

HYDRATION BEHAVIOR OF C₂S AND C₂AS NANOMATERIALS, SYNTHETIZED BY SOL–GEL METHOD

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Hydration behavior of dicalcium silicate (C₂S) (Cement chemistry nomenclature is used where C=CaO, S=SiO₂, A=Al₂O₃, \bar{S} =SO₃) and gehlenite (C₂AS), synthesized by sol–gel method was investigated by means of isothermal heat flow calorimeter at different temperatures. These phases were obtained by crystallization processing at different temperatures from their xerogels (nano-crystalline) prepared by the sol–gel method at ambient temperature. The crystallization of C₂S begins below 600°C and it is well crystallized at 900°C. X-ray diffraction patterns reveal that β-C₂S is formed and it remains stable since after slow cooling. The crystallization of C₂AS xerogels starts with the formation of C₂S, then it reacts with alumina to form mineral C₂AS at 1100°C. The effect of hydration temperature upon the hydration reaction of C₂S obtained at 600 and 900°C and C₂AS annealed at 600 and 1100°C was investigated by means of isothermal calorimeter. An increase in the temperature of hydration brought about initial acceleration of all samples, as indicated by the increased magnitude of peak of calorimetric curves. The microstructure of the samples cured at hydrothermal condition after 1 and 7 days has been examined by means of scanning electron microscopy (SEM). Fine crystals of calcium silicate hydrate (C–S–H) were developed in C₂S samples, while C₂AS has been hydrated to form gehlenite hydrate supplemented by C–S–H.

Keywords: dicalcium silicate, gehlenite, hydration products, hydration reactivity, isothermal calorimeter, temperature

Introduction

Dicalcium silicate (C₂S) is one of the four main clinker minerals of ordinary Portland cement (OPC) [1–4] and sulfoaluminate belite (SAB) cement [2–9]. It exists in five polymorph modifications [1, 10]. β-C₂S is a metastable modification at all temperatures. The thermal transition of β-C₂S to the γ-modification at lower temperature (<500°C) is accompanied with a volume increase, responsible for the well-known phenomenon of dusting. Furthermore, γ-C₂S has no hydraulic properties. The stabilization of β-C₂S modification has retained attention of many investigators. Minor compounds were introduced into the lattice of β-C₂S to stabilize it and hence to improve the hydraulicity of belite cement [11, 12]. Processes including particle size and rapid cooling [13], upon the stabilization of β-C₂S has been investigated. Twice firing with intermittent grinding to micro-size has stabilized β-C₂S with rapid cooling and without using dopants. It seems that the method of β-C₂S synthesis has an influence upon its stabilization.

The authors [14] have studied the hydration kinetics of C₂S–C₄A₃ \bar{S} –C \bar{S} system. In this system, dicalcium silicate was synthesized via sol–gel method

and then annealed at different temperatures. The heat evolution of this system is higher than for the system containing β-C₂S, synthesized by conventional method [15].

Generally, hydration of C₂S generates calcium hydroxide with the formation of C–S–H.



Other phase, gehlenite with formulae Ca₂Al(AlSi)O₇ or Ca₂Al₂SiO₇ is a mineral belonging to the group of millit. In addition to C₂S, C₂AS is one of the clinker minerals of low-energy cements. Its formation as an intermediary clinker product occurs during the burning of OPC [1]. Until now, the hydration kinetics and mechanism of mineral gehlenite has not been widely and deeply investigated. The reason may be linked to its low hydraulic activities and to the conditions in which gehlenite hydrate could be formed. However, this hydrated product (C₂ASH₈), also known as mineral stratlingite, is generally found in concrete based on slag cement, or high-alumina cements in the presence of silicon oxide [16, 17]. Indeed, concretes made from mixtures of high-alumina cements and granulated blast furnace slag show increasing mechanical properties after longer time of hydration [16]. The reason for this is that gehlenite

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hydrate rather than calcium aluminate hydrate forms are the major phase due to the presence of granulated blast furnace slag. Other authors [14, 17, 18] have also reported that, the hydration of calcined clays with lime produces essentially C_2ASH_8 and C–S–H with small quantity of C_4AH_{13} .

Theoretically, gehlenite hydrate can be formed by hydration reaction of C_2AS according to Eq. (2)



The hydration of glasses in $CaO-Al_2O_3-SiO_2$ system has showed that gehlenite hydrate constitutes the principal phase of the strong and fast setting cements. Experimental investigation [19] conducted on $CaO-Al_2O_3-SiO_2-SO_3-H_2O$ system have proved that the most important and the most stable phases formed are C–S–H (Ca/Si varies between 0.9 to 1.8), $Ca(OH)_2$, gehlenite hydrate (C_2ASH_8 , GH) ettringite ($C_6\bar{A}S_3H_{32}$, AF_T), siliceous hydrogarnet (C_3ASH_6 , Si–HG).

With regard to the energy cost and technical conditions for the glass melting, the present work was undertaken to find an alternative method (sol–gel process) allowing the synthesis of gehlenite with high hydraulic reactivity. Also, the same method was applied to prepare β - C_2S without dopant. Both phases, synthesized by sol–gel method are more reactive than their analogs prepared by conventional route [19].

Experimental

C_2AS gel was prepared using commercial boehmite powder (Condea Pural SB, ~5 nm, Condea, Germany), silica sol (Tosil, 30 mass% of silica, particles ~20 nm, TONASO Neštenice, Czech Republic) and solution of $Ca(NO_3)_2 \cdot 4H_2O$ ($c=1.234 \text{ mol L}^{-1}$). Water boehmite suspension was peptized by mixing with HNO_3 ($pH \approx 2.5$) at 55°C . Then the calculated amount of the silica sol and solution of $Ca(NO_3)_2 \cdot 4H_2O$ were slowly added into the boehmite suspension. The same procedure was used to prepare nano-crystalline C_2S from stoichiometrically mixture of silica sol and solution of $Ca(NO_3)_2 \cdot 4H_2O$. The silica sol was poured onto a glass plate and was gelled. Afterwards, gels were dried at 100°C and then heated at different temperatures (600, 900, 1000 and 1250°C) for 1 h.

Description of the calorimeter

The rate of the heat evolution was measured with a conduction calorimeter (ZIAC, German Academy of Science). The sensitive part of the calorimeter consists of a system of two cells inserted in an isolating metallic block. The first, containing the standard sample, acts as a reference, and the second one contains

the sample of hydrating cement. This system is covered by solid foam of polyurethane, which isolates the metallic block from the lid. Heat flux transducer links the two cells. When the exothermic hydration reaction starts, the temperature difference between the two cells generates electromotive tension such that the flux proportional to the heat transfer is continuously monitored through a converter module as a temperature rise in the hydrating cement. The temperature data are then used to determine the flow of heat generated and the heat of hydration. The device allows measuring simultaneously four samples connected in difference to an inert reference sample. Furthermore, measurements can be performed in temperature range from 10 to 90°C .

Four measurements of 2 g of phases C_2AS or C_2S were carried out with a water/cement ratio of 0.5 at 20, 30, 50 and 70°C . The results of heat evolution curve are a mean of four data. The data stored on the hard drive personal computer was afterwards plotted and suitably analyzed.

Results and discussion

The progresses in crystallinity of C_2AS and C_2S with annealing temperatures are reported in Figs 1 and 2. It can be seen that, the main diffraction intensity for C_2S appears at 600°C at 2θ $37-38^\circ$, confirming that the nucleation and crystallization of this phase starts at lower temperatures. With increasing annealing temperature, the crystallization of this phase is well emphasized and the broad peak appeared in sample

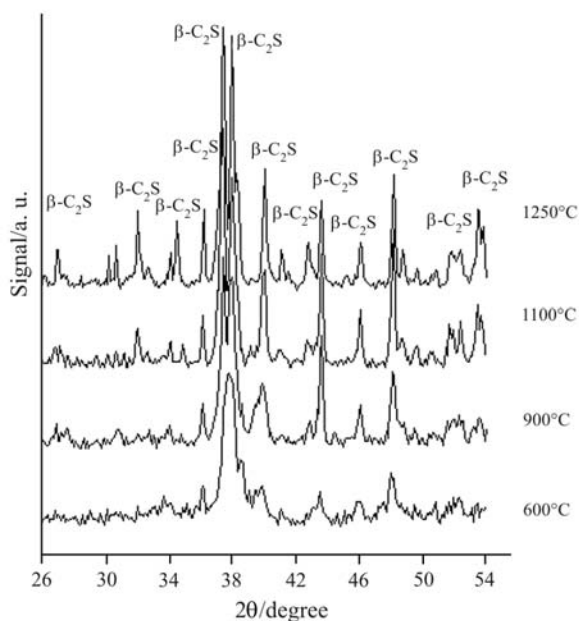


Fig. 1 Crystallization process of nano-crystalline C_2S at different temperatures

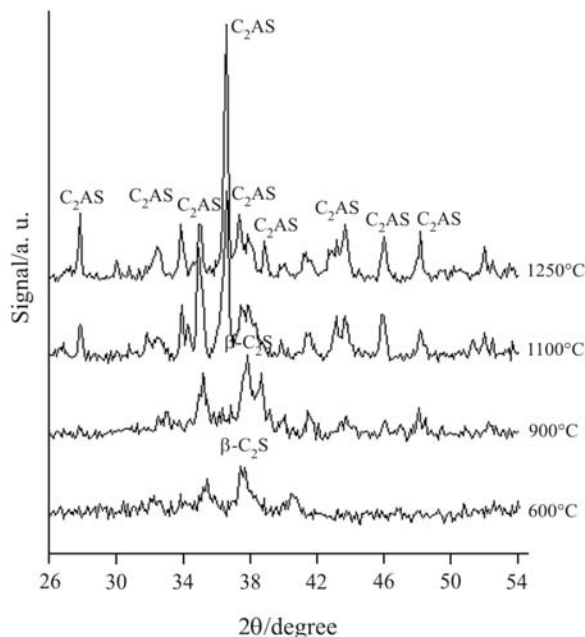


Fig. 2 Crystallization process of nano-crystalline C₂S at different temperatures

heated at 600°C is divided into 2 peaks measured at $d=2.28$ and 2.74 Å. These diffraction peaks characterize the presence of β-C₂S as a unique and pure phase. As xerogel C₂S was not doped, it can be proposed that the sol-gel technique will be a suitable method to synthesize β-C₂S without stabilizer.

Figure 2 shows the crystallization progress of C₂AS xerogel. Diffraction peaks characterizing the presence of β-C₂S appear in samples heated at 600 °C. Gradually with annealing temperatures, β-C₂S reacts with alumina (Eq. 3) to form C₂AS crystal as demonstrated by the main diffraction peaks at $2\theta=36.56^\circ$ for gehlenite.

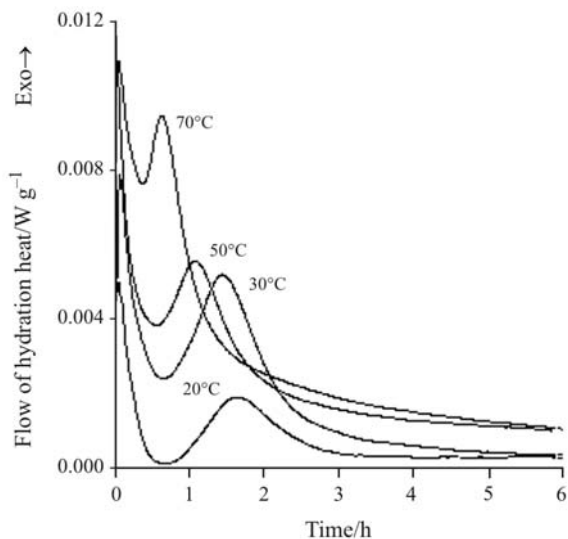


Fig. 3 Heat evolution at 20, 30, 50 and 70°C with $w/c=0.5$ of nano-crystalline C₂S, annealed at 600°C

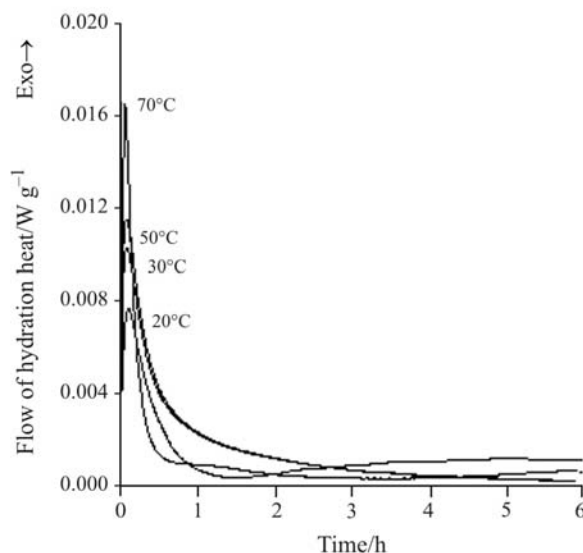


Fig. 4 Heat evolution at 20, 30, 50 and 70°C with $w/c=0.5$ of nano-crystalline C₂S, annealed at 900°C



The variations in hydration heat flow with time are described by means of calorimetric curves (Figs 3–6). Figures 3 and 4 show the influence of temperature upon the hydration reaction of nano-crystalline C₂S annealed at 600 and 900°C. Two peaks separated with induction period characterize the hydration reaction of sample heated at 600°C. It is clear that with increasing temperatures, the magnitude of hydration has been increased and the induction period has been shortened. The hydration reaction of sample C₂S, heated at 1100°C occurs in one phase without period. Calorimetric measurements on samples of C₂AS, prepared at 600 and 1100°C are depicted in Figs 5 and 6.

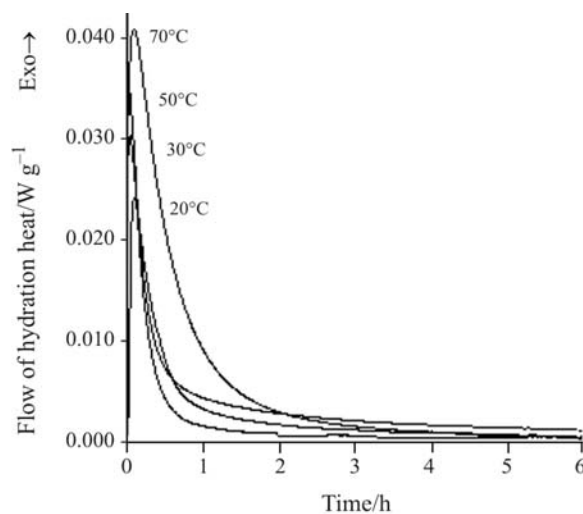


Fig. 5 Heat evolution at 20, 30, 50 and 70°C with $w/c=0.5$ of nano-crystalline C₂AS, annealed at 600°C

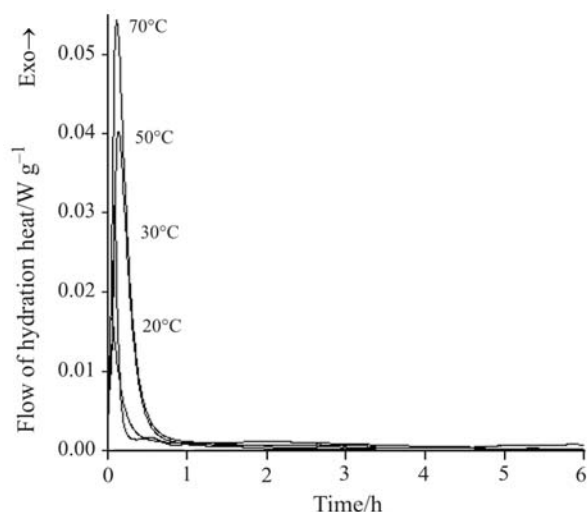


Fig. 6 Heat evolution at 20, 30, 50 and 70°C with $w/c=0.5$ of nano-crystalline C_2AS , annealed at 1100°C

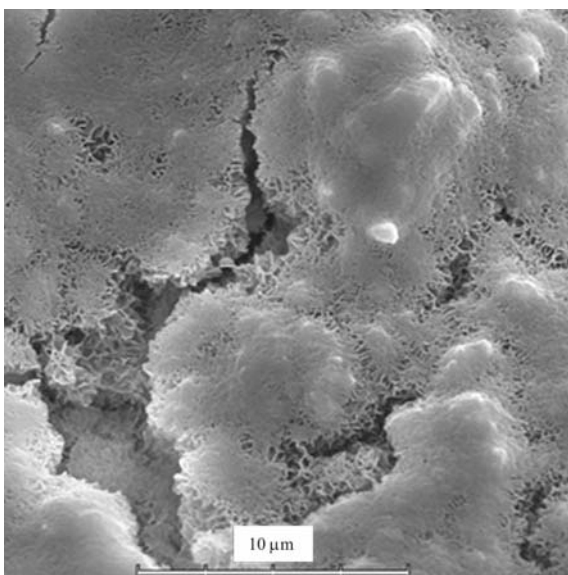


Fig. 7 SEM image of nano-crystalline phase of C_2S , annealed at 600°C after 1-day hydration

Figures 7 and 8 show the SEM images of hydrated nano-crystalline C_2S after 1 and 7 days of curing in autoclave. Microstructure development clearly demonstrates the high hydraulic activity of nano-crystalline C_2AS and C_2S . The crystals of tobermorite are well developed. The SEM images of hydrated C_2S ($C-S-H$) look different from the SEM image of $C-S-H$ nanocomposite materials obtained by incorporating poly(vinyl alcohol) (PVA) into the inorganic layers of $C-S-H$ during precipitation of quasi-crystalline $C-S-H$ from aqueous solution and reported in [20]. There are very fine crystallized with honeycomb structure, while the authors reported crystallized foil like $C-S-H$ in [20].

SEM images of C_2AS , heated at 600°C (Figs 9 and 10) and hydrated for 1 and 7 days show plate

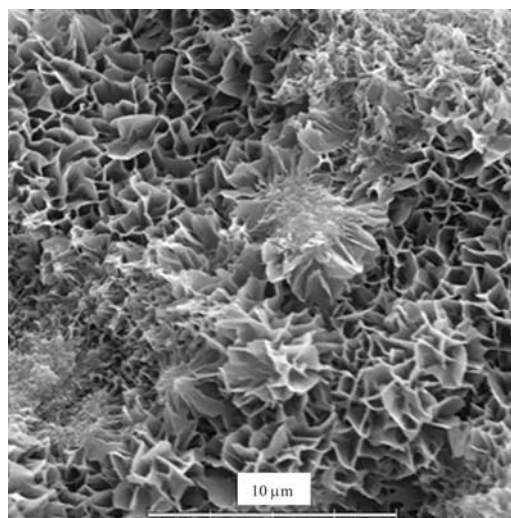


Fig. 8 SEM image of nano-crystalline phase of C_2S , annealed at 600°C after 7-day hydration

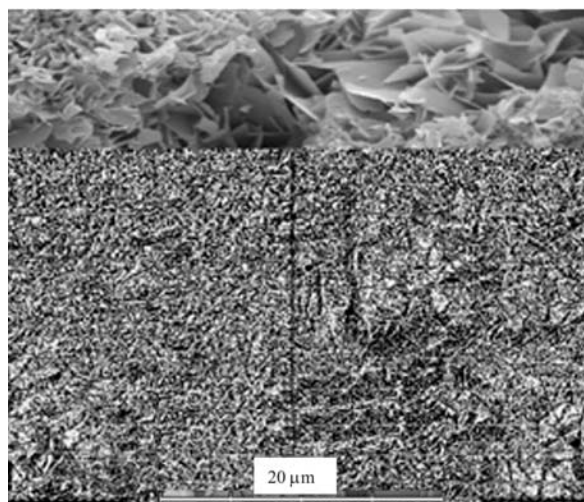


Fig. 9 SEM image of C_2AS , annealed at 600°C after 1-day hydration

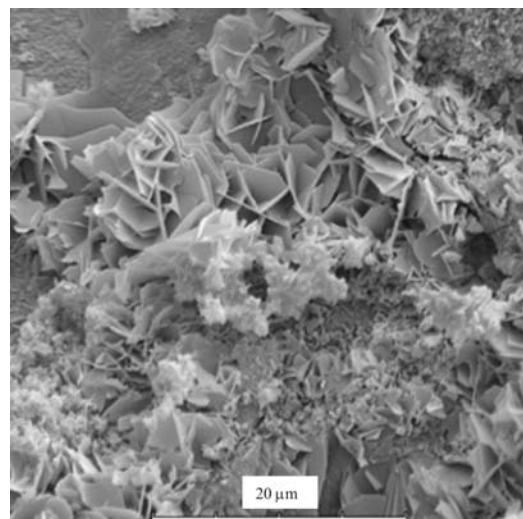


Fig. 10 SEM micrograph of C_2AS , annealed at 600°C after 7-day hydration

crystal of gehlenite hydrate incorporated in the mass of C–S–H fine crystals. Reaction seems to be achieved after one day in autoclave. XRD-patterns revealed the presence of gehlenite hydrate as major hydrated product as previously reported by [15].

Conclusions

C₂AS and C₂S minerals were synthesized by crystallization processing at different temperatures from xerogels, prepared by the sol–gel method. The crystallization of C₂S starts at temperature lower to 600°C and is achieved at 900°C. Further crystallization processing by temperature has led to the formation of stable β-C₂S without doping and rapid cooling. The hydraulicity of C₂S, annealed at different temperatures diminishes with crystallization degree, but it is enhanced with hydration temperatures. Heating of C₂AS xerogel at 600°C leads to the formation of C₂S, then it reacts with alumina to form gehlenite at 1100°C. The temperature at which hydration occurs has a great influence on the hydraulicity of C₂AS phases. The microstructure of samples, hydrated in autoclave is well developed. The crystals are tobermorite-like for C₂S hydration, while the crystal of gehlenite hydrate supplemented by C–S–H in hydrated C₂AS.

Acknowledgements

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