Application of sol-gel technique to synthesize inorganic binder materials with upgraded hydration characteristics

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The paper reports the results of hydration heat evolution, microstructure and stability of binder materials composed of C_2AS, C_2S, $C_4A_3\bar{S}$ *, $C\bar{S}$ and in proportion to give, after complete hydration, gehlenite hydrate and ettringite. The conventional method was applied to synthesize different mineral phases. Also, an alternative method (sol-gel technique) has been used to synthesize pure and highly active C_2AS and C_2S, which prepared by conventional method are hydraulically latent or less active. After heated at 600 °C, the xerogels were calcined at 900 °C and 1100 °C to obtain crystals of C_2S and C_2AS respective. Two categories of samples with identical mineralogical composition were set. The samples of first category were made from minerals synthesized by conventional method, while in those of the second one, C_2AS and C_2S were synthesized via sol-gel method. Conduction calorimeter, SEM and XRD methods were used. Specimens of the first category were cured in autoclave to obtain gehlenite hydrate, but ettringite decomposed into monosulfate. In the second group, gehlenite hydrate was formed under normal conditions, owing to active C_2AS nano-particles. Also, C_2S nano-particles have contributed to gehlenite hydrate formation through secondary reaction between C-S-H, AH_3 and CH, ettringite formed remained stable.

1. Introduction

Synthesis cement phases are essentially realized by conventional methods that assure the formation of these binder materials by solid-state reaction at high temperatures. The process includes mixture and homogenization of finely ground natural raw materials or chemical reagents, following by thermal treatment at adequate temperature. This thermal operation leads to the formation of crystal phases (minerals) that after grinding can react with water to form material with binding properties. Research in cement chemistry realized in the last years mapped over the possibilities to synthesize highly pure cement phases using starting materials different from the usual ones and treatments at lower temperatures, using alternative synthesis methods [1-4]. These non-traditional methods include: pyrolisis of solutions of some salts, precipitation from solutions, sol-gel processing and hydrothermal steam processing.

*Cement nomenclature is used when $C = CaO$, $S = SiO_2$, $A = Al_2O_3$, $\bar{S} = SO_3$

The non-conventional methods, namely those that realize the mixing and homogenizing of the raw materials at a molecular scale by wetting process, can produce very reactive samples of binding compounds able to react with water at low temperatures. These alternative methods for the synthesis of binding compounds present some advantages: low synthesis temperatures comparatively with those of the traditional methods; advanced homogeneity of the starting material, often at molecular level; products with fine grained powders and a strict control of the grain size distribution can be obtained; very pure and homogeneous compounds and very reactive compounds can be obtained [2-7].

Inorganic binders in the framework of C_2AS-$C_4A_3\bar{S}$-$C\bar{S}$-C_2S-C system form a special type of Sulfoaluminate Belite Cements (shorthand SAB) that belong to the class of Low-Energy Cements (shorthand LEC) [8,9,10,11]. Unfortunately, the rate of hydration of these cements are inhibited by the worse reactivity of minerals gehlenite and dicalcium silicate and the formation of ettringite at beginning of hydrations can foster sulfate attack. Some progress has been realized to improve the hydraulicity of C_2S by stabilizing with minor oxides the high temperature ß-C_2S polymorph [12,13]. Indeed, the transformation at lower temperature (about 550°C) of ß-C_2S to the γ-C_2S is accompanied by a volume increase responsible for the well-known phenomenon of dusting. Furthermore, γ -C_2S has not hydraulic properties [14]. Also, the effect of grain size upon the stabilization of ß -C_2S has been investigated and it was found that micro-particles of ß-C_2S having no overcome the critical size are stabilized without doping or rapid cooling [15]. Next to C_2S, C_2AS is one of the clinker minerals of Low-Energy Cements (LEC). It formation occurs as an intermediary product formed at 800°C during the burning of Portland cement [14], but gehlenite is hydraulically latent and could not contribute to the properties of binder materials. Nevertheless, gehlenitehydrate C_2ASH_8 has been obtained by hydrating gehlenite glass prepared by melting a mixture of CaO, Al_2O_3 and SiO_2 in molar ratio of 2:1:1 at 1630°C, following by rapid quenching in water [16]. Also, gehlenite hydrate is found as hydration product of cement containing blast furnace slag [17,18,19]. Currently gehlenite is as melted glass phase in slag. The abstention of gehlenitehydrate by this procedure is high-energy consumption pathway.

Sol-gel process, as an alternative to the conventional method [20] has been already used by Roy and Oyefesobi, and that for the first time, to synthesize C_2S from aqueous silica sol and a $Ca(NO_3)_2$ solution as precursors, the mole ratios Ca/Si were 2:1. Thereafter, sol-gel process has offered an alternative route to prepare highly active cement phases.

With regard to the energy cost and technical conditions to prepare the gehlenite glass and the non-equilibrium condition of hydration in autoclave [16], the present work was undertaken to find an alternative method (sol-gel process) allowing to synthesize gehlenite and β-C_2S without dopant, both with high hydraulic reactivity.

Recently, authors [21] have explored the hydraulic properties of C_2AS-C_2S-$C_4A_3\bar{S}$-$C\bar{S}$-C system in hydrothermal conditions. The computational method has established two quaternary (C_2AS-C_2S-$C_4A_3\bar{S}$-$C\bar{S}$ I, C_2S-$C_4A_3\bar{S}$-$C\bar{S}$-C II) and two ternary (C_2S-$C_4A_3\bar{S}$-$C\bar{S}$ S_1, $C_4A_3\bar{S}$-$C\bar{S}$-C S_2) phase associations and one singular point of gehlenite P_1. Apart from P1 and S_2 hydration of each point could give two crystallohydrates: gehlenite hydrate and ettringite (Fig. 1).
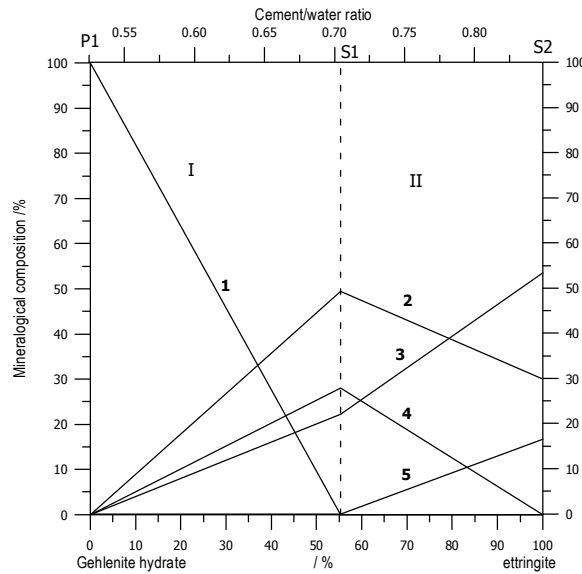

Figure 1: C_2AS(1)-$C_4A_3\bar{S}$(2)-$C\bar{S}$(3)- C_2S(4)-C(5) system and phase associations (I, II), singular points (S1, S2) and gehlenite point (P1).

Sequence of hydration reaction in individual phase association

Phase association I   **C_2AS-C_2S- $C_4A_3\bar{S}$-$C\bar{S}$**

The formation of gehlenite hydrate can be expressed theoretically by Eq. (1)

$$C_2AS + \quad 8H \quad = \quad C_2ASH_8 \tag{1}$$

Dicalcium silicate reacts with water to produce calcium silicate hydrate with different C/S ratios and calcium hydroxide according to Eq. (2)

$$C_2S + 2H \quad = \quad CSH + CH \tag{2}$$

Hydration reaction of $C_4A_3\bar{S}$ and $C\bar{S}$ lead to ettringite formation supplemented by aluminum hydroxide (Eq. 3).

$$C_4A_3\bar{S} + 2C\bar{S} + 38H \quad = \quad C_6A\bar{S}_3H_{32} + 2AH_3 \tag{3}$$

Also, ettringite can be generated by reaction according to following equation (Eq. 4):

$$C_4A_3\bar{S} + 8C\bar{S} + 6CH + 9OH = 3C_6A\bar{S}_3H_{32} \qquad (4)$$

Then, gehlenite hydrate can be formed through secondary reaction according to Eq. 5.

$$CSH + CH + AH_3 + 3H = C_2ASH_8 \qquad (5)$$

The final hydration products are thus ettringite ($C_6A\bar{S}_3H_{32}$) and gehlenite hydrate C_2ASH_8).

Phase association II C_2S- $C_4A_3\bar{S}$ -$C\bar{S}$ -C

Calcium silicate hydrate is formed by reaction (Eq. 2). Ettringite is precipitated firstly by reaction (Eq.4), but also through reaction (Eq. 3). Gehlenite hydrate is formed exclusively from secondary according to Eq. 5.

Singular point S_1 C_2S- $C_4A_3\bar{S}$ -$C\bar{S}$ -C

As in previous phase associations, dicalcium silicate reacts with water to form calcium silicate hydrate and calcium hydroxide (Eq. 2) and ettringite is precipitated through Eq. (3) or Eq. (4). Then, expected gehlenite hydrate formation occurs through secondary reaction between CSH, CH and AH_3, see Eg. (5).

From these equations, one can postulate that the final crystallohydrate products are ettringite and gehlenite hydrate. But the reactions occur in the non - equilibrium heterogeneous conditions starting by dissolution of individual mineral phase, following by the formation of intermediate products that finally convert (including decomposition and secondary reactions) to the stable crystallohydrates.

Singular point S_2 $C_4A_3\bar{S}$ -$C\bar{S}$ -C

The hydration of this phase association leads exclusively to ettringite formation according to Eq. 3 or Eq. 4.

2. Experimental

Individual mineral phases were synthesized from a homogenized stoichiometrical mixtures of reagent grade $CaCO_3$, $Al(OH)_3$ and $CaSO_4.2H_2O$ for $C_4A_3\bar{S}$ at 1250 °C, $CaCO_3$ and SiO_2 for C_2S at 1300 °C, $CaCO_3$, $Al(OH)_3$ and SiO_2 for C_2AS at 1450 °C. All samples were calcined twice for two hours at corresponding temperatures with intermediate grinding to a grain size of < 40 μm, controlled by sieving. Furthermore, C_2S and C_2AS were quenched in air to avoid the polymorph transformation. $C\bar{S}$ was

obtained by heating gypsum at 350 °C. Calcium hydroxide (CH) was used instead of calcium oxide (C).

C_2AS xerogel was prepared using commercial boehmite powder (Condea Pural SB, ~ 5 nm, Condea, Germany), silica sol (Tosil, 30.wt % of silica, particles~20 nm, TONASO Neštenice, Czech Republic) and solution of $Ca(NO_3)_2.4H_2O$ (c= 1.234 mol.l^{-1}). Boehmite suspension was peptized by mixing with HNO_3 (pH $\cong 2.5$) at 55ºC. Then the calculated amount of the silica sol and solution of $Ca(NO_3)$ were slowly added into the boehmite suspension. The same procedure was used to prepare nano-crystalline C_2S from stechiometrically mixture of silica sol and solution of $Ca(NO_3)_2$. The colloidal solution was stirred for 2 h at ambient temperature, then poured onto a glass petri dish and was gelled at the same temperature. Xerogels were dried at 100 °C and then heat treated at 600 °C, 900 °C, 1100 °C and 1250 °C for 1 h at each temperature.

Stoe powder diffraction system, i.e. Stoe transmission X-ray diffraction system (STADI P), using Co K_a radiation, operating at 40 kV and 30 mA was used to characterize different samples. Assignment of diffraction lines was made by comparison with JCPDS files. The heat of hydration of samples with water/cement ratio 0.5 was measured using a Ziac conduction calorimeter [22]. The microstructure of samples cured under hydrothermal and normal conditions was examined by means of Scanning Electron Microscopy.

Then, mixing and homogenizing minerals in the proportion as elucidated in Table 1 prepared samples.

Table 1. Studied samples.

Samples	1	2	3	4	5	6
Gehlenite hydrate: ettringite	100:0	80:20	60:40	44.7:55	20:80	0:100
C_2S (%)	0	10.15	20.31	28.06	12.56	0
C_2AS (%)	100	63.83	27.67	0	0	0
$C_4A_3\bar{S}$ (%)	0	17.98	35.97	49.72	38.82	29.98
$C\bar{S}$ (%)	0	8.02	16.04	22.20	39.82	53.48
C (%)	0	0	0	0	9.13	16.53

3. Results and discussion

Hydraulicity of C_2S and C_2AS synthesized by conventional and sol-gel method, microstructure of hydrated products.

Fig. 2 reports the rate of hydration heat of C_2AS synthesized by sol gel method and that obtained by conventional one at 1450 °C. It can be seen from these results that the hydraulicity of C2AS synthesized via sol-gel method is upgraded. The XRD patterns of hydrated samples of C2AS mineral and C_2AS xerogels are reported in Fig. 3. The XRD patterns show

that the main hydration product of C_2AS xerogels is gehlenite hydrate, while C_2AS mineral has remained constant.

Figs. 4 and 5 show the scanning electron micrographs of hydrated C_2AS mineral and C_2AS xerogels. SEM micrograph evidently shows well-crystallized hydrated products and hence demonstrates the high hydraulic activity of xerogels C_2AS.
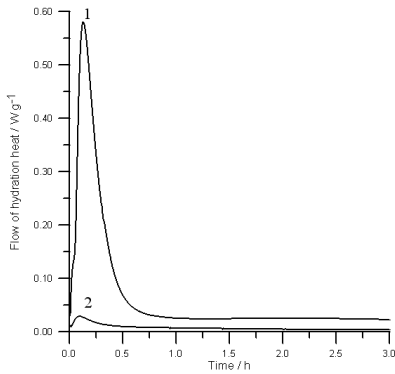

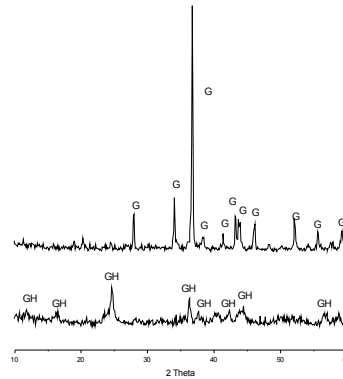Figure 2. Calorimetric curves of C_2AS hydration. C_2AS synthesized by 1-sol gel and 2-conventional methods.

Figure 3. XRD of C_2AS after hydration. *Up*-C_2AS synthesized by conventional and *down*- by sol gel methods, *G* –Gehlenite, *GH* – Gehlenite hydrate.
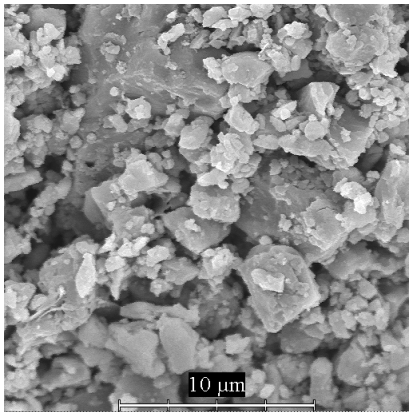

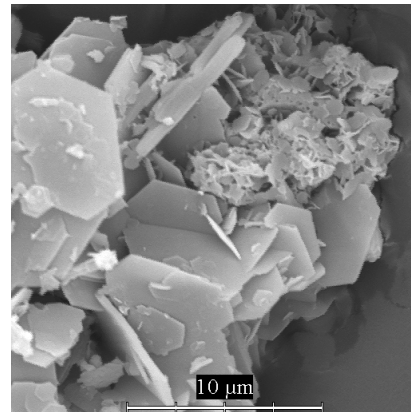Figure 4. Micrograph of hydrated C_2AS, synthesized by conventional method.   .

Figure 5. Micrograph of hydrated C_2AS synthesized by sol-gel method.

Fig. 6 reports the rate of heat evolution of C_2S synthesized via sol gel method and then heat-treated at 1250 °C and that of C_2S prepared by conventional method at the same temperature. It is evident that the hydration rate of C_2S obtained from calcined xerogel is more intense than

that of relative clinker mineral synthesized through solid-state reaction. These findings are also confirmed by SEM micrographs (Fig. 8) and(Fig. 9). Fig. 9 shows very dense gel structure surrounding original grain of C_2S is formed, while in Fig. 9 well-crystallized C-S-H is observed.

Figure 6. Hydration calorimetric curves of C_2S prepared by different (1- conventional, 2-sol-gel) methods, both samples treated at 1250 °C.

Figure 7. XRD of C_2AS after hydration. *Up*-C_2AS synthesized by conventional and *down*- by sol gel methods.

Figure 8. Micrograph of hydrated C_2S, synthesized by conventional method.

Figure 9.Micrograph of C_2S hydrated synthesized by sol-gel method.

Hydraulicity of inorganic binders containing C$_2$S and C$_2$AS synthesized by conventional or sol-gel method, microstructure of hydrated products

Fig 10 summarizes the micrographs of two hydrated samples as referred in Table 1. The samples denoted "*sample a*" contain C$_2$S and C$_2$AS synthesized by conventional while in those denoted "*sample b*" C$_2$S and C$_2$AS were prepared by sol-gel method. Samples containing crystals of C$_2$AS and C$_2$S were cured under hydrothermal conditions to accelerate the hydration process, while those with C$_2$AS and C$_2$S xerogels were hydrated in suspension at room temperature.

The microstructure development differs with the nature of C$_2$AS and C$_2$S in the samples and with condition under which samples were hydrated.

The XRD diffraction patterns in Fig. 11 show that the main hydration product within 24 hours is ettringitu in "*Samples a*". Ettringite is found in all samples, except sample of pure gehlenite. Gehlenite hydrate is not observed due the low hydration rate of gehlenite.
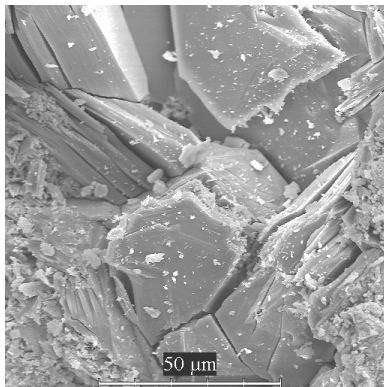
After 28 -day curing in autoclave, XRD diffraction (Fig. 12) clearly shows that ettringite is not stable under the defined condition. Monosulphate is a dominant hydrated product as consequence of ettringite decomposition.
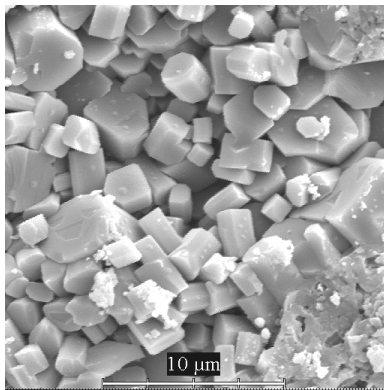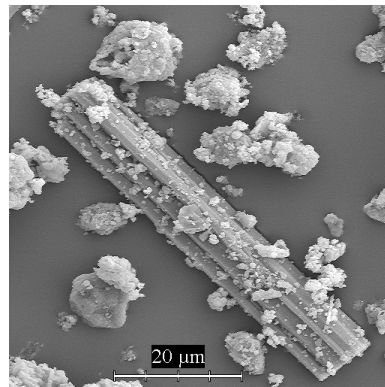

Sample 1a
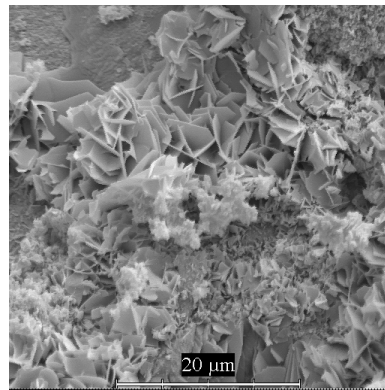
Sample 1b

Sample 6a

Sample 6b

Figure 10. Microstructure development of samples 1-6 a/ C$_2$AS a C$_2$S synthesized by conventional method and b/ C$_2$AS a C$_2$S synthesized via sol-gel route.

Scanning electromicrographs in Fig. 10 (*Sample 6a*) and XRD patterns reported in Fig. 12 bring the demonstration of ettringite instability under the hydrothermal conditions. But under these conditions, large crystals of gehlenite hydrates are found localized in pore structure(*Sample 1a*). In samples with high gehlenite content, one could remark that crystallohydrates of gehlenite hydrates, surrounded by a mass of CSH gel begin to join one to another and the microstructure is compact (*Samples 1a-4a not reported*). This fact supports the idea that cementitious materials containing gehlenite hydrate have higher long-term mechanical properties [11]. The hydration of samples containing C_2AS and C_2S synthesized via sol-gel route has led to the formation of two crystallohydrates: ettringit and gehlenite hydrate. These findings are confirmed by XRD patterns (Fig. 13). In all these samples, ettringite is stable and gehlenite hydrate is formed at lower temperature. The formation of gehlenite hydrate by primary or secondary reaction (Eq.1 and Eq.5) is due to the high hydraulic activity of C_2S and C_2AS synthesized by sol-gel method.
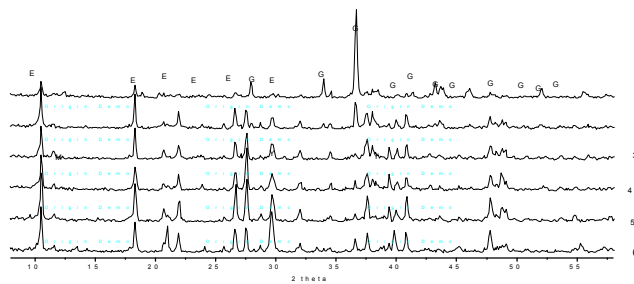

Figure 11. XRD pattern of samples containing C_2S and C_2AS synthesized by conventional method after 24 hours of hydration at 70°C. E- ettringite, G – gehlenite, M – monosulphate and Y – Yeelenite ($C_4A_3\bar{S}$).
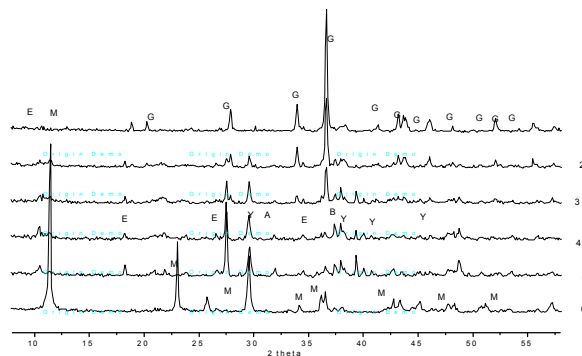

Figure 12. XRD patterns of sample containing C_2S and C_2AS synthesized by conventional method after 28-day hydration in autoclave. E- ettringite, G – gehlenite, M – monosulphate and Y – Yeelenite ($C_4A_3\bar{S}$).
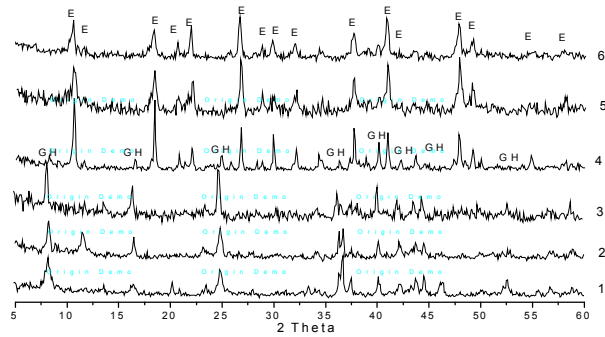
Figure 13. XRD patterns of samples after 7 days of hydration at 25°C.
E- ettringite, GH – gehlenitehydrate

Sample 4b is, in Fig. 13, a specific sample without nano particles of gehlenite. Nevertheless, one can observe on XRD patterns that ettringite coexists with gehlenite hydrate. In this sample gehlenite hydrate was formed through secondary reaction (Eq.5). In samples 5 and 6 ettringite is the dominant phase. The identification of gehlenite hydrate by XRD was hindered due to very intense peaks of ettringite. Ettringite is there formed according to the Eq. (3) or Eq. (4).

Conclusion

This work has used sol-gel method to synthesize pure and highly active cement phases, which prepared by traditional route have low or latent hydraulicity. The xerogels of C_2S and C_2AS have shown good hydraulicity. For the first time, sol-gel process has been applied to obtain gehlenite hydrate from hydration of gehlenite. Binder materials in the C_2AS-C_2S-$C_4A_3\bar{S}$-$C\bar{S}$-C system, with nano particles of C_2AS and C_2S prepared by sol-gel method, showed better hydraulic activity comparatively to the system which consist of pure minerals. The forecasted hydration products, ettringite and gehlenite hydrate were obtained in system containing C_2AS and C_2S synthesized through sol-gel method. The hydration leading to coexistence of two crystallohydrates of gehlenite hydrate and ettringite has been achieved by primary and secondary reactions. The high reactivity of C_2AS and C_2S xerogels and relative binder systems is due to the fineness and homogeneity of these phases. Ettringite obtained by this way is stable, while under hydrothermal conditions, it degrades into monosulfate.

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