

FORMATION AND STABILITY OF CRYSTALLOHYDRATES IN THE NON-EQUILIBRIUM SYSTEM DURING HYDRATION OF SAB CEMENTS

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The present experimental work characterizes different kinetic regimes and crystallohydrate products of the hydration reaction in $C_2AS-C_4A_3\bar{S}-C\bar{S}-C_2S-C$ system, relevant to Sulfoaluminate Belite Cement (SAB). In the given system, two associations of phases (I and II) were identified, each is composed of 4 minerals, as well as two singular points with 3 minerals (S1, S2) and a single point of gehlenite (P1). The computational method established that the hydration products are gehlenite hydrate and ettringite. The ratio of these two crystallohydrates depends on the mineralogical composition in the given phase associations. The hydration reaction of this system is a heterogeneous and non-equilibrium solid phase transformation forming from an anhydrous solid phases to crystallohydrate phases in the presence of water. The advantage and complexity of this heterogeneous process is that during hydration heat is evolved and the paste sets and hardens limiting thus the dissolution of primary anhydrous phases and ion transport. Then the reaction is at great extent retarded. Some primary hydration products ($C-S-H$, AH_3 , CH) convert through secondary reactions to the gehlenite hydrate, thermodynamically more stable. Eight samples were prepared along gehlenite hydrate - ettringite composition. Apart from the single gehlenite point, ettringite is formed at the beginning of reaction in all samples, but over the time and under the non-equilibrium conditions it was decomposed to monosulphate. After 28 - day curing at high temperature and under saturated steam pressure, gehlenite hydrate was identified by SEM. The intensity of hydration reaction from calorimetric measurements depends on the content of $C_4A_3\bar{S}$ in the mixtures.

INTRODUCTION

$C_2AS-C_4A_3\bar{S}-C\bar{S}-C_2S-C$ system forms a special type of Sulfoaluminate Belite Cements (shorthand SAB) that belongs to the class of Low-Energy Cements (shorthand LEC). The defined phase system has been found to be an coexisting phase association within the five oxide system $CaO-SiO_2-Al_2O_3-Fe_2O_3-SO_3$ [1, 2, 3]. Other phase associations, relevant to SAB cements were deeply investigated, in term of synthesis of phases as well as hydration kinetics and mechanism.

SAB cements in the framework of $C_4AF-C_4A_3\bar{S}-C\bar{S}-C_2S-C$ phase association were prepared from natural raw materials, by-products and industrial wastes [4, 5]. They are cements environmentally acceptable, relatively cheap in production and technically similar in use compared to Portland cements. A mixture of the SAB cement and CEM I in the 85:15 proportion has shown enhanced properties compared to CEM I [6-10]. Also, some authors have reported possible applications of these blended cements in the preparation of MDF-materials [11, 12]

Phase association $C_2AS-C_4A_3\bar{S}-C\bar{S}-C_2S-C$ differs from $C_4AF-C_4A_3\bar{S}-C\bar{S}-C_2S-C$ in that, C_4AF is replaced by C_2AS . Until now, hydration kinetics and mechanism of phase association relevant to SAB cements and containing mineral gehlenite has not been investigated. The reason may be the low hydraulic properties of C_2AS . Theoretically, gehlenite hydrate could be formed by hydration reaction of C_2AS according to equation (1):



This hydrated product (C_2ASH_8), also known as mineral stratlingite, is generally found as hydration product of slag cement, or high-alumina cements in the presence of silicon oxide [13, 14]. Indeed, concretes made from mixtures of high-alumina cements and granulated blast furnace slag show an increasing mechanical properties, though after longer time of hydration [15]. The reason for this is that gehlenite hydrate rather than calcium aluminate hydrate is the major phase due to the presence of granulated blast furnace slag. Other authors [7-12] have also reported that, the hydration of calcined clays with lime produces essentially C_2ASH_8 and CSH with small quantity of C_4AH_{13} .

The most available and effective way to obtain gehlenite hydrate is the hydration of cement glass prepared by melting gehlenite ($2\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$) at 1650°C , followed by quenching in water [16]. The hydration of glasses in $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system has showed that gehlenite hydrate constitutes the principal phase of the strong, fast setting cements. The reason for development of cement glass was that, gehlenite mineral itself hydrates slowly and without activators can not set. El-Diamond [14] studied the mechanism and kinetics of slag cement hydration and found that the hydration of calcium aluminosilicate glass powders with composition above 50 % CaO and below 20 % SiO_2 content had hydraulic properties. The mechanism of C_2AS glass hydration seems to be topochemical by forming a permeable coating of ASH_6 on the surface of gehlenite. In the suspension hydration of C_2AS glass was accelerated by the addition of $\text{Ca}(\text{OH})_2$, because SiO_2 and particularly Al_2O_3 were apt to be liberated from above mentioned coating. Locher [19], after deep investigation of hydration of $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ glasses concluded that activators such as Portland clinker, gypsum or lime can produce practically the same rates of hydration of normal cement. Other experimental investigations conducted on $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{SO}_3-\text{H}_2\text{O}$ 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), $\text{Ca}(\text{OH})_2$, gehlenite hydrate (C_2ASH_8 , GH) ettringite ($\text{C}_6\text{A}\bar{3}\text{H}_{32}$, AFT), siliceous hydrogarnet (C_3ASH_6 , Si-HG) [16, 17]. All of these crystallohydrates are known to be formed during hydration of sulfoaluminat belite cements also.

Based on these preliminary findings, Majling et al. have extended their investigations on the phase singularities in the $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{SO}_3-(\text{H}_2\text{O})$ oxide system [22]. They have ascertained that the hydration of three mineral phases (C_2S , $\text{C}_4\text{A}_3\bar{\text{S}}$, $\text{C}\bar{\text{S}}$) at suitable molar ratio leads to the formation of ettringite and gehlenite hydrate. However, they concluded that gehlenite hydrate is formed through secondary reactions between calcium silicate hydrogel, calcium hydroxide and gibbsite.

Ettringite is always precipitated at early hydration period of the SAB cement hydration from $\text{C}_4\text{A}_3\bar{\text{S}}$ and $\text{C}\bar{\text{S}}$ equation (2).



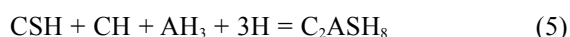
Also, full ettringite is formed when lime or calcium hydroxide is associated to $\text{C}_4\text{A}_3\bar{\text{S}}$ and $\text{C}\bar{\text{S}}$ according to equation (3):



The hydration reaction of dicalcium silicate is generally described by the following equation:



The expected gehlenite hydrate formation then occurs through secondary reaction.



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.

The present research work was undertaken to determine the conditions under which gehlenite hydrate and ettringite could be formed as two crystallohydrates from the hydration reaction of $\text{C}_2\text{AS}-\text{C}_4\text{A}_3\bar{\text{S}}-\text{C}\bar{\text{S}}-\text{C}_2\text{S}-\text{C}$ system and their stability under the non-equilibrium and heterogeneous process.

EXPERIMENTAL

Individual mineral phases were synthesized from a homogenized stoichiometrical mixtures of reagent grade CaCO_3 , $\text{Al}(\text{OH})_3$ and $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ for $\text{C}_4\text{A}_3\bar{\text{S}}$ at 1250°C , CaCO_3 and SiO_2 for C_2S at 1300°C , CaCO_3 , $\text{Al}(\text{OH})_3$ 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 $< 40 \mu\text{m}$, controlled by sieving. Furthermore, C_2S and C_2AS were quenched in air to anneal the polymorph transformation. $\text{C}\bar{\text{S}}$ was obtained by heating gypsum at 350°C . Calcium hydroxide (CH) was used instead of calcium oxide (C).

Table 1. Studied samples.

Samples	1	2	3	4	5	6	7	8
Gehlenite hydrate: ettringite	100:0	90:10	80:20	60:40	44.7:55.3	40:60	20:80	0:100
C_2S (%)	0	5.08	10.15	20.31	28.06	25.12	12.56	0
C_2AS (%)	100	81.92	63.83	27.67	0	0	0	0
$\text{C}_4\text{A}_3\bar{\text{S}}$ (%)	0	8.98	17.98	35.97	49.72	47.66	38.82	29.98
$\text{C}\bar{\text{S}}$ (%)	0	4.01	8.02	16.04	22.20	25.47	39.82	53.48
C (%)	0	0	0	0	0	1.73	9.13	16.53

The purity of products (C_2S , C_2AS , $C_4A_3\bar{S}$, $C\bar{S}$) has been controlled by STOE Powder Diffraction System (STADI P) using $Co K_{\alpha}$ 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.

Then, series of samples were prepared by mixing and homogenizing minerals in the proportion as elucidated in table 1. The hydration of samples at defined water/cement ratio was performed by using conduction calorimeter at 70°C as previously described by [23]. Also the pastes of different samples were stored under hydrothermal condition for a period up to 28 days.

RESULTS AND DISCUSSION

The course of hydration reaction of samples was determined by conduction calorimeter. There appear two peaks separated by an induction period (figure 2a-h). While the first peak is linked to dissolution of mineral phases, the second one characterizes hydration reaction of samples mainly ettringite precipitation in the early period. The intensity-values of the second peaks were collected and graphically presented as function of gehlenite hydrate/ettringite ratio (figure 2). Though ettringite is the unique hydrated product at this stage of reaction, it is evident from figure 3 that the intensity of hydration is not function of ettringite quantity, but it is linked to $C_4A_3\bar{S}$ content. Indeed, singular point (sample 5) with three minerals (C_2S , $C_4A_3\bar{S}$ and $C\bar{S}$) has the highest intensity of reaction. By comparing figure 1 with figure 2, it is evident that $C_4A_3\bar{S}$ content is the highest. The intensity of hydration reactions continuously decreases, while ettringite quantity increases.

XRD patterns in figure 4 show that the main hydration product within 24 hours is ettringite. Ettringite is found in all samples, except sample of pure gehlenite (XRD pattern of Sample 1 is not presented, because it presents none crystallized hydration product). In sample 5, 6, 7, and 8, monosulphate appears besides ettringite. Gehlenite hydrate is not observed due to the low hydration rate of gehlenite.

The XRD patterns figure 5 after 28-days curing clearly shows that ettringite is not stable under the defined condition. Monosulphate is a dominant hydrated product as consequence of ettringite decomposition. The instability of ettringite here reported is not a result of sulphate attack, but is related to the lack of sulphate ions. Indeed, cement-water system is generally handled as a heterogeneous liquid-solid system with interacting components.

Under the given experimental conditions, sample pastes set and harden, limiting thus dissolution rate of individual phases. Furthermore, primary hydration products form an "insulating layer" on the surface of

mineral phase that isolates each grain from the bulk of solution. Consequently, the dissolution rate and diffusion of ions in hardened paste are at great extent lowered. The lowering dissolution of anhydrite results in the lack of sulphate ions necessary for the formation and stability of ettringite. Ettringite being sensible to the factors as pH, $Al(OH)_4^-/SO_4^{2-}$ and Ca^{2+}/SO_4^{2-} ratios of cement bulk can rapidly convert to monosulphate [24-27].

Scanning electron micrographs in figures 6-14 support the theory of ettringite instability under the non-equilibrium and heterogeneous system. After 28-days curing under hydrothermal conditions, crystals of gehlenite hydrates are found localized in pore structure. In figure 7, one can remark that crystallohydrates of gehlenite hydrates, surrounded by a mass of C-S-H gel begin to join one to another.

In figure 8 and figure 9 (singular point), the compaction of microstructure of pastes is reinforced. Scanning electron micrographs show a microstructure without pores, in which crystallohydrates seem to be integrated. This fact supports the idea that cementitious materials containing gehlenite hydrate have higher long-term mechanical properties [13]. According to table 1 and figure 1, gehlenite hydrate predominates. Micrographs (figures 10-12) show degraded microstructure. Indeed, in these samples the amount of ettringite is higher than that of gehlenite hydrate. Ettringite is converted to monosulphate (see figure 5). It appears that crystal of monosulphate are under the given experimental conditions more stable than ettringite. When sulphate ions will be available, secondary ettringite can be formed through reaction between monosulphate and SO_4^{2-} .

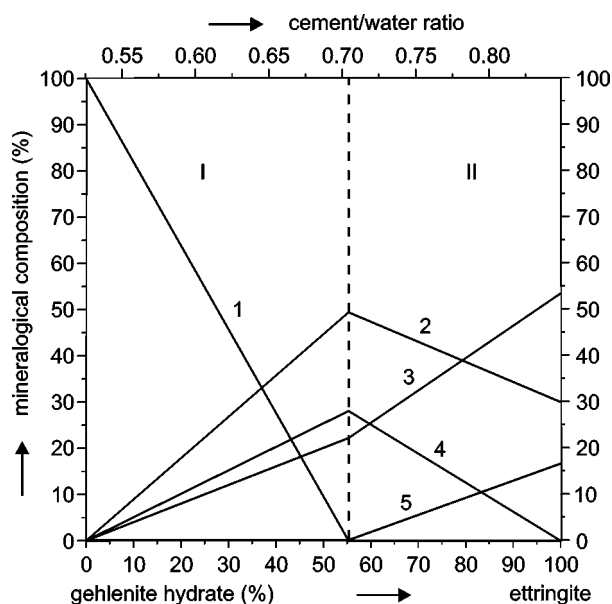


Figure 1. $C_2AS(1)-C_4A_3\bar{S}(2)-C\bar{S}(3)-C_2S(4)-C(5)$ system and phase associations (I, II), singular points (S1, S2) and gehlenite point (P1).

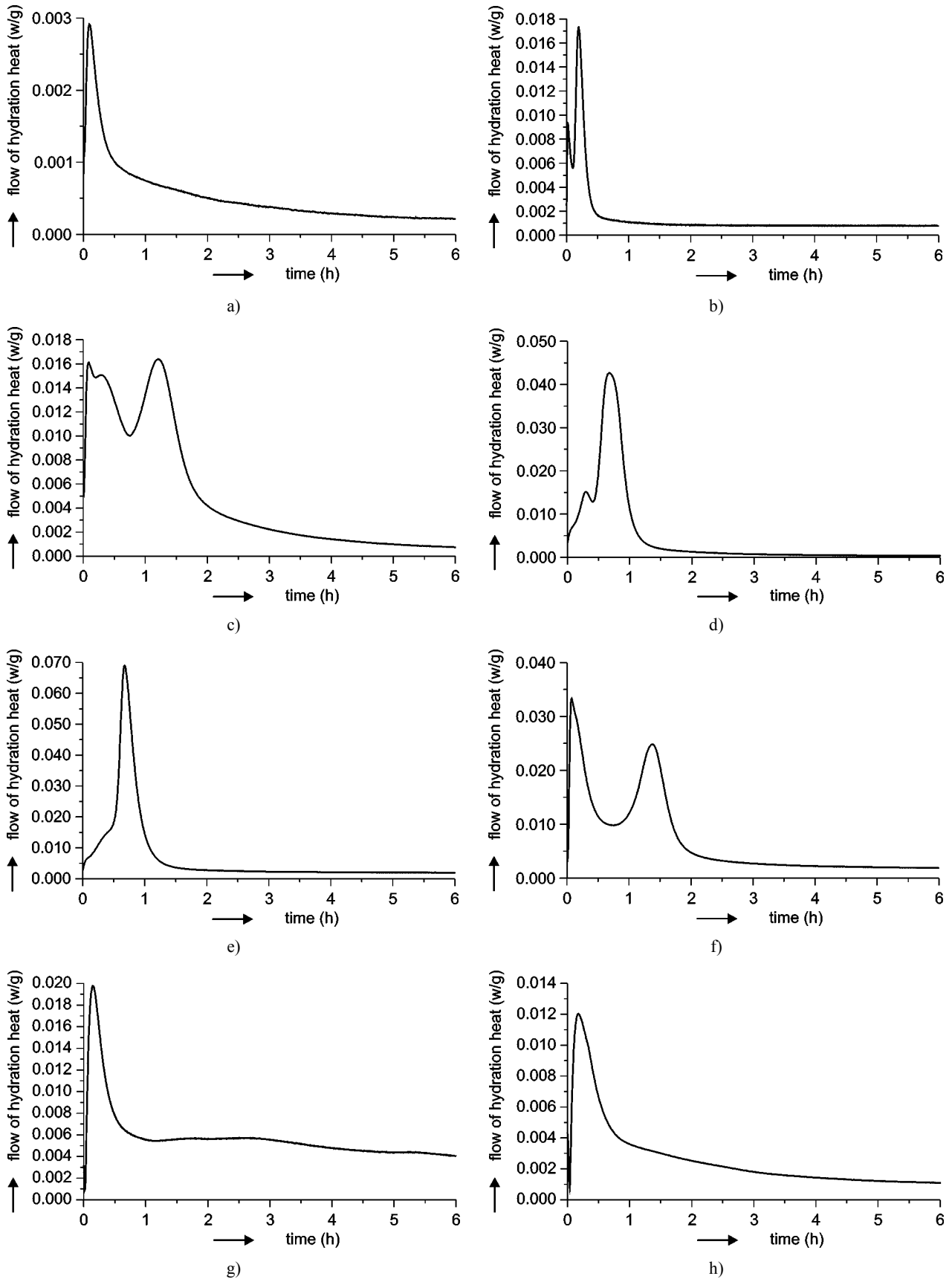


Figure 2. Calorimetric curves of Sample1 (a), Sample2 (b), Sample3 (c), Sample4 (d), Sample5 (e), Sample6 (f), Sample7 (g), Sample8 (h).

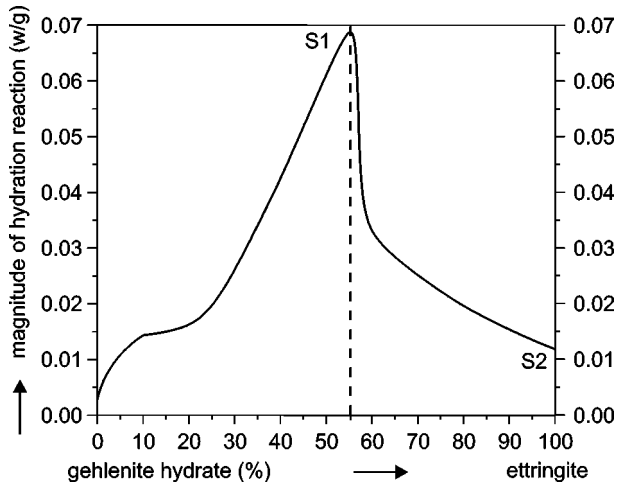


Figure 3. The change in the intensity of hydration of different mixtures along the "gehlenite hydrate - ettringite" join.

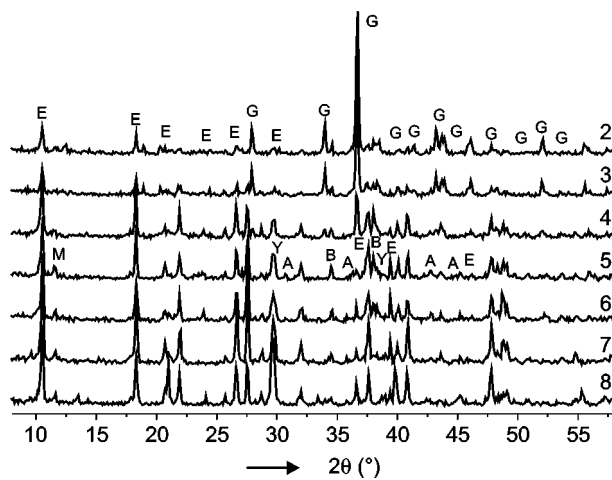


Figure 4. XRD pattern of samples after 24 hours of hydration at 70°C; E - ettringite, G - gehlenite, M - monosulphate and Y - Yeelenite (C₄A₃S).

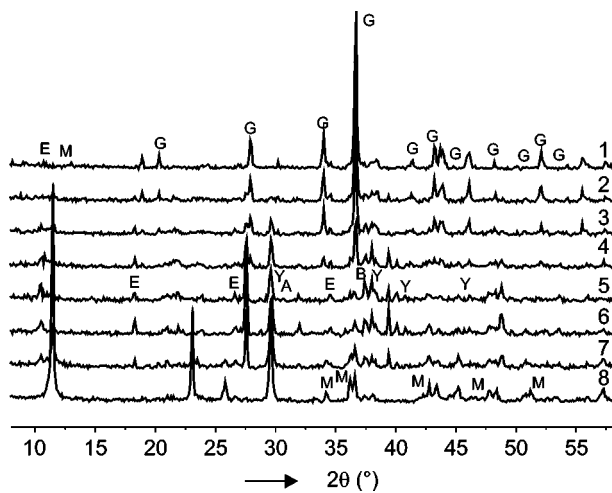


Figure 5. XRD patterns of sample 1-sample 8 after 28-day hydration in autoclave; E- ettringite, G - gehlenite, M - monosulphate and Y - Yeelenite (C₄A₃S).

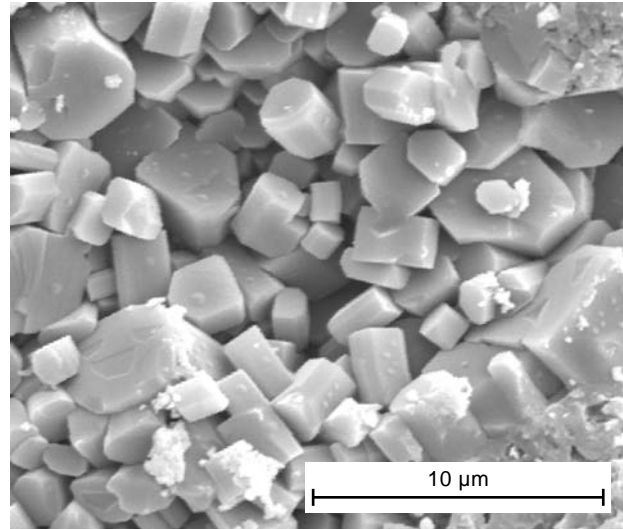


Figure 6. SEM micrograph of Sample 1 (gehlenite hydrate) after 28-days curing.

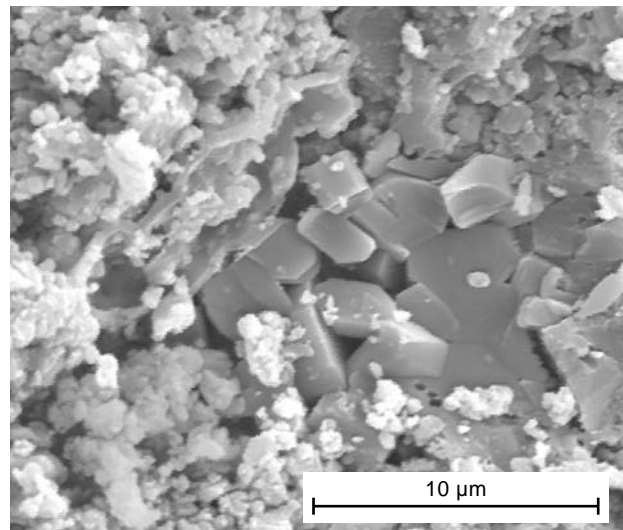


Figure 7. SEM micrograph of Sample 2 after 28-days curing.

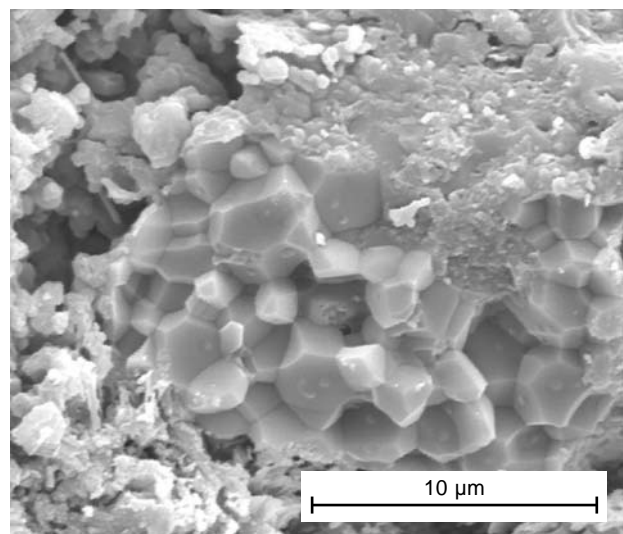


Figure 8. SEM micrograph of Sample 3 after 28-days of curing.

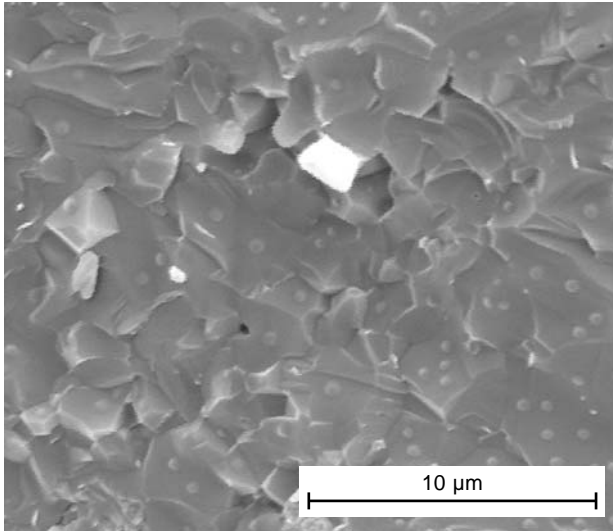


Figure 9. SEM micrograph of Sample 4 after 28-days of curing.

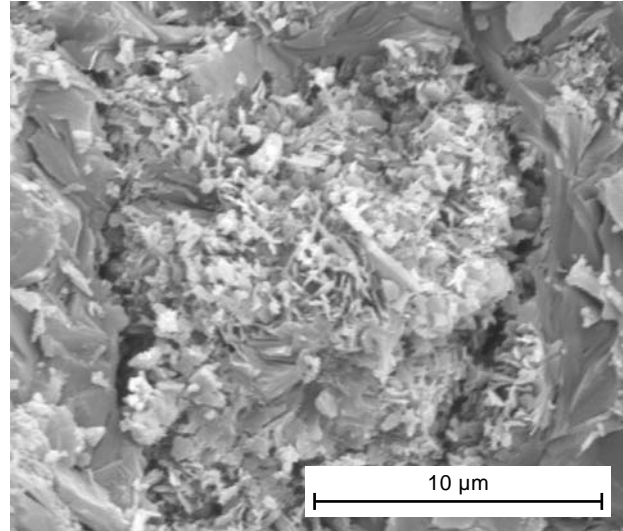


Figure 12. SEM micrograph of Sample 7 after 28-days curing.

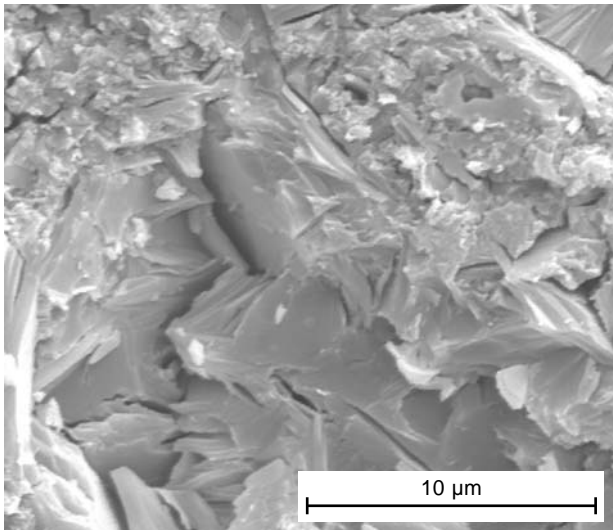


Figure 10. SEM micrograph of Sample 5 after 28-days curing.

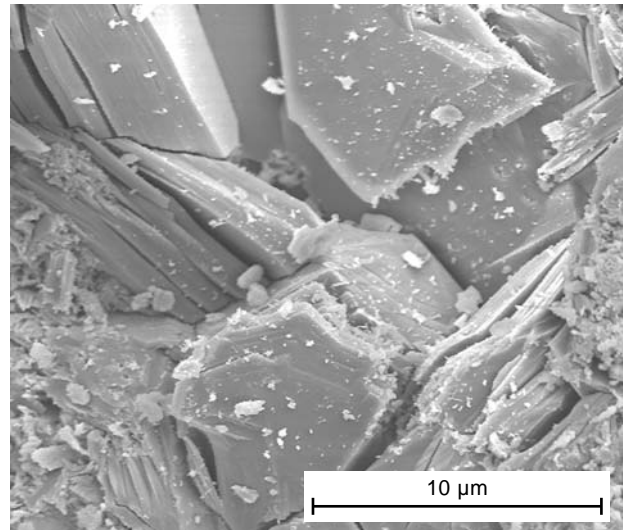


Figure 13. SEM micrograph of Sample 8 after 28-days curing.

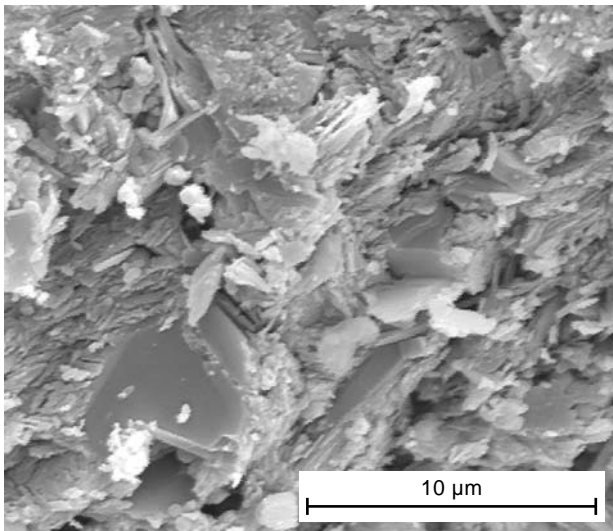


Figure 11. SEM micrograph of Sample 6 after 28-days curing.

CONCLUSION

Two quaternary phase associations ($C_2AS-C_4A_3\bar{S}-C\bar{S}-C_2S$ and $C_4A_3\bar{S}-C\bar{S}-C_2S-C$), two ternary singular points ($C_4A_3\bar{S}-C\bar{S}-C_2S$ and $C_4A_3\bar{S}-C\bar{S}-C$) and one single point (C_2AS) were identified in $C_2AS-C_4A_3\bar{S}-C\bar{S}-C_2S-C$ system. Hydration reactions of samples with different mineralogical composition inside the system are programmed to generate two crystallohydrates: gehlenite hydrate and ettringite. Apart from the single point of gehlenite, ettringite is formed in all samples at early period of hydration reaction. Then, under the non-equilibrium and because of heterogeneous process, it converts to monosulphate, causing expansion. The conversion of ettringite to monosulphate is due to the sulphate lack in the bulk system.

Indeed, mineral particles are enclosed by primary products of hydration, thus the dissolution rate of anhydrite is lowered and because of the sensibility of ettringite to the surrounding environment, it becomes unstable and converts to monosulphate. Crystals of gehlenite hydrate were observed in the pores of samples 1-4 after 28-days curing under hydrothermal conditions. They are well developed and were stable over the time. Hydration of dicalcium silicate forms calcium silicate hydrate gel by hydration reaction and liberates calcium hydroxide. This phenomenon enhances the *pH* of surrounding liquid and contributes also to the degradation of ettringite.

Note: Cement chemistry nomenclature and abbreviations are used through this report: C = CaO, A = Al₂O₃, S = SiO₂, S = SO₃, H = H₂O, GH = gehlenite hydrate, HG = hydrogarnet, AFT = ettringite, Si-HG = siliceous hydrogarnet.

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TVORBA A STABILITA KRYŠTALOHYDRÁTOV V NEROVNOVÁZNOM SYSTÉME POČAS HYDRATÁCIE SAB CEMENTOV

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V predloženej experimentálnej práci sa vyšetrojú rôzne kinetické režimy a produkty hydratačnej reakcie - kryštalohydráty - v systéme C₂AS-C₄A₃S-C₂S-C, relevantnom pre sufolaminátový belitový cement (SAB). V uvedenom systéme boli identifikované dve štvorzložkové asociácie fáz (I a II), dva singulárne body (S1 a S2) a jednoduchý bod gehlenitu (P). Podľa teoretického výpočtu konečné rovnovážne produkty hydratacie sú gehlenithydrát a ettringit. Pomer týchto dvoch kryštalohydrátov závisí of mineralogického zloženia v jednotlivých vzorkách. Hydratačná reakcia v danom systéme je heterogénnou a nerovnovážnou transformáciou tuhých fáz (anhydridov) na kryštalické fázy v prítomnosti vody. Výhody ale aj zložitost' tohoto heterogénneho procesu spočívajú v tom, že sa uvoľňuje hydratačné teplo a zároveň vzorka vo forme pasty tuhne a tvrdne, čo však obmedzuje rozpustnosť primárnych anhydritových fáz a transport iónov. Z tohto dôvodu je reakcia v značnej mieri spomalená. Niektoré primárne hydratačné produkty (C-S-H, AH₃, CH) konvertujú cez sekundárne reakcie na gehlenithydrát, ktorý je termodynamicky stabilnejší. Osem (8) vzoriek bolo pripravených podľa pomeru kryštalohydrátov „gehlenithydrát/ettringit“. S výnimkou prvej vzorky (jednoduchý bod) sa v ostatných na začiatku hydratacie tvoril ettringit, ktorý sa časom rozkladal na monosulfát. Rastrovacím elektronovým mikroskopom sa identifikovala prítomnosť gehlenithydrátu po 28 dňoch hydratacie vzoriek v autokláve. Intenzita hydratačnej reakcie - podľa kalorimetrických výsledkov - závisí hlavne na obsahu C₄A₃S v zmesiach.