 3.1. Preparation of precursors

The gelation of the solutions is strongly affected by the heating temperature and the ratios of the starting materials. According to our preliminary experiments, the optimum temperature for the completion of the polyesterification reaction is 80 °C. Lower temperature prolongs the gelation of the solution, while higher temperature may lead to the hydrolysis of the cations and the precipitation of metal compounds.

The gelation time is determined on the basis of the conductivity measurements, as the time elapsed between the addition of EG and the elimination of the conductivity. The increase of CA:cations ratio prolonged the gel formation while the increase of CA:EG ratio had the opposite effect. The former ratio, also, affects the drying conditions and the morphology of the xerogels. Samples with CA:cations=1 were dried at 150 °C for 24h and the dried gels were swelled, aerated and very brittle. As the ratio increased, the dried gel became denser and harder. It seems that the excess of citric acid in the starting solution leads to the formation of linear polymeric networks with less branching and lower porosity, resulting to denser and harder xerogels.

The evolution of orange vapour during the heating of the starting solutions, indicate the removal of nitrates, probably through a redox reaction between ethylene glycol and nitric ions.

Figure 1 presents the TG, DTG and DTA curves of the precursor powder for the synthesis of C<sub>4</sub>AF. The relative curves of the other samples are very similar, although the total weight loss varies, depending on the content of organic material in the precursors. The curves indicate a weak weight loss around 100 °C, and a strong loss within 200 °C and 550 °C. The first weight loss is attributed to the moisture loss, absorbed after the thermal treatment of the gel at 150 °C. The major weight loss of the samples take place between 200 °C and 550 °C in multiple stages, associated with the removal of residual ethylene glycol, the dissociation of the polymer's network and the burning of organic carbon. The relative DTA curve shows two strong exothermic effects caused by the burning of 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 [13]. This is probably due to the reaction between calcium and CO<sub>2</sub> evolved during the burning of organic carbon. The formation reactions of the clinker compounds are not recorded due to their low heat content.

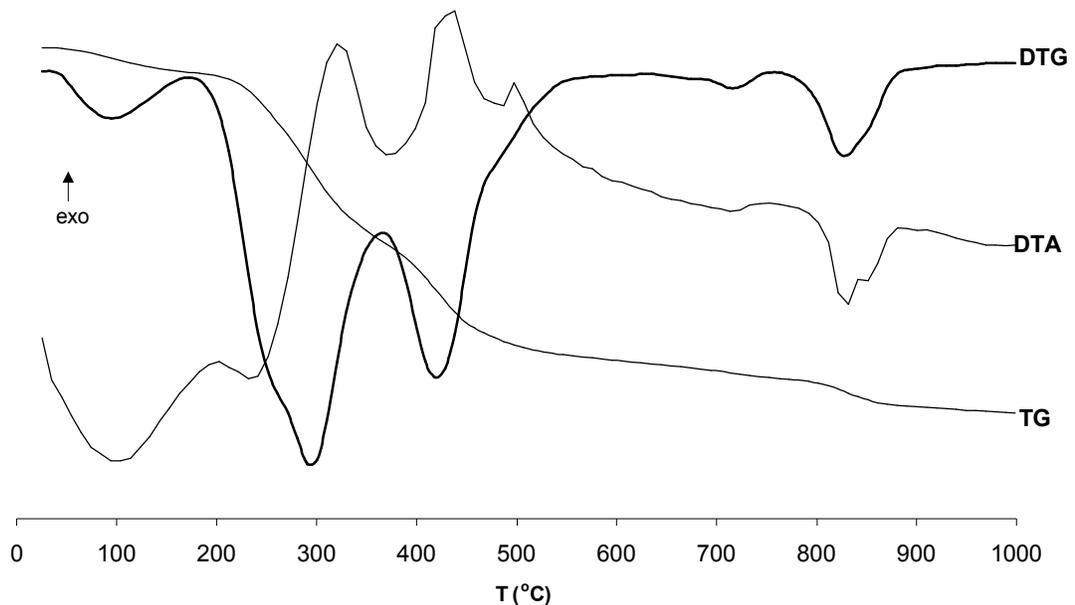


Figure 1. Synthesis of  $C_4AF$  - TG/DTG/DTA curves of the precursor powder

### 3.2. Characterization of intermediate and final products

Figure 2 shows the FTIR spectra of the xerogel and the samples sintered at 400, 600, 800 and 1000 °C, in the case of  $C_3A$ . 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 (1620 and 2960  $cm^{-1}$ ). The multiple bands at 400-1000  $cm^{-1}$  can be assigned to the vibrations of the metal ions. 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 FTIR spectrum of the sample sintered at 800 °C comprises a strong band at 1450  $cm^{-1}$  which is associated with the carbonate ions and a broad multiple band between 400 and 900  $cm^{-1}$  which indicates that the formation of Al tetrahedra is just beginning. The FTIR spectrum at 1000 °C indicates the decrease of carbonates and the formation of well-developed  $AlO_4^{-5}$ . The FTIR spectra of the other samples

are similar. In the case of silicate compounds, the FTIR spectra of the samples treated at 400 °C show also the characteristic bands of amorphous SiO<sub>2</sub> at 1100 and 780 cm<sup>-1</sup>. At higher temperatures these bands disappear and are replaced by the multiple bands at 800-1000 and 400-600 cm<sup>-1</sup>, which are characteristic of the stretching and bending vibrations of Si-O bonds in SiO<sub>4</sub> tetrahedra, respectively.

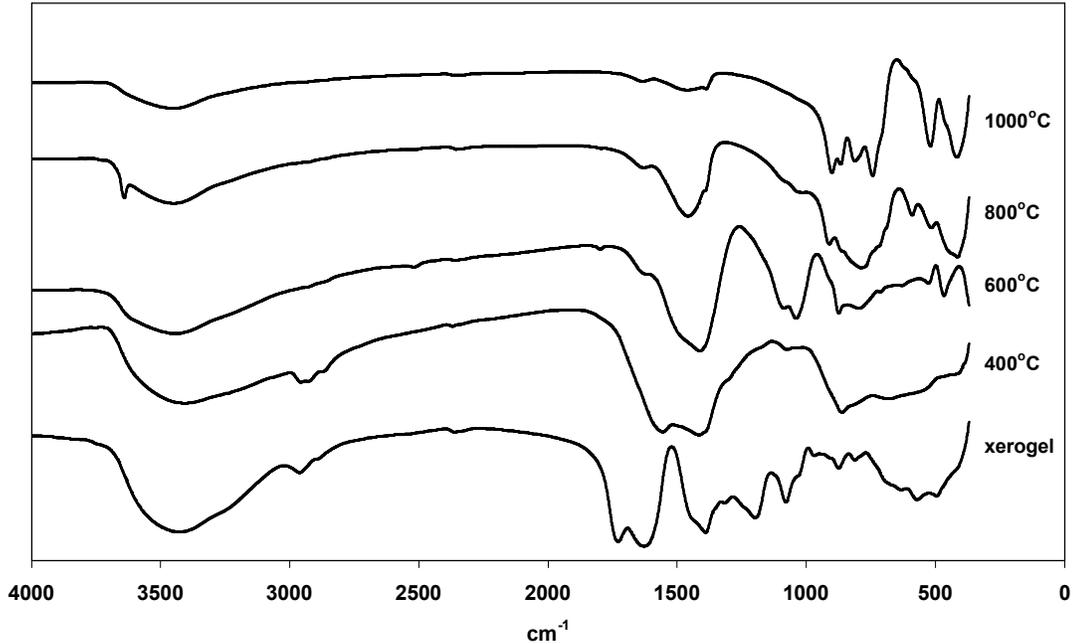


Figure 2. Synthesis of C<sub>3</sub>A - FTIR spectra of dried gel and sintered products

XRD was used for the definition of mineral compounds in the samples. In all cases, the powder precursors were completely amorphous. Table 2 presents the evolution of phases during the calcination of the precursors. C<sub>4</sub>AF and C<sub>2</sub>S were the first to be formed around 600 °C. C<sub>4</sub>AF was completely formed after 3-hour sintering at 800 °C, while the formation of C<sub>3</sub>A, C<sub>2</sub>S, SLA and MA samples required sintering at 1000 °C, for 3 hours. C<sub>3</sub>S is not stable below 1300 °C, and therefore it cannot be formed at any lower temperature. The sample sintered at 1500 °C for 3 hours, still contained C<sub>3</sub>S, C<sub>2</sub>S and free lime. Further investigation is needed in order to prepare pure C<sub>3</sub>S through wet chemical synthesis. Figures 3 and 4 present the XRD patterns of the pure compounds and the clinkers prepared through the Pechini-type polymerized complex technique, respectively.

Table 2. Intermediate and final products

	600 °C	800 °C	1000 °C
<b>C<sub>3</sub>A</b>	amorphous	5CaO·3Al <sub>2</sub> O <sub>3</sub> CaO	3CaO·Al <sub>2</sub> O <sub>3</sub>
<b>C<sub>4</sub>AF</b>	CaCO <sub>3</sub> CaO CaFe <sub>5</sub> AlO <sub>9</sub>	4CaO·Al <sub>2</sub> O <sub>3</sub> ·Fe <sub>2</sub> O <sub>3</sub>	4CaO·Al <sub>2</sub> O <sub>3</sub> ·Fe <sub>2</sub> O <sub>3</sub>
<b>C<sub>2</sub>S</b>	CaO 2CaO·SiO <sub>2</sub>	CaO 2CaO·SiO <sub>2</sub>	2CaO·SiO <sub>2</sub>
<b>C<sub>3</sub>S</b>	CaCO <sub>3</sub> 2CaO·SiO <sub>2</sub>	CaCO <sub>3</sub> 2CaO·SiO <sub>2</sub>	CaO 2CaO·SiO <sub>2</sub>
<b>SLA</b>	amorphous	CaO·Al <sub>2</sub> O <sub>3</sub> 4CaO·Al <sub>2</sub> O <sub>3</sub> ·Fe <sub>2</sub> O <sub>3</sub>	CaO·Al <sub>2</sub> O <sub>3</sub> 4CaO·Al <sub>2</sub> O <sub>3</sub> ·Fe <sub>2</sub> O <sub>3</sub> 2CaO·SiO <sub>2</sub> 2CaO·Al <sub>2</sub> O <sub>3</sub> ·SiO <sub>2</sub>
<b>MA</b>	amorphous	amorphous	CaO·Al <sub>2</sub> O <sub>3</sub> 4CaO·Al <sub>2</sub> O <sub>3</sub> ·Fe <sub>2</sub> O <sub>3</sub>

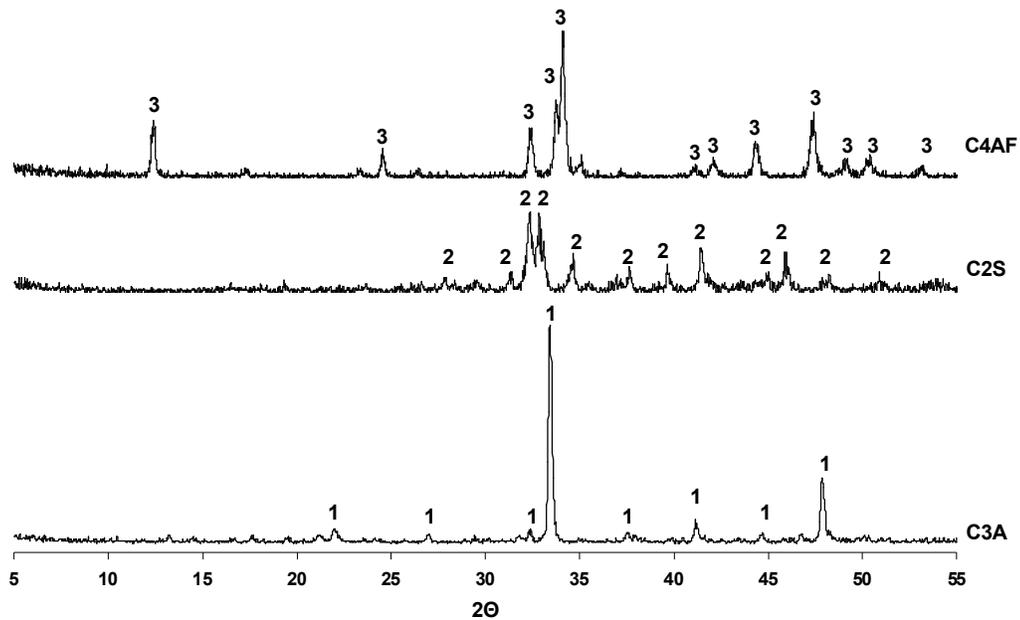


Figure 3. XRD patterns of C<sub>3</sub>A, C<sub>2</sub>S and C<sub>4</sub>AF precursors sintered at 1000 °C for 3 hours. (1: C<sub>3</sub>A, 2: β-C<sub>2</sub>S, 3: C<sub>4</sub>AF)

The fCaO content of the C<sub>3</sub>A, C<sub>4</sub>AF, C<sub>2</sub>S, SLA and MA samples sintered at 1000 °C for 3 hours was less than 0.8% w/w. In the case of C<sub>3</sub>S, the sample sintered at 1500 °C for 3 hours, still contained 2.5% w/w fCaO.

It must be noted that 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 two-step sintering (first at 400 °C and then at 1000°C) the products contains impurities of free lime.

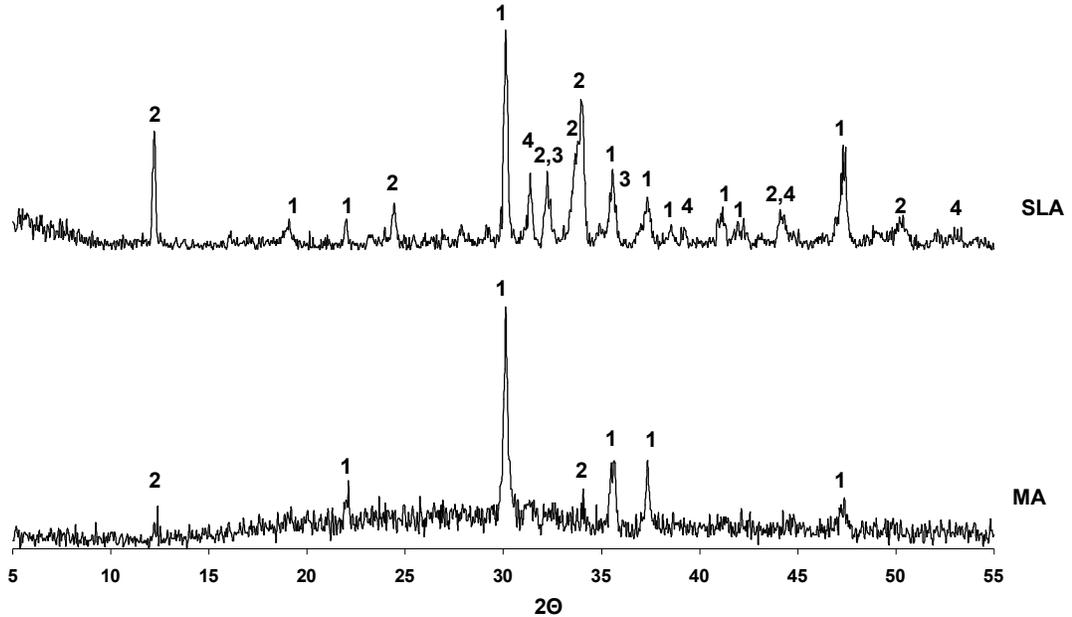


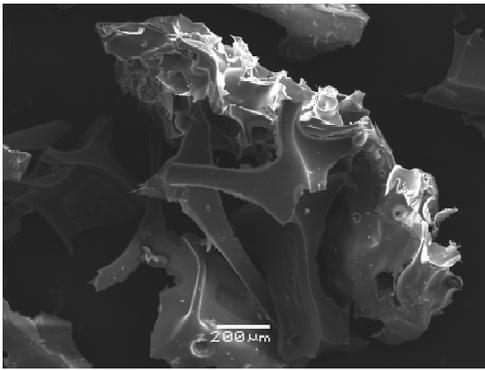
Figure 4. XRD patterns of MA and SLA precursors sintered at 1000 °C for 3 hours. (1: CA, 2 C<sub>4</sub>AF, 3: β-C<sub>2</sub>S, 4: C<sub>2</sub>AS)

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 is presented below:

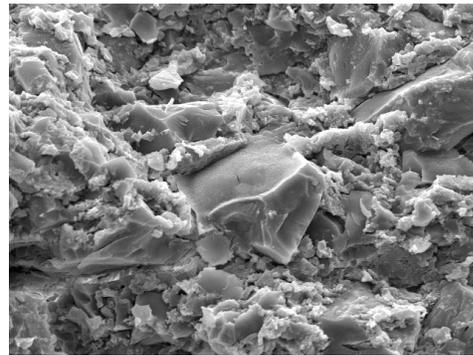
- i. Starting solution (80 °C): chelation, removal of nitrates, esterification, starting of polyesterification
- ii. Gel (150 °C): removal of solvents, polyesterification
- iii. Precursor (400 °C): organic degradation at carboxyl sites
- iv. Precursor (600 °C): burning out of organics, formation of calcium carbonate, formation of ill-shaped aluminate, ferrite and/or silicate groups
- v. Precursor (1000 °C): decomposition of carbonates, development of Al, Fe and/or Si tetrahedra

Figure 5 presents the SEM photos of one dried gel (C<sub>3</sub>A) and the samples sintered at 1000 °C for 3 hours. The photos were selected to be representative of the size and texture of the grains. As it is seen, the

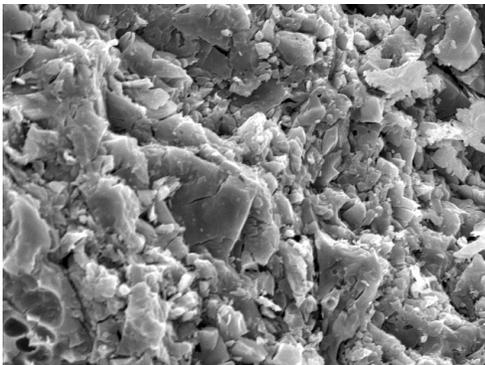
xerogel consists of small fragments in the range of 100-400 $\mu\text{m}$  (Figure 5a). The shape of these particles indicates an abrupt rupture of the material due, probably, to gas evolution. All xerogels looked quite the same. The microanalysis on the surface of selected particles showed that the atomic ratio of the elements Ca, Al, Fe and/or Si is very close to the ratio in the final product, indicating a uniform distribution of the elements in the gel.  $\text{C}_3\text{A}$  and  $\text{C}_4\text{AF}$  consist of polygonal-shaped grains, with a wide size distribution (Figures 5b and 5c).  $\text{C}_2\text{S}$  consists of the characteristic spherical-shaped particles of  $2\text{CaO}\cdot\text{SiO}_2$ , having a mean particle size less than 1  $\mu\text{m}$  (Figure 5d). This small size must be the reason for the stabilization of  $\beta\text{-}2\text{CaO}\cdot\text{SiO}_2$  at ambient temperature without the need of any chemical stabilizers or sudden cooling. Calcium aluminate clinkers consist mainly of polygonal-shaped grains (Figures 5e and 5f). The microanalysis on the surface of selected grains shows that the molar ratio  $\text{Al}_2\text{O}_3:\text{CaO}$  is 1.07, very close to 1, as expected in the case of CA. Most of the grains are covered with finer particles consisting of Ca, Al and Fe, indicating that the ferrite phase is crystallized on the surface of calcium aluminate grains. In the case of SLA, some spherical-shaped particles of  $\text{C}_2\text{S}$  are evident in the centre of the photo.



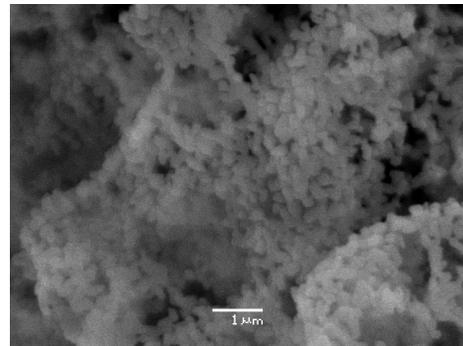
**a**



**b**



**c**



**d**

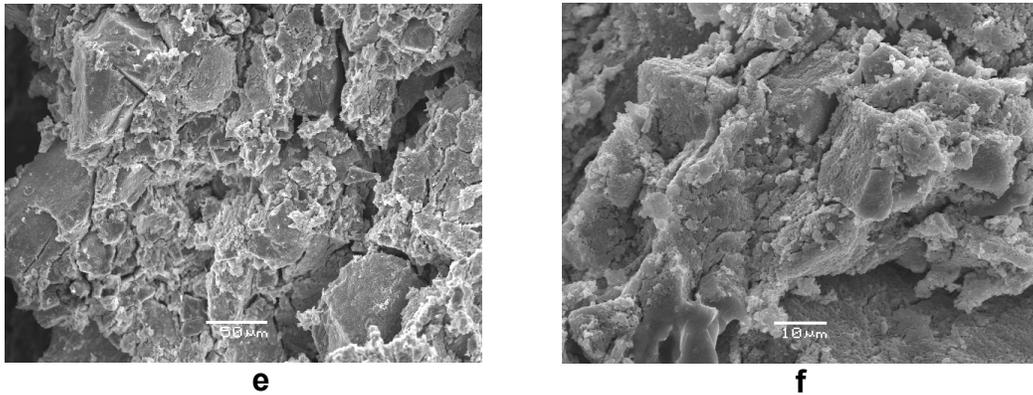


Figure 5. SEM photos of samples (a: xerogel, b:  $C_3A$ , c:  $C_4AF$ , d:  $C_2S$ , e: MA, f: SLA)

#### 4. Conclusions

This work led to the following conclusions:

- ✓ The Pechini-type polymerized complex method can be successfully applied for the synthesis of hydraulic compounds and materials.
- ✓ The preparation of pure  $3CaO \cdot Al_2O_3$ ,  $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$  and  $2CaO \cdot SiO_2$ , as well as the preparation of Standard Low Alumina and Medium Alumina clinkers require a three-hour sintering at  $1000\text{ }^\circ\text{C}$ .
- ✓ In the case of  $C_2S$ ,  $\beta\text{-}2CaO \cdot SiO_2$  is obtained, without the use of any chemical stabilizers or sudden cooling. This is attributed to the very small size of the grains.
- ✓ 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.

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