HEAT EVOLUTION AND MECHANISM OF HYDRATION IN CaO–Al$_2$O$_3$–SO$_3$ SYSTEM

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The hydration behavior of CaO-Al$_2$O$_3$-SO$_3$ system has been investigated over the temperature range of 25 to 80°C and at three different water/solid ratios 0.5, 0.7 and 1.0 using isothermal conduction calorimeter. In the defined system, $C_4A_3\bar{S}$ known as Klein compound was supposed to be the main mineral phase. An increase in the temperature of hydration brought about initial acceleration of all samples treated under different water/solid ratios, as indicated by the increased hydration rate. Also, there was a clear evidence of increasing intensity of the main peaks with increasing water/solid ratio at hydration temperature of 25°C and 40°C. Contrarily, at higher temperatures (60°C and 80°C) the magnitude of hydration decreased with increasing water/solid ratio. Kinetics of hydration $C_4A_3\bar{S}$ can be described by Avrami model. The value of kinetic exponent n = 3 implies that the hydration was controlled by nucleation and three-dimensional crystal growth. Calculated values of activation energy for water/solid ratio 0.5, 0.7 and 1.0 were 21.0, 17.2 and 16.4 kJ/mol.
(* In this paper usual cement chemistry notation is used in which: C = CaO, $\bar{S}$ = SO$_3$, A = Al$_2$O$_3$, H = H$_2$O)*

INTRODUCTION

Calciumsulfoaluminate cements belong to the class of low-energy cements (LEC) [1-3]. These cements differ from traditional ordinary portland cement (OPC) by clinkering temperatures, and also are classified as "low-CO$_2$ cements" [4]. The main mineral phase is $C_4A_3\bar{S}$, which does not occur in OPC and markedly supports to consequential properties of calciumsulfoaluminate cements. The applications of these cements have recently been receiving growing interests [4-10]. Until now, the hydration of calciumsulfoaluminate cements has been investigated with respect to their capability to set and harden, as well as with to their mechanical properties and microstructural development [5-10]. The hydration of $C_4A_3\bar{S}$ alone leads to the formation of monosulphate (equation (1)), while in environment with higher water content, $C_4A_3\bar{S}$ hydrates (equation (2)) are formed besides ettringite, monosulphate, hydrogarnet, and gibbsite. These hydrated products are found to co-exist, but ettringite can finally convert to monosulphate.

$$C_4A_3\bar{S} + 18\ H = C_4A\bar{S}H_{12} + 2AH_3 \qquad (1)$$

$$4C_4A_3\bar{S} + 80\ H = C_6A\bar{S}_3H_{32} + C_4A\bar{S}H_{12} + \\ + 2C_3AH_6 + 8AH_3 \qquad (2)$$
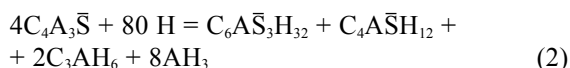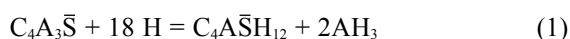
The hydration of $C_4A_3\bar{S}$ is an exothermic reaction, and the heat evolved can be measured by conduction calorimeter. Therefore, the effect of temperature and water/solid ratio can be investigated.

The hydration of system including $C_4A_3\bar{S}$ phase has been investigated at 20°C. Satisfactory results were obtained by studying the influence of chemical admixtures upon C_2S–$C_4A_3\bar{S}$–$C\bar{S}$ system [11]. It was found that the chemical compounds like calcium chloride and aluminum chloride substantially inhibit the hydration rate, while sodium sulphate and aluminum sulphate enhances the reaction of the system with water. Additionally, the influence $C\bar{S}$ annealed at different temperatures was investigated [12]. It is important to emphasize that the hydration rate of the given system depends on the particle size of individual clinker minerals [13]. All of these results demonstrate that the mechanism and hydration rate of calciumsulfoaluminate cements depend on several factors. As it is well known, hydration of cementitious materials is a complicated reaction involving several processes: individual and interdependent chemical reactions of clinker minerals, heat evolution, setting, hardening, and microstructural changes. With respect to the complexity of hydration and factors influencing the reaction rate of cement, in the present experimental work we reported on the kinetics and mechanism of $C_4A_3\bar{S}$ hydration by following the heat evolution under different temperatures and cement/solid ratios. There are two model mechanisms of $C_4A_3\bar{S}$ hydration: a topochemical and through-solution mechanism. According to the first one, products of hydration are

formed on the surface of $C_4A_3\bar{S}$, while in the second mechanism the hydrated products are precipitated from a solution supersaturated with respect to Ca^{2+}, $[Al(OH)_4]^-$ and SO_4^{2-}. The mechanism of $C_4A_3\bar{S}$ hydration is markedly influenced by external factors and it is complicated to postulate that hydration occurs only by a one mechanism. This idea was supported by Palou and Majling [14], who ascertained that hydration of calciumsulfoaluminate cements proceeds by a mechanism lying somewhere in-between these two extremes. The predominance of the first or second mechanism will depend on factors such as temperature, water/solid ratio, specific surface, chemical admixtures, and their "scale". There is still divergence of views on the mechanism of $C_4A_3\bar{S}$ hydration under different conditions [15, 16] that justifies our investigation.

The aim of this work was to determine the simultaneous influence of temperature and water/solid ratio on the kinetics and mechanism of the $C_4A_3\bar{S}$ hydration. The measurements of heat evolution of $C_4A_3\bar{S}$ powder at water/solid ratio 0.5, 0.7, and 1.0 were performed at four different temperatures 25°C, 40°C, 70°C and 80°C using a conduction calorimeter. The calorimetric estimate of heat evolution as a function of temperature at different water/solid ratios were modeled using Avrami kinetic equation (3) to interpret the extent of hydration α:

$$\alpha = 1 - e^{-kt^n} \tag{3}$$

where t is time of crystallization, k is temperature-dependent rate constant; n characterizes the geometry of the reacting interface and is independent on temperature. Temperature dependence of the rate constant k is supposed to obey the Arrhenius relationship:

$$k = Ae^{\frac{-E_a}{RT}} \tag{4}$$

where A is a temperature-independent constant (frequency factor), T is absolute temperature, R the universal gas constant (8.314 J/molK), and E_a an activation energy (typically in kJ/mol).

Experimental works are carried out to determine kinetic parameters and understand the mechanism of calciumsulfoaluminate hydration. For that we studied the hydration of individual minerals under variable conditions.

EXPERIMENTAL

Homogenized mixture of reagent grade $CaCO_3$, $Al(OH)_3$ and $CaSO_4 \cdot 2H_2O$ was calcined 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 μm sieve). The mineral purity was controlled by STOE Powder Diffraction System using $CoK\alpha$ radiation. The rate of the heat evolution was measured with a conduction calorimeter (ZIAC, German Academy of Science) [17]. 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 polyuret, 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 single-phase $C_4A_3\bar{S}$ sample were carried out with a water/solid ratio of 0.5, 0.7, and 1.0 at 25, 40, 60, and 80°C. The data stored on the hard drive personal computer was afterwards plotted and analyzed. The results of heat evolution curve are a mean of four data.

RESULTS AND DISCUSSION

The course of heat evolution during hydration is described by means of calorimetric curves (figures 1-3). The figures demonstrate the influence of temperature upon the calorimetric curves at constant value of water/solid ratio. The same features can characterize all these curves. At the first contact of $C_4A_3\bar{S}$ powder with water, heat is evolved. This fast reaction of a short time is characterized by a little peak at earlier period followed by an induction period during which almost no heat effects are observed. Then the rate of hydration increases, it reaches its maximum, and finally decreases to the level of induction period (reaction is calorimetrically finished). The principal hydration peak appears during this period. The shape of the main peak, its magnitude and time of its maximum characterize the influence of temperature and water/solid ratio on the kinetics and mechanism of hydration. From the curves obtained, it is obvious that with increasing temperatures the intensity of hydration at all water/solid ratio increases. The duration of the induction period is shortened with the temperature increase. At higher temperature (60°C and 80°C) this thermal effect on the length of the induction period is negligible. With the increasing temperature, the shape of the main peak also changes. This is connected to the change in the hydration mechanism. As the dissolution rate depends on the water content, with lower water/solid ratio, primary hydration products are formed around $C_4A_3\bar{S}$ grains. They behave as a protective layer, which slow down the diffusion of water and ions. If one accepts that the temperature at great extent influences the dissolution rate of mineral $C_4A_3\bar{S}$, it can

be postulated that at lower temperatures with lower water/solid ratio the topochemical mechanism predominates whereas at higher temperatures with excess of water the hydration reactions are driven by the through-solution mechanism. The peak profile (shape) supports this idea. By through-solution mechanism, the peak of hydration are shifter with reduced induction period. Indeed, when the bulk solution is supersaturated with respect to different ions, the precipitation is very fast and the rate of hydration is intensive. By topochemical

mechanism, the creation of protective layer retards the diffusion of ions and water. In the meantime, this protective layer can set and additionally more retards hydration process. Then, the induction period is longer and the subsequent process is less intense. Calorimetric curves with the reduced intensities are extended over time.

Influence of water/solid ratio

Figures 4-7 show the effect of water/solid ratio at different temperatures. At lower temperatures (25°C and 40°C) intensity of hydration heat increases slightly with increasing water/solid ratios. Additionally, the hydration is accelerated with respect to the length of the induction period. The profile of the curves is extended over time. At higher temperatures (60°C and 80°C), the peaks of hydration heat are higher and narrower with shorter induction periods. The results of the rate of $C_4A_3\bar{S}$ hydration at 60°C and 80°C under different water/solid ratio values clearly demonstrate that not only hydration kinetics are strongly temperature-dependent, but that also hydration occurs through another mechanism. Calorimetrically, hydration is finished after 2 hours at 80°C, and 3 hours at 60°C. The culminated effect of temperature and water/solid ratio upon the kinetics of $C_4A_3\bar{S}$ hydration is not full understood. At higher temperature (60°C and 80°C), water is partially evaporated, but the main interpretations come from the effect of temperature upon the mechanism of hydration and the nature of hydration products.

Indeed, the course of hydration according to equations (1) and (2) clearly demonstrates that products of $C_4A_3\bar{S}$ hydration are closely dependant on the water/
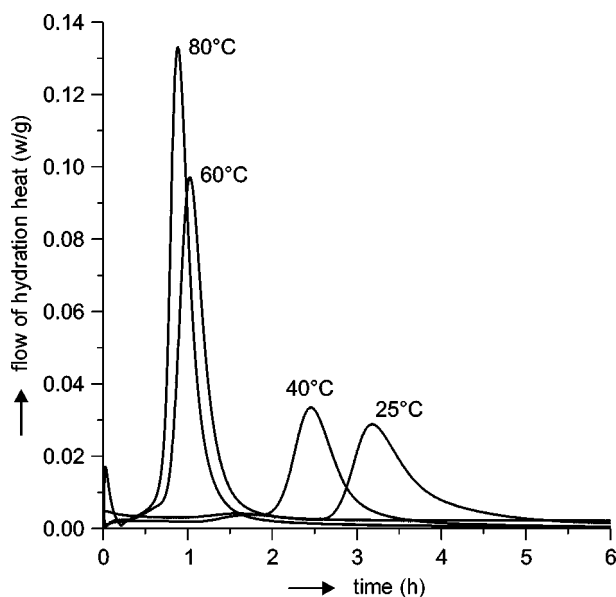

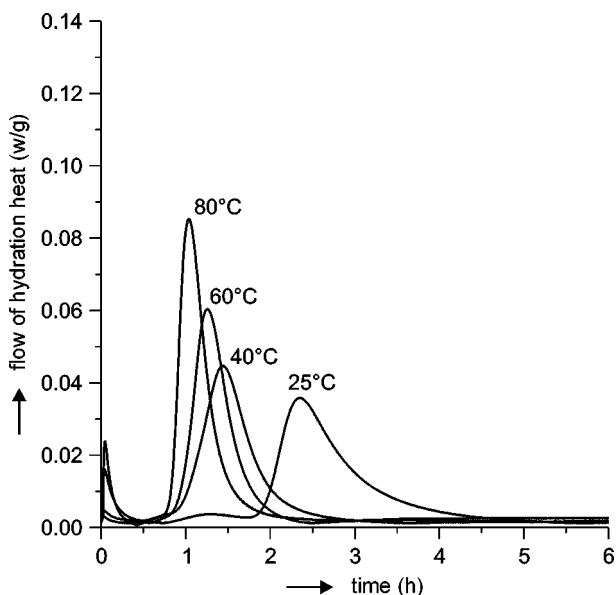Figure 1. Influence of temperature upon hydration heat evolution at water/solid ratio 0.5.

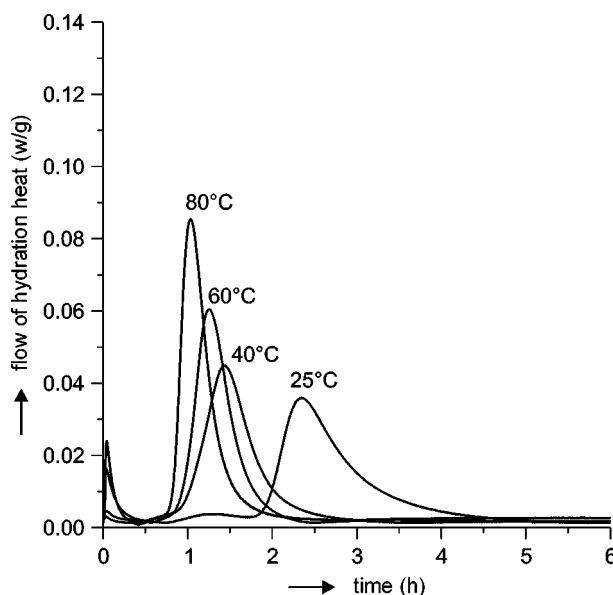Figure 2. Influence of temperature upon hydration heat evolution at water/solid ratio 0.7.

Figure 3. Influence of temperature upon hydration heat evolution at water/solid ratio 1.0.

/solid ratio. At higher water/solid ratio, the reaction produces monosulphate besides ettringite, hydrogarnet, and gibbsite, while at lower water/solid ratio, monosulphate is a unique phase. The formation rate of ettringite and monosulphate is not identical. In the non-equilibrium $C_4A_3\bar{S}$-water system and in excess of water (water/solid ratio 0.7 and 1.0), ettringite is always precipitated at earlier period of hydration through different mechanisms, and then it can convert to monosulphate. As the dissolution kinetics depends on the temperature, the same is valid for the solubility product, which charac-

terizes the saturation of liquid. With the water/solid ratio increasing, we observed a decrease of intensity and postponement of the reaction at higher temperatures (60 and 80°C). As it is well documented in the literature [18], the crystallization theory postulates that the hydration products are formed by precipitation from a supersaturated liquid. The reaction is then postponed because the supersaturation is retarded and this occurs at higher temperatures with increasing water/solid ratio. In other words, supersaturating of liquid has decreased with increasing temperatures. The ion activities becoming
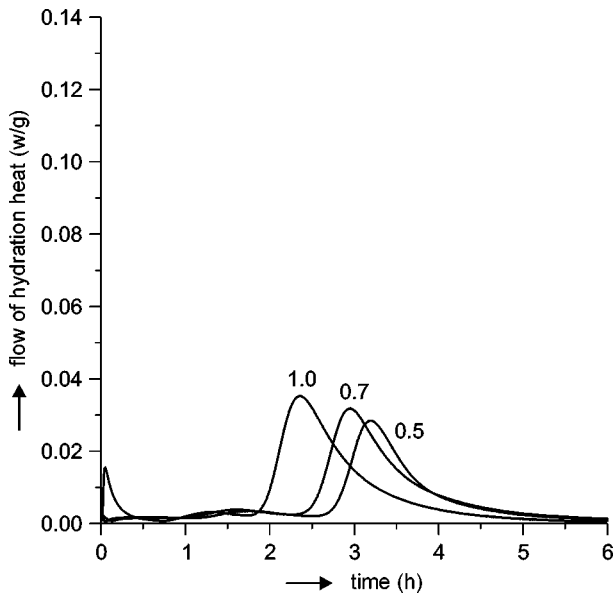

Figure 4. Influence of water/solid ratio upon hydration heat at 25°C.
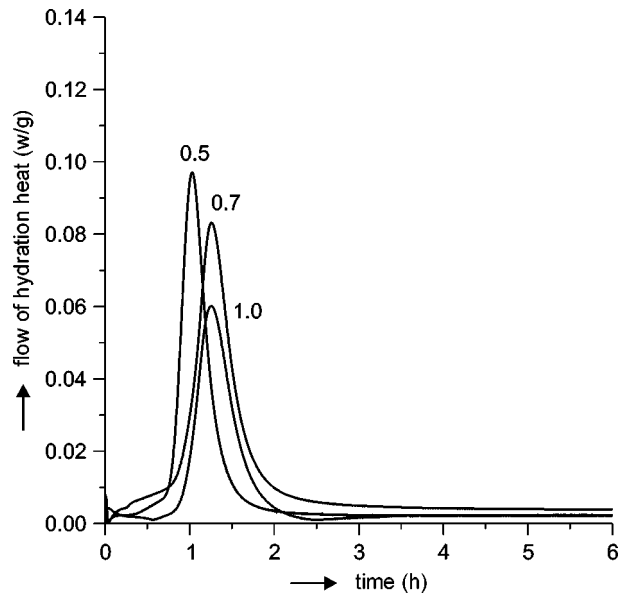

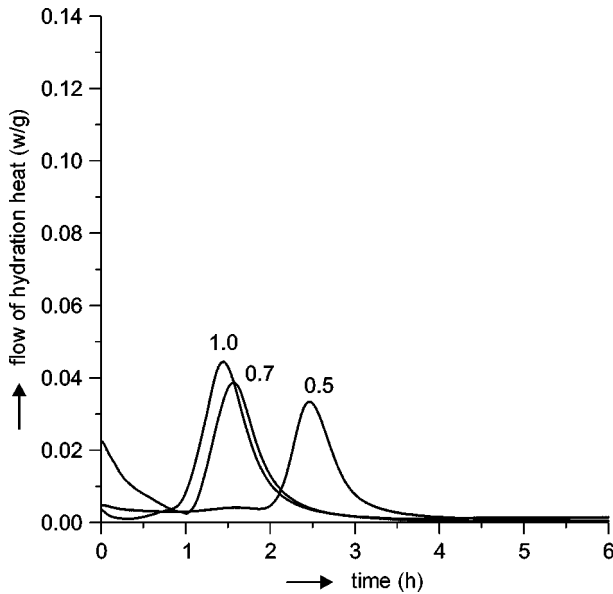Figure 6. Influence of water/solid ratio upon hydration heat at 60°C.

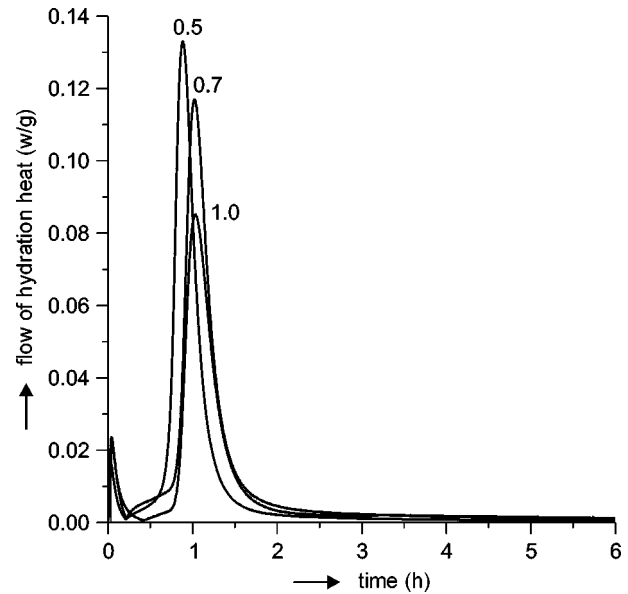Figure 5. Influence of water/solid ratio upon hydration heat at 40°C.

Figure 7. Influence of water/solid ratio upon hydration heat at 80°C.

reduced in bulk solution, and a decrease of intensity of hydration is observed. At lower temperature, the dissolution rate depends mainly on the water/solid ratio. $C_4A_3\bar{S}$ dissolves slowly, but the dissolution is accelerated with growing temperature, and then supersaturation is controlled by the dissolution rate. At lower temperatures (25 and 40°C) the intensity of hydration reaction increases with increasing values of the water/solid ratio, and according to equation (1), monosulphate is the unique phase formed at lower water/solid ratio (0.5).

But at higher water/solid ratio, the hydration intensity decreases with temperature and ettringite, monosulphate, hydrogarnet, and gibbsite are formed. Recently, Jeffrey and co-workers have demonstrated that supersaturation levels of ettringite and monosulphate decrease with increasing hydration temperature and that the final saturation level with respect to ettringite are higher than that of monosulphate [19].

Based on equation (4) a plot of *k* versus *1/T* gave a straight line with its slope proportional to the activation energy E_a. It was found that E_a depends on the water/solid ratio. The higher the water/solid ration, the lower the activation energy. The values 21.0, 17.3, and 16.4 kJ/mol at water/solid ratios 0.5, 0.7, and 1.0, respectively are lower than those found for Portland cement [20, 21], but the experience has been achieved under higher water/solid ratio and furthermore, the temperature sensitivity of $C_4A_3\bar{S}$ hydration can differ from that of C_3S.

CONCLUSIONS

From the obtained results the following conclusions can be drawn:

- The hydration reaction of $C_4A_3\bar{S}$ is accelerated with increasing temperatures at water/solid ratio of 0.5, 0.7, and 1.0.
- The hydration reaction is accelerated with increasing water/solid ratio at hydration temperature of 25°C and 40°C. At the higher temperatures (60°C and 80°C) the intensity of hydration decreased with increasing water/solid ratio
- The profile of the main hydration peak is shaper with increasing temperatures that indicates the change in mechanism of hydration.
- Arrhenius' model was applied to calculate activation energy under different water/solid ratios 0.5, 0.7 and 1.0. The value of exponent n characterizes nucleation and crystal growth according to Avrami formulation. Activation energy (21.0, 17.2, 16.4 kJ/mol, respectively) is dependent on the water/solid ratio.

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UVOLŇOVÁNÍ TEPLA A MECHANISMUS HYDRATACE
V SYSTÉMU CaO–Al₂O₃–SO₃

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Hydratace systému CaO–Al₂O₃–SO₃ jsme zkoumali v teplotním rozmezí 25 až 80°C a při třech různých poměrech voda/tuhá fáze 0,5; 0,7 a 1,0 pomocí izotermálního vodivostního kalorimetru. Předpokládali jsme, že hlavní minerální složku je $C_4A_3\bar{S}$*, známá jako Kleinova sloučenina. Vzrůst teploty hydratace vedl k urychlení jejího počátku při všech poměrech voda/tuhá fáze, jak bylo patrné z maxima rychlosti hydratace. Rovněž bylo zřejmé, že velikost hlavních píků rostla s rostoucím poměrem voda/tuhá fáze při teplotě hydratace 25°C a 40°C. Při vyšších teplotách (60°C a 80°C) velikost hydratace s rostoucím poměrem voda/tuhá fáze naopak klesala. Kinetiku hydratace $C_4A_3\bar{S}$ lze popsat Avramiho modelem. Hodnota kinetického exponentu n = 3 ukazuje, že hydratace je řízena nukleací a trojrozměrným růstem krystalů. Vypočítané hodnoty aktivační energie pro poměr voda/tuhá fáze 0,5, 0,7 a 1,0 byly 21,0, 17,2 a 16,4 kJ/mol.