HYDRATION AND MICROSTRUCTURE OF BINDER COMPOUNDS CONTAINING C_2AS AND C_2S SYNTHESIZED BY SOL-GEL METHOD

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Sol-gel method has been used to synthesize the nano particles of C_2AS and C_2S. These cement phases prepared by solid-state reaction at high temperatures are hydraulically latent or less active. After heating at 600°C, they were calcined at 900°C and 1100°C to obtain crystals of C_2S and C_2AS respectively. Binder compounds in the framework of $C_2AS–C_2S–C_4A_3\bar{S}–C\bar{S}–C$ system were prepared using C_2AS and C_2S synthesized via sol-gel process. Samples showed better hydraulic activity when comparing it with the system, where pure minerals were used. The hydration of this system leads to coexistence of two crystallohydrates of gehlenite hydrate and ettringite, which were originated by primary and secondary reactions. Gehlenite hydrate as well as ettringite were stable.

INTRODUCTION

Synthesis and preparation of cement phases are essentially realized by conventional methods that assure the formation of these binder materials by solid state reaction at high temperatures. The processing includes mixture and homogenization of finely ground natural raw materials or chemical reagents, following by thermal treatment at adequate temperature. This technical operation leads to the formation of crystal phases (minerals), that after grinding can react with water to form material with binding properties. Some of these minerals have not good hydraulic properties and some ones are hydraulically latent, even though their important presence in cement. Research in cement chemistry realized in the last years mapped over the possibility 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. From 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; the 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].

Cements based on C_2S and C_2AS are generally classified as Low-Energy-Cements due to the temperatures at which they are producible [9-11]. Unfortunately, C_2S is hydraulically less active [9] and C_2AS latent phase [11]. Some progress has been realized to improve the hydraulicity of C_2S by stabilizing with minor oxides the high temperature β-C_2S polymorph [12,13]. Indeed, the transformation at lower temperature (about 550°C) of β-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 β -C_2S has been investigated and it was found that micro-particles of β-C_2S having no overcome the critical size are stabilized without doping or rapid cooling [14]. 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 [15], 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 [17-19]. Currently gehlenite is as melted glass phase in slag. The obtention of gehlenitehydrate by this procedure is high energy consumption way.

Recently, authors [20] 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 quaternary and ternary phase associations, which hydration could give two crystallohydrates: gehlenite hydrate and ettringite (figure 1). Under hydrothermal steam conditions, ettringite formed at early hydration period is not stable and converts to monosulfate, while gehlenite hydrate formed by primary and secondary reactions remains stable.

With regard to the energy cost and technical conditions to prepare the gehlenite glass and the non-equilibrium condition of hydration in autoclave [16, 20], 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.

Sol-gel process, as an alternative to the conventional method [21] 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. The obtained gels were, after washing dried and then heated at 700°C. β-C_2S with fibrous shape and a very high specific surface area (of about 12.9 m^2/g BET) was identified. The compressive strength developed by this compound was about 62 MPa, as compared to 40 MPa for commercial β-C_2S measured in the same conditions. Thereafter, sol-gel process has offered an alternative route to prepare highly active dicalcium silicate.

C_2S and C_2AS are ones of the main phases of Low-Energy Cements based on belite and calcium-sulfoaluminate cements in the framework of $C_2AS–C_2S–C_4A_3\bar{S}–C\bar{S}–C$ system [20]. Unfortunately, the rate of hydration of these cements are inhibited by the worse reactivity of minerals gehlenite and dicalcium silicate prepared by conventional method and the lack of calcium silicate hydrate in the matrice of cement paste at beginning of hydration enables the formation of ettringite that is not always stable.

In the present investigation, hydraulic properties of $C_2AS–C_2S–C_4A_3\bar{S}–C\bar{S}–C$ system are explored, using nano particles of C_2AS and C_2S synthesized by sol-gel method. Other phases $C_4A_3\bar{S}$, $C\bar{S}$ and C have been obtained by conventional procedure. The hydration reaction, as previously investigated has to lead to the formation of two crystallohydrates: gehlenitehydrate and ettringite [20].

EXPERIMENTAL

Homogenized mixture of reagent grade $CaCO_3$, $Al(OH)_3$ and $CaSO_4.2H_2O$ was burnt twice for two hours at 1250°C in platinum crucible to synthesize $C_4A_3\bar{S}$. The obtained mineral was milled to specified fineness (to pass a 40 m sieve). Purity of this mineral was controlled by STOE Powder Diffraction System using CoK_α radiation, operating at 40 kV and 30 mA. Data were collected over 2θ between 10 to 60°. Assignment of lines was made by comparison with JCPDS files.

C_2AS gel 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). Water boehmite suspension was peptized by mixing with HNO_3 ($pH \cong 2.5$) at 55°C. Then the calculated amount of the silica sol and solution of $Ca(NO_3)_2.4H_2O$ 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 $Ca(NO_3)_2.4H_2O$. The sol was poured onto a glass plate and was gelled. Afterwards, gels were dried at 100°C and then gradually heated at from 500°C to 1250°C. Calcium hydroxide (CH) was used instead calcium oxide (C) and anhydrite ($C\bar{S}$) was substituted by gypsum ($C\bar{S}H_2$).

Then, series of samples were prepared by mixing and homogenizing minerals and xerogels in the proportion as elucidated in Table1. The hydration of samples at defined water/cement ratio was performed by using conduction calorimeter at 25°C [22]. Mineralogical composition of samples was derived from gehlenite hydrate/ettringite ratio as described in figure 1.

Table 1. Studied samples.

Samples	1	2	3	4	5	6
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
Gehlenite hydrate: ettringite	100:0	80:20	60:40	44.7:55.3	20:80	0:100

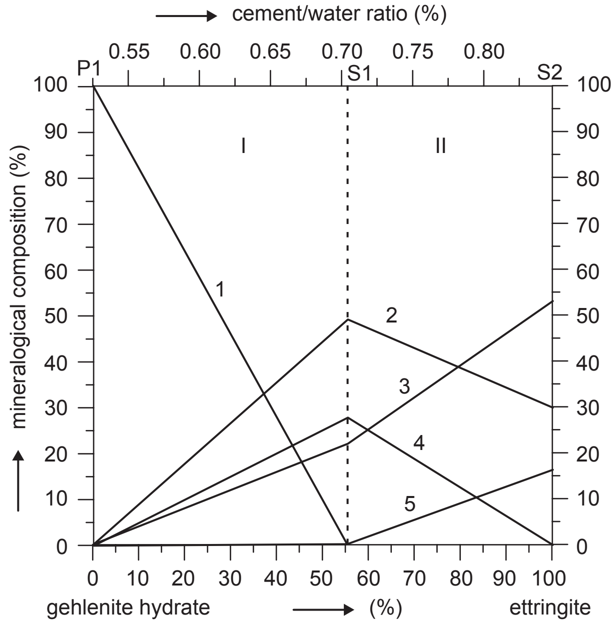


Figure 1. C_2AS(1)–$C_4A_3\bar{S}$(2)–$C\bar{S}$(3)–C_2S(4)–C(5) system and phase associations (I, II), singular points (S1, S2) and gehlenite point (P1) [20].

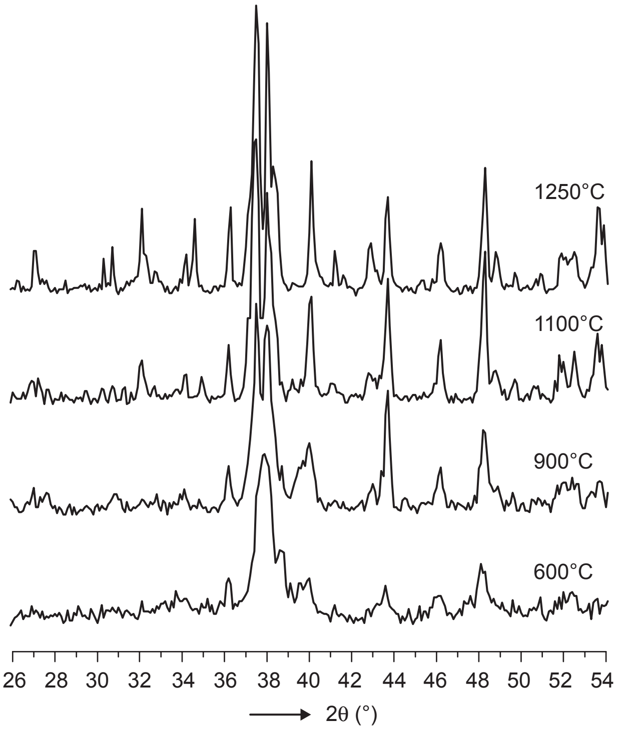


Figure 2. XRD diffraction patterns of C_2S xerogels calcined at different temperatures.

RESULTS AND DISCUSSION

Formation and hydraulic activity of C_2S

Figure 2 presents the degree of crystallization of xerogel of C_2S with temperature. As it can be seen, diffraction peaks of C_2S become narrower with increasing temperatures. In addition, main diffraction intensity for C_2S appears at 600°C between 2θ 37-38°, confirming that the nucleation and crystallization of this phase starts at lower temperatures. With increasing heating temperature, the crystallization of this phase is well emphasized and the board peak appeared in sample heated at 600°C is divided into 2 peaks measured at d = 2.28 Å and d = 2.74 Å. Assignment of lines of diffraction peaks compared with JCPDS files demonstrates the presence of β-C_2S as an unique and pure phase. As xerogel C_2S was not doped, it can be proposed that sol-gel technique will be a suitable method to synthesize C_2S without stabilizer. Also, the reaction processes and transformations that occur during the heating of C_2S were evidenced by the DTA curve.

The hydration activities of xerogels of C_2S calcined at 600°C and 900°C were investigated at 25°C, 40°C, 50°C and 70°C. The results are presented by figures 3 and 4. Gel C_2S annealed at 600°C is hydraulically active as demonstrated by calorimetric curves showing two peaks separated by induction period (figure 3). The intensity of hydration reaction increases with increasing temperature at which measurements were performed. While C_2S prepared by conventional method has lower hydraulic activities [23], nano particle of C_2S as xerogel with high specific surface exhibits high hydration rate.

The rate of hydration heat with temperature of xerogel calcined at 900°C is reported in figure 4. The calorimetric curves present one peak. The absence of second peak demonstrates that hydration is considerably reduced. When the samples are crystallized, the specific surface decreases and C_2S becomes less and less active. In addition, hydration reaction rate of C_2S calcined at 900°C increases with increasing temperatures. The nano particles of C_2S hydrated show a microstructure with C–S–H after one day, and then the crystals are well developed after 7 days of curing (figures 5 and 6).

Formation and hydraulic activity of C_2AS

Figure 7 shows the crystallization progress of C_2AS xerogel. Diffraction peaks characterizing the presence of β-C_2S appear in samples heated at 600°C. Gradually with heating temperatures, this peak disappears and the diffraction peak at 2θ = 36.56° characterizing gehlenite appears according to JCPDS. These findings confirm that β-C_2S reacts with alumina (reaction (1)) to form C_2AS crystal as demonstrated by diffraction peaks for gehlenite.

$$C_2S + A = C_2AS \qquad (1)$$

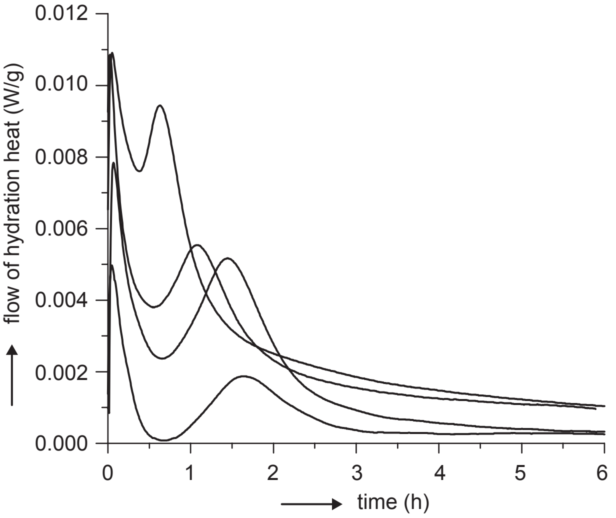


Figure 3. Calorimetric curves of nano-crystalline C_2S calcined at 600°C; w/c = 0.5.

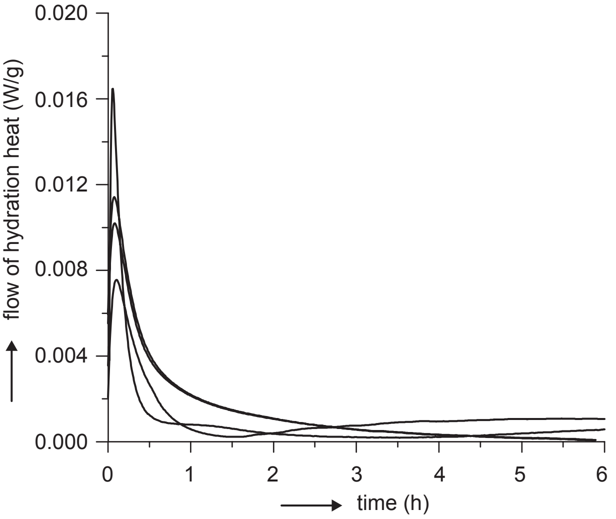


Figure 4. Calorimetric curves of nano-crystalline C_2S calcined at 900°C; w/c = 0.5.

The positions of the peaks are the same but the peak intensities differ due to the crystallinity of the dicalcium silicate and gehlenite.

Calorimetric measurements on samples of C_2AS prepared at 600°C and 1100°C are depicted in figures 8 and 9. The profile of the hydration peak of samples C_2AS and C_2S calcined at 600°C is shaper than that of samples calcined at 1100°C and 900°C. The influence of temperatures is evidently demonstrated; the higher is the temperature, the higher is the magnitude of hydration reaction. The results indicate that the maximum time of heat evolution at hydration of C_2AS varies from 1 to 2 h and at C_2S from 2 to 6 h.

SEM micrographs of C_2AS (figures 10 and 11) calcined at 600°C show plate crystal of gehlenite hydrate.

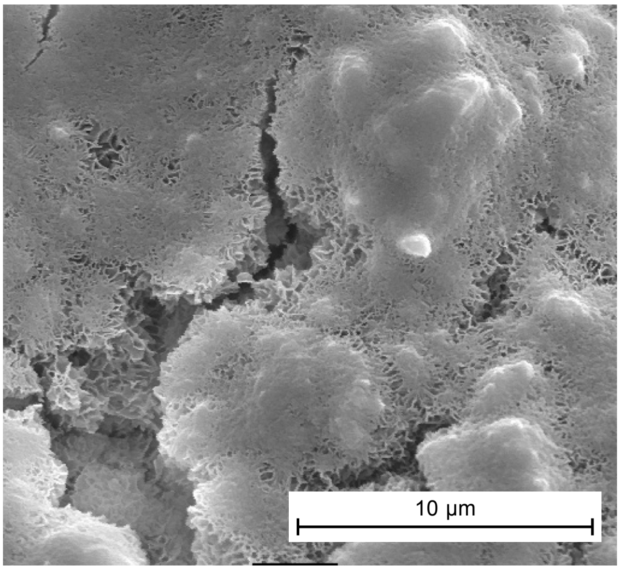


Figure 5. SEM micrograph of nano-crystalline phase of C_2S calcined at 600°C after 1-day hydration. Layer of C–S–H with honeycomb structure is observed.

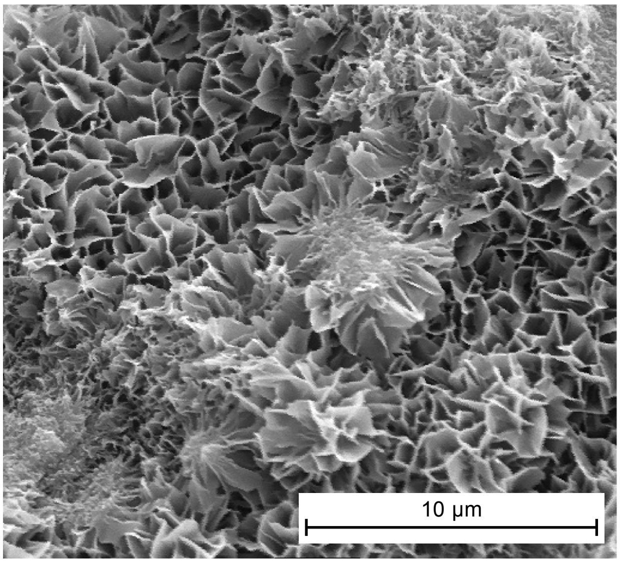


Figure 6. SEM micrograph of nano-crystalline phase of C_2S calcined at 600°C after 7-day hydration. Crystal structure is developed.

Formation of crystallohydrates in C_2AS–C_2S–$C_4A_3\bar{S}$–$C\bar{S}$–C–H system

The course of heat evolution during hydration of samples obtaining by homogenizing minerals is described by means of calorimetric curves (figures 12a-f). The measurements were performed at room temperature. It is evident, that the mineralogical composition, as calculated from "gehlenite hydrate/ettringite" ratio, influences the course of hydration. The hydration reaction of samples with higher content of C_2S and C_2AS prepared via sol-gel process occurs in two phases separated by induction period. With increasing expected ettringite, reaction occurs in one phase. The formation of ettringite in the presence of $Ca(OH)_2$ is achieved within two hours.

Figure 13 presents X-ray diffraction analyses of samples hydrated for 7 days. The XRD patterns show that the main hydration product in samples 1, 2 and 3 is gehlenite hydrate which is formed by primary and secondary reaction (reaction (4)). The primary hydration product of C_2S are C–S–H gel and $Ca(OH)_2$. Later on the crystallization of gels leads to the formation of tobermorite or other calcium silicate hydrates.

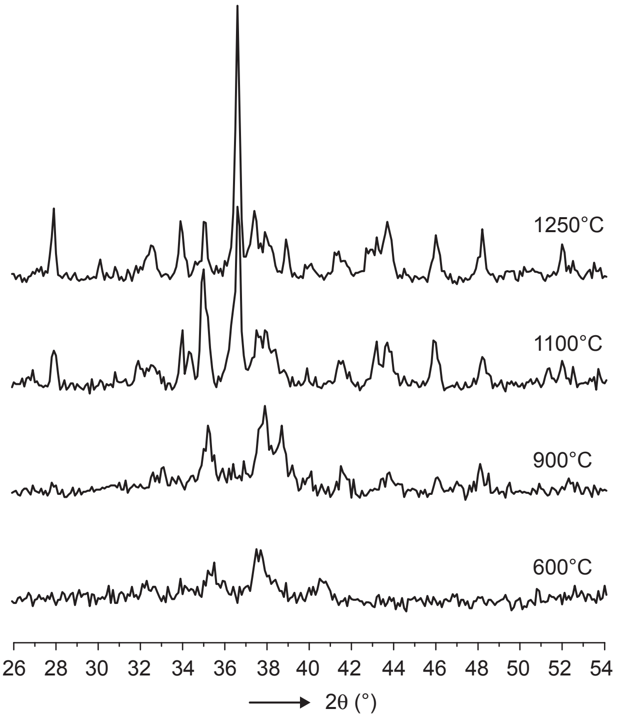


Figure 7. XRD diffraction patterns of C_2AS xerogels calcined at different temperatures.

$$C_2S + 2H = C\text{–}S\text{–}H + CH \qquad (2)$$

The formation of gehlenite hydrate can be also represented by two reactions. Firstly, gehlenite hydrate can be formed by hydration reaction of C_2AS xerogel according to (reaction (3))

$$C_2AS + 8H = C_2ASH_8 \qquad (3)$$

or as secondary reaction between calcium silicate hydrogel, calcium hydroxide and gibbsite.

$$C\text{–}S\text{–}H + CH + AH_3 + 3H = C_2ASH_8 \qquad (4)$$

Sample 4 is 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 reactions between CSH, CH (calcium hydroxide) and AH_3 (gibbsite) (reaction (4)). Consequential chemical equation in sample 4 which corresponding to singular point S1 (figure 1) can be written:

$$C_4A_3\bar{S} + 2C\bar{S} + 2C_2S + 48H = C_6A\bar{S}_3H_{32} + 2C_2ASH_8 \ (5)$$

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 following the reaction:

$$C_4A_3\bar{S} + 8C\bar{S} + 6C + 96H = C_6A\bar{S}_3H_{32} \qquad (6)$$

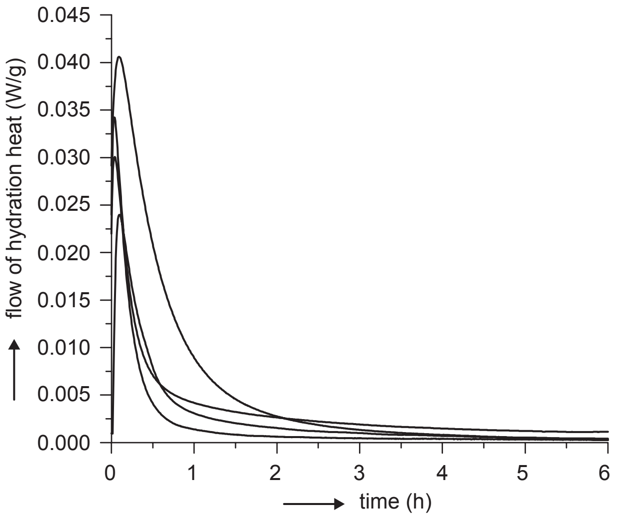


Figure 8. Calorimetric curves of nano-crystalline C_2AS calcined at 600°C; w/c = 0.5.

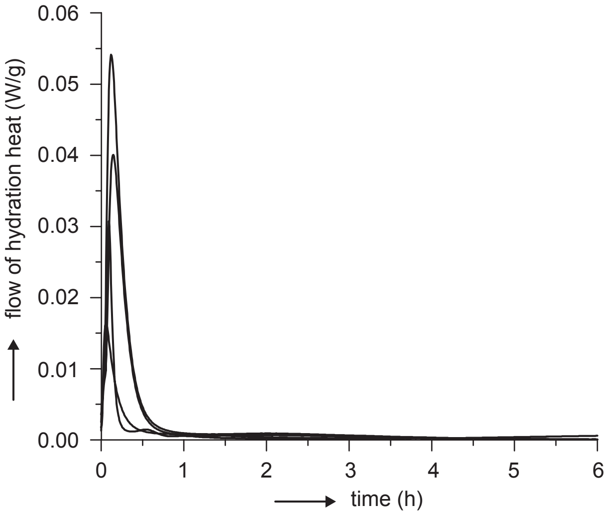


Figure 9. Calorimetric curves of nano-crystalline C_2AS calcined at 1100°C; w/c = 0.5

Figure 14 presents SEM micrographs of samples after 7 days of hydration. The hydration was kept in suspension, allowing thus to accelerate process of reaction. Large tabular crystals of gehlenite are observed in samples 1, 2, 3. Here, gehlenite hydrate is dominating phase (figure 7). At singular point, two distinct hydrated products can be observed: tabular shape supplemented by large and elongated crystal hydrates. These last ones are attributed to ettringite. The similar microstructure can be observed in micrographs of samples 5 and 6. 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 is due to the high hydraulic activity of C_2S and C_2AS synthesized by sol-gel method.

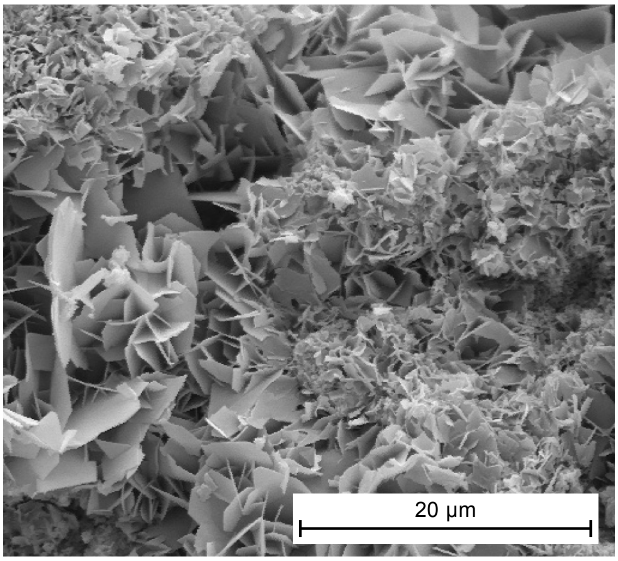


Figure 10. SEM micrograph of C_2AS calcined at 600°C after 1-day hydration.

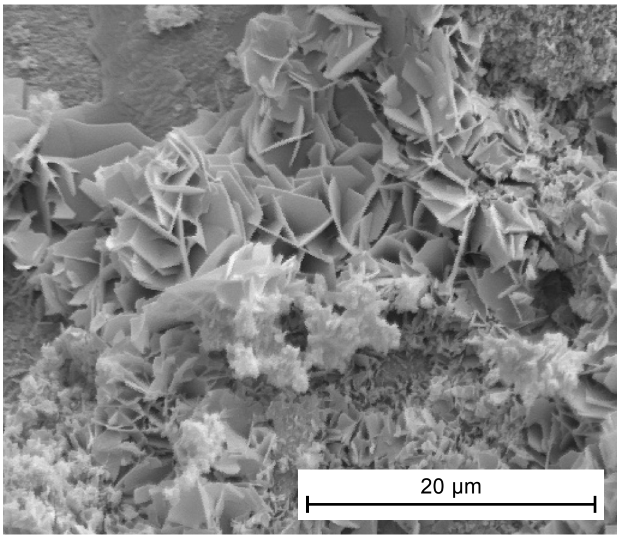
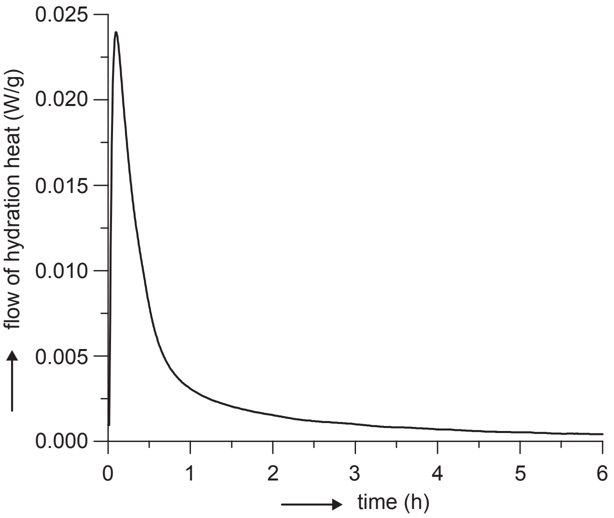
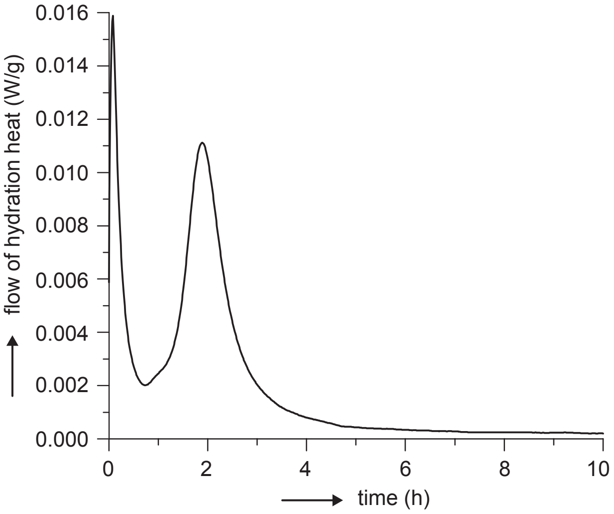


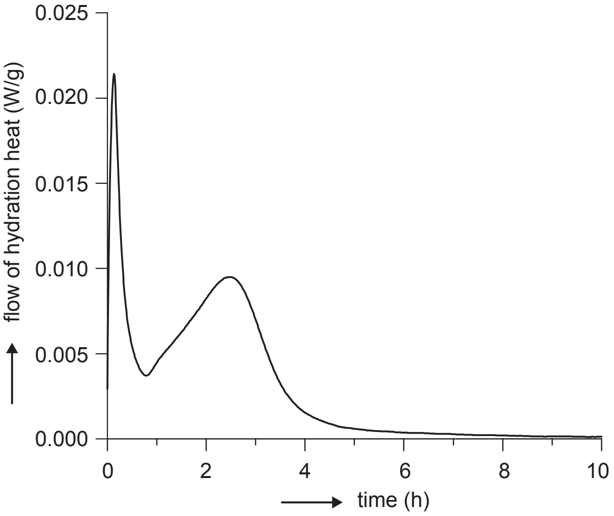
Figure 11. SEM micrograph of C_2AS calcined at 600°C after 7-day hydration.



Sample 1

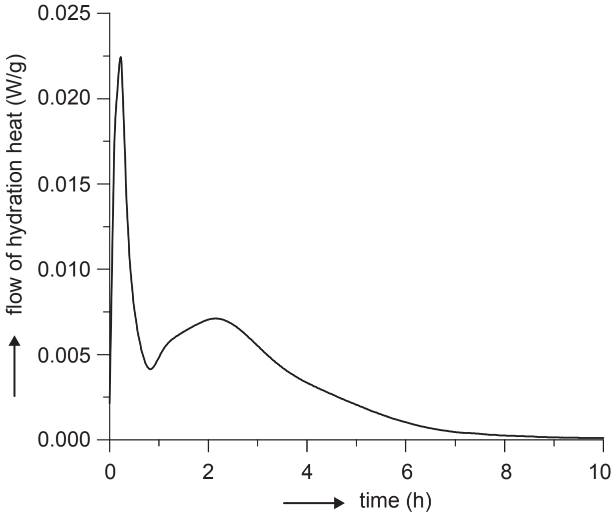


Sample 2

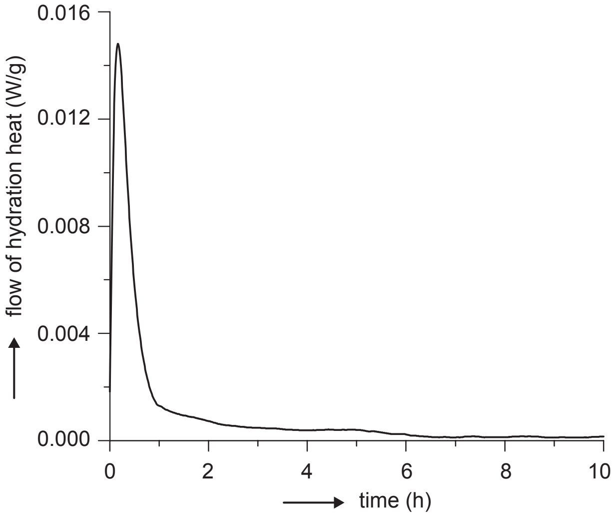


Sample 3

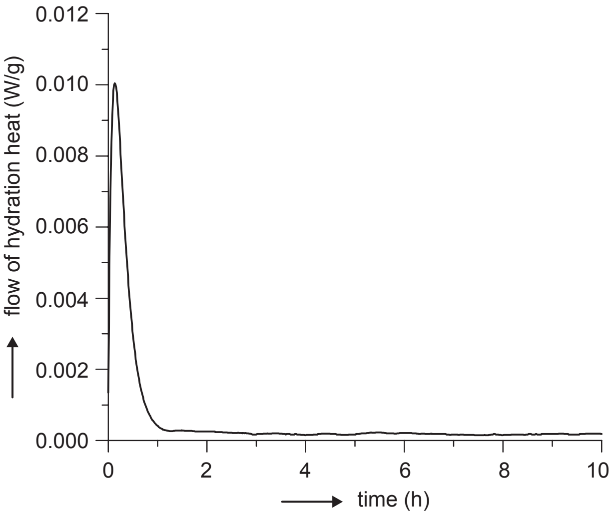
Figure 12. Calorimetric curves.



Sample 4



Sample 5



Sample 6

Figure 12. Calorimetric curves (continue)

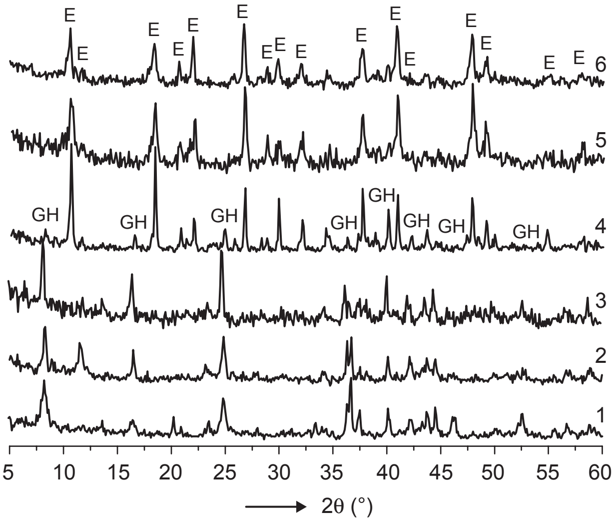
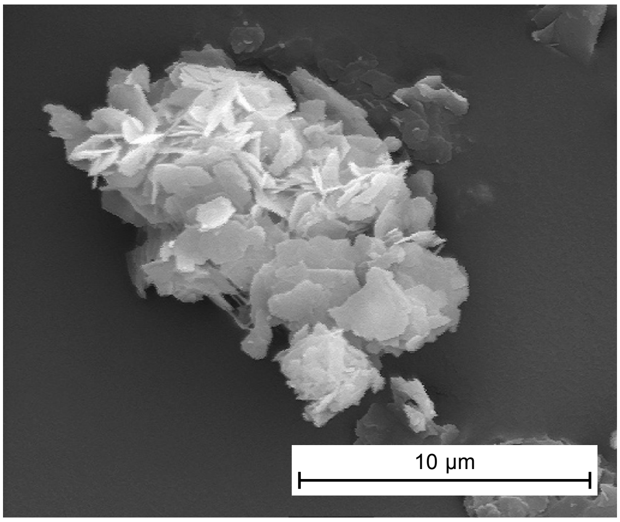
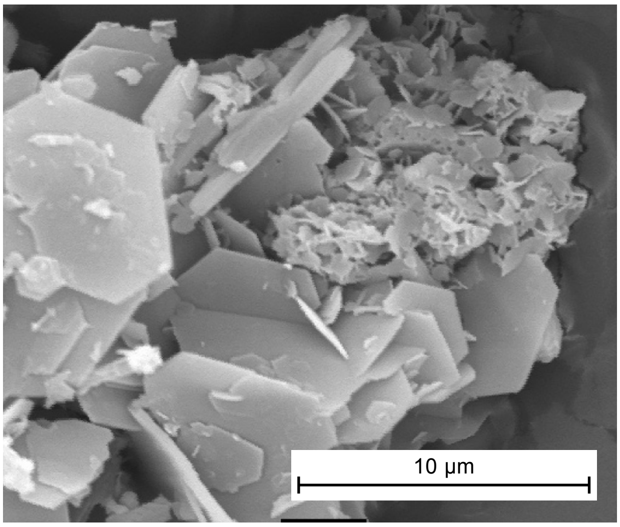


Figure 13. XRD diffraction patterns of samples after 7 days of hydration at 25°C. E- ettringite, GH - gehlenitehydrate

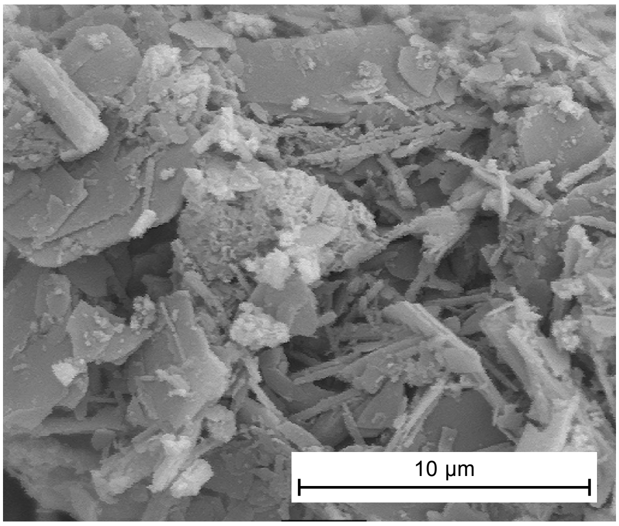


Sample 1

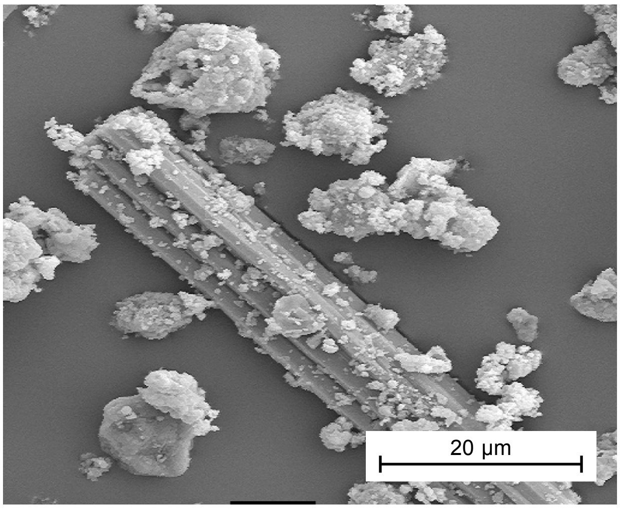


Sample 2

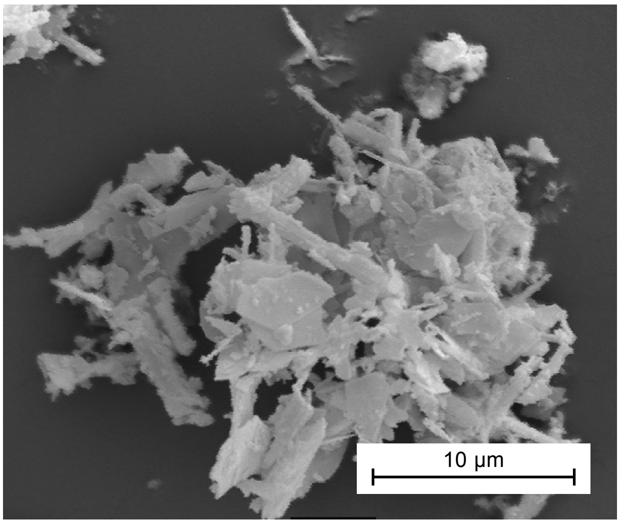
Figure 13. SEM micrographs.



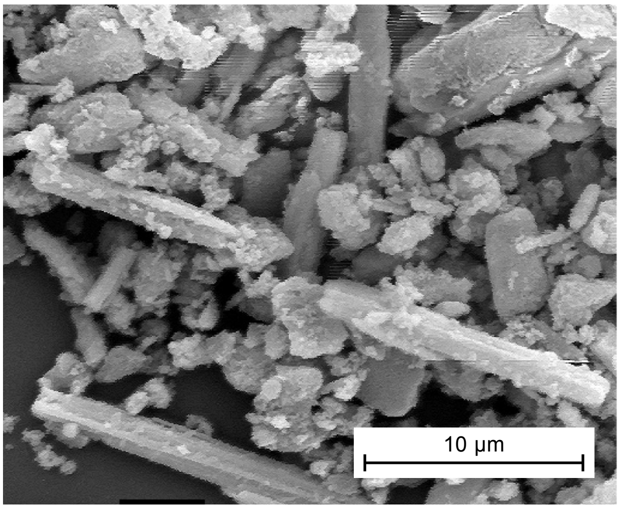
Sample 3



Sample 6



Sample 4



Sample 5

Figure 13. SEM micrographs.

CONCLUSION

This work has explored an alternative method (sol-gel processing) 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 gehlenite hydration. Binding materials in the framework of C_2AS–C_2S–$C_4A_3\bar{S}$–$C\bar{S}$–C system, that can be considered as belonging to the class of Sulfoaluminate Belite Cements (SAB) 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 identified. The hydration leading to coexistence of two crystallohydrates of gehlenite hydrate and ettringite has been achieved by primary and secondary reactions.

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HYDRATÁCIA A MIKROŠTRUKTÚRA SPOJÍV OBSAHUJÚCICH C_2AS A C_2S SYNTETIZOVANÝCH SÓL-GÉL METÓDOU

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Sól-gél metóda bola použitá na syntézu nanočastíc C_2AS a C_2S. Tieto cementové fázy pripravené reakciou v tuhej faze pri vysokych teplotách sú hydraulicky latentné alebo menej aktívne. Po kalcinácii pri 600°C boli jednotlivé vzorky C_2S a C_2AS tepelne spracované pri 900°C resp. 1100°C. V modelovom systéme $C_2AS-C_2S-C_4A_3\bar{S}-C\bar{S}-C$ boli použité fázy C_2S a C_2AS pripravené sól-gél metódou. Výsledky u týchto vzoriek ukázali lepšie hydraulické vlastnosti ako to bolo u systému kde boli použité čisté minerály. Hydratácia tohto systému vedie ku koexistencii dvoch rovnovážnych krýštalohydrátov gehlenithydrátu a ettringitu, ktoré vznikli primárnou aj sekundárnou reakciou. Obidva kryštalohydráty gehlenithydrát a ettringit boli stabilné.