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Tricalcium aluminate hydration in the presence of calcium sulfite hemihydrate

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Abstract

This article reports on the study to evaluate the potential possibility of regulating the tricalcium aluminate (C_3A) hydration process by the addition of calcium sulfite hemihydrate. The kind and the form of hydration products were studied in the system: $C_3A-CaSO_3 \cdot 0.5H_2O-H_2O$ and $C_3A-CaSO_3 \cdot 0.5H_2O-Ca(OH)_2-H_2O$ by use of XRD, DTA and SEM/EDS methods as well as the kinetics of hydration along with chemical composition development of the liquid phase. The results thus obtained were compared to the hydration process of C_3A with the addition of natural gypsum. The results show that the reaction rate of C_3A with the addition of calcium sulfite hemihydrate differs from the analogous hydration process of C_3A in the presence of calcium sulfate dihydrate. Also, the kind of hydration products obtained in the presence of $CaSO_3 \cdot 0.5H_2O$ is different.

Keywords: Hydration; Calcium sulfite hemihydrate; Hydration products; Microstructure; Tricalcium aluminate

1. Introduction

In cement literature there are no accurate descriptions of the hydration process of tricalcium aluminate (C_3A) in the presence of calcium sulfite hemihydrate. The results published by some authors complement each other, but they do not show the whole processes [1–4].

The knowledge of C_3A hydration rate in the presence of $CaSO_3 \cdot 0.5H_2O$ as well as of the kind of products being formed and their influence on the course of reactions, is essential to the understanding of more complex processes occurring in the cement hydration. The significance of this knowledge stems from the fact that it can contribute to the development of methods of utilisation of $CaSO_3 \cdot 0.5H_2O$-containing waste in the production of cements and/or building materials (the waste is obtained in a desulfurisation process with the use of semi-dry methods). The attempts made so far to use the aforementioned waste as a set-time regulator of cements raise doubts as for an actual function of calcium sulfite. The present study may facilitate the understanding of the function of calcium sulfite as a potential cement component in the case of both plastic and hardened cement pastes.

In order to investigate the potential possibility of regulating the C_3A hydration process by the addition of calcium sulfite hemihydrate, the kind and the form of hydration products were studied in the system: $C_3A-CaSO_3 \cdot 0.5H_2O-H_2O$ and $C_3A-CaSO_3 \cdot 0.5H_2O-Ca(OH)_2-H_2O$. Hydration processes were also studied by means of chemical analysis of the liquid phase within the first hour after mixing the ingredients with water. The results thus obtained were compared to the hydration process of C_3A with the addition of natural gypsum.

2. Materials

The following raw materials mentioned below were used in the tests.

2.1. Calcium sulfite hemihydrate

Calcium sulfite hemihydrate was obtained in the $Na_2SO_3/CaCl_2$ reaction [5]. Pure deposit thus obtained was

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Table 1
Composition of mixtures

Sample code	Phase content (wt.%)				Molar ratio $C_3A/CaSO_3{\cdot}0.5H_2O$ ($C_3A/CaSO_4{\cdot}2H_2O$)
	C_3A	$CaSO_3{\cdot}0.5H_2O$	$CaSO_4{\cdot}2H_2O$	$Ca(OH)_2$	
CS1	67.7	32.3	–	–	1/1
CS1C	64.3	30.7	–	5.0	1/1
CG1	61.1	–	38.9	–	1/1
CG1C	58.0	–	37.0	5.0	1/1

dried at 100 °C until the decay of mass loss (caused by water evaporation or the dehydration of previously hydrated sulfites) took place [6].

The XRD studies indicated that the obtained compound is calcium sulfite hemihydrate (α variety) crystallising in orthorhombic system [7], and chemical analysis did not show the presence of NaCl.

2.2. Calcium sulfate dihydrate

For the purpose of experiments with calcium sulfate dihydrate, natural gypsum from Dolina Nidy was used. After chemical and thermal analyses, $CaSO_4{\cdot}2H_2O$ content in gypsum was estimated at 87.6%.

2.3. Tricalcium aluminate

Tricalcium aluminate was obtained as a result of the synthesis of $Al(OH)_3/CaCO_3$ stoichiometric mixture in a superkanthal furnace. The synthesis was carried out by burning the abovementioned mixture twice at 1370 °C for 3 h. Prior to the second burning, the material was crushed and ground in a laboratory mill. The XRD analysis of the sample of the material obtained indicated that it was pure tricalcium aluminate, free of any XRD-detectable impurities. The content of free calcium determined by means of Franke's method amounted to 0.17%, so it had no fundamental influence on the course of experiments.

3. Experimental

As it was mentioned before, hydration tests in the systems $C_3A–CaSO_3{\cdot}0.5H_2O–H_2O$ and $C_3A–CaSO_3{\cdot}0.5H_2O–Ca(OH)_2–H_2O$ included: defining the kind and the morphology of reaction products after 30 min, as well as after 24 h and 28 days of hydration. The tests also included chemical analysis of the liquid phase within the first hour after mixing the samples with water. In order to compare the results, the tests were also carried out with the use of mixtures containing gypsum instead of $CaSO_3{\cdot}0.5H_2O$.

3.1. Composition of samples

The test samples, the composition of which is shown in Table 1, were prepared in the process of homogenisation of the components in a laboratory mill. These

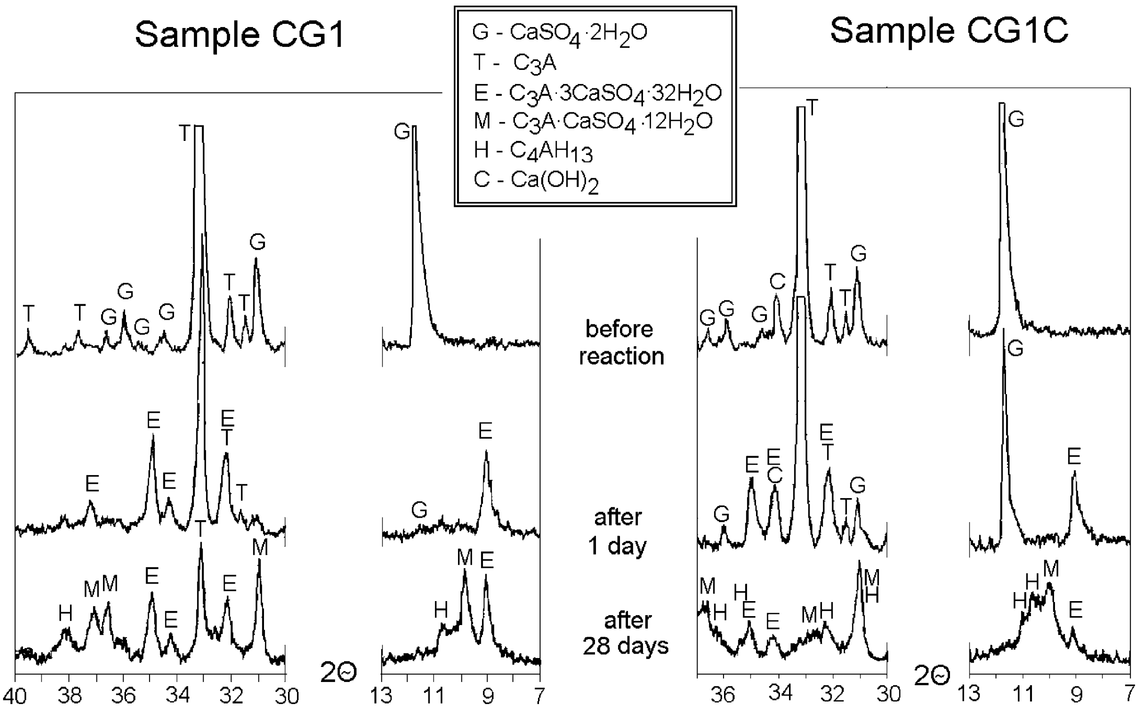

Fig. 1. XRD analysis of the CG1 and CG1C samples before and after 1 and 28 days of hydration.

components had been previously ground below 63 μm. In the samples thus prepared, the ratio of C_3A to sulfite or gypsum equaled 1. Simultaneously, test were carried out with the mixtures containing 5% addition of Ca $(OH)_2$. In the process of hydration of C_3A with gypsum, the addition of $Ca(OH)_2$ radically alters the reaction rate.

The phase composition of the hydrating mixtures as well as the microstructure of the hydration products were analysed after 24 h and 28 days of reaction on the pastes (coefficient water/sample = 1) reacting at 20 °C. The pastes were made by mixing the prepared samples with water without access of CO_2 from the air. After the aforementioned time, the hydration process was stopped. In order to do this the samples were mixed with acetone in a mortar and then dried at 35 °C. The analysis of the phase composition was conducted by means of XRD and DTA/TG, whereas the microstructure of the products was analysed with the use of SEM/EDS.

The chemical composition of the liquid phase was analysed on the pastes (w/s = 10), reacting at 20 °C. Such a high coefficient w/s was necessary to make it possible to determine the concentration of several elements on the relatively small samples. The chemical composition of liquid phase was analysed by means of ICP AES and capillary electrophoresis.

3.2. Results and discussion

3.2.1. XRD and DTA analysis

The XRD analysis of the samples presented in Table 1, after 1 and 28 days of hydration, showed that the addition of $Ca(OH)_2$ alters the reaction rate of components both in the samples containing gypsum and calcium sulfite hemihydrate (Figs. 1 and 2). As it is known, $Ca(OH)_2$ in the mixtures containing gypsum (sample CG1C) slows down the reaction rate between the components immediately after mixing the sample with water. The results of this retardation can still be seen after 24 h (Fig. 1). After 28 days, the presence of calcium hydroxide increases degree of the C_3A hydration and it has an influence on the mineralogical composition of the hydration products. The decrease of ettringite amount is observed, whereas the content of solid solution C_4AH_{13} and monosulfoaluminate is on the increase.

In the sample containing sulfite (CS1C), the addition of calcium hydroxide contributes to a partial increase in the C_3A hydration degree (in comparison to CS1 sample), which is observed after 24 h of reaction in water. After 28 days of reaction, the degree of hydration of all the components increases considerably (Fig. 2). Thus, the retarding influence of sulfite on the hydration of C_3A with the admixture of $Ca(OH)_2$ was not observed. The reaction

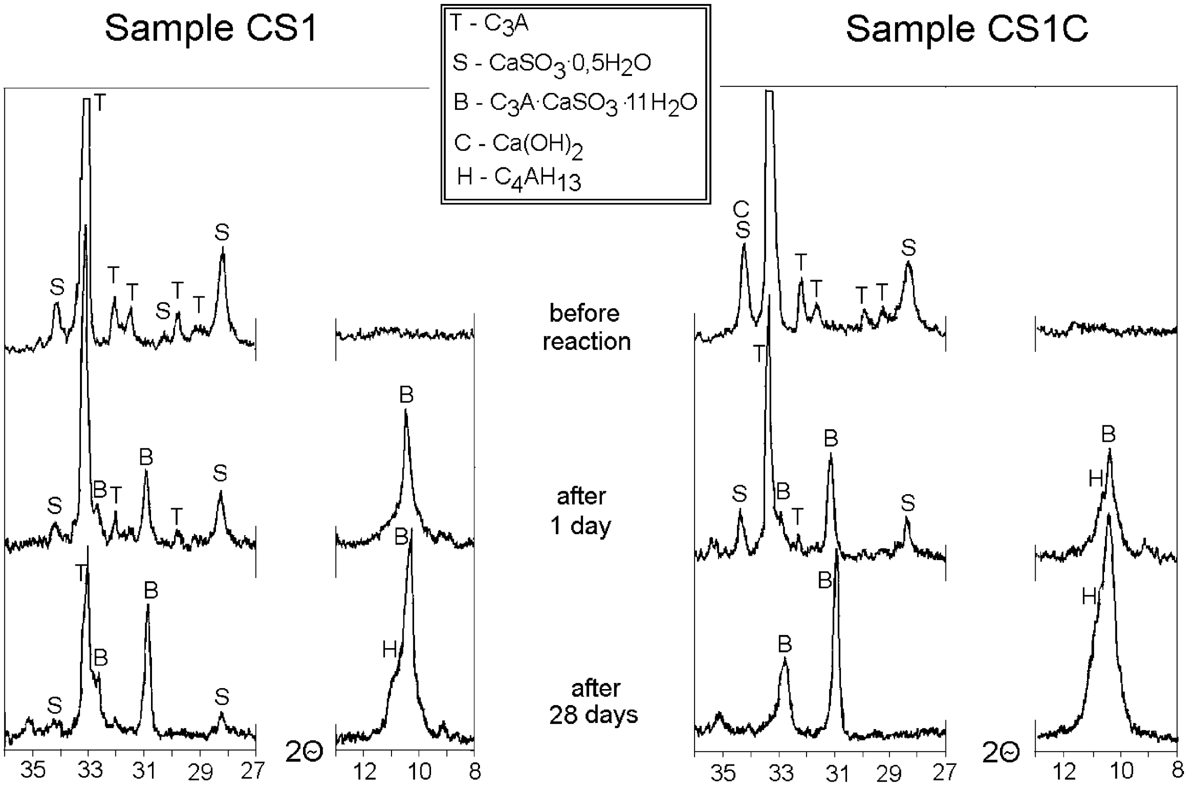

Fig. 2. XRD analysis of the CS1 and CS1C samples before and after 1 and 28 days of hydration.

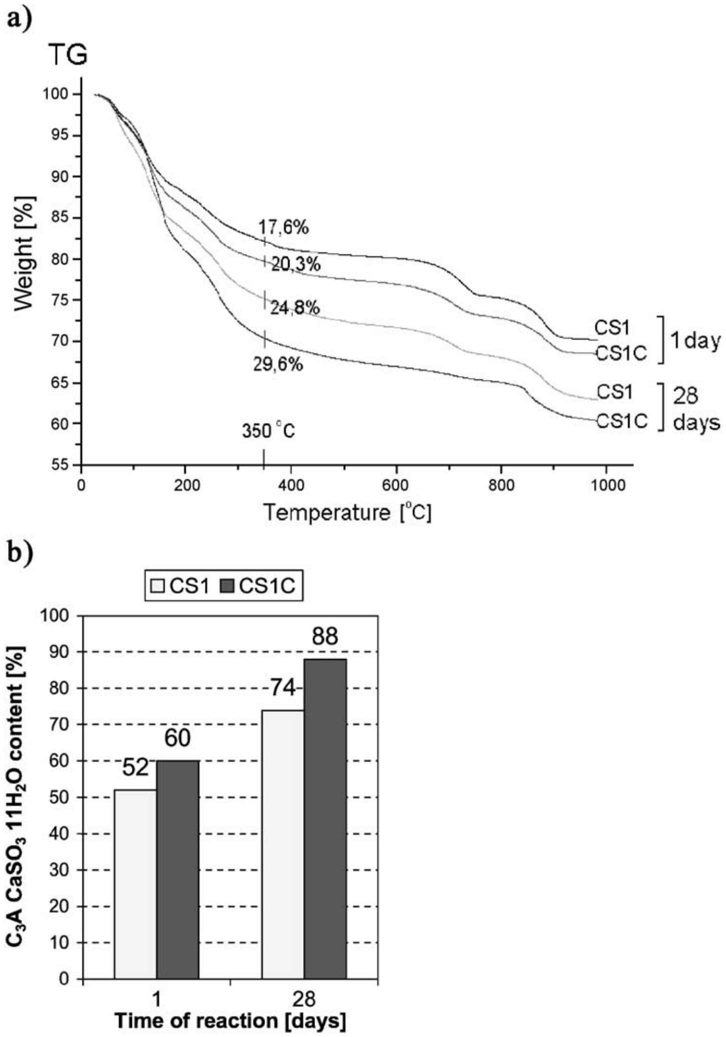

Fig. 3. DTA analysis; (a) TG curves of samples containing calcium sulfite after 24 h and 28 days of hydration; (b) calculated content of $C_3A·CaSO_3·11H_2O$ (including the C_4AH_{13} phase in sample CS1C).

products between the components of the sample are $C_3A·CaSO_3·11H_2O$ and C_4AH_{13} or their solid solution. The tests of the phase composition also showed that in the mixture C_3A with $CaSO_3·0.5H_2O$ with or without the addition of $Ca(OH)_2$, the mineral analogical to the ettringite phase did not come into being. Therefore, the reaction

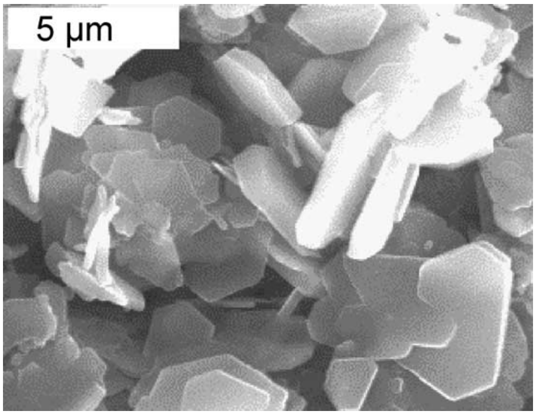

Fig. 4. Sample CS1 after 1 day of hydration (without $Ca(OH)_2$).

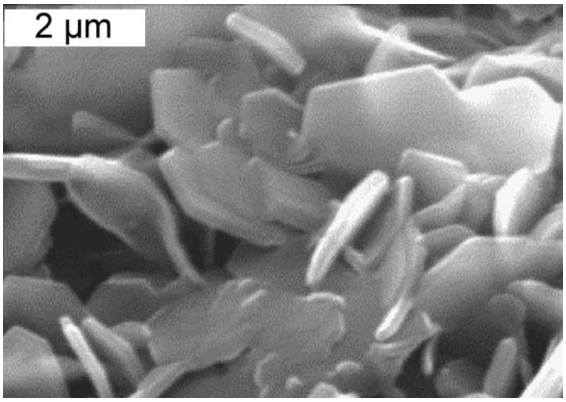

Fig. 5. Sample CS1C after 1 day of hydration (with addition of 5% $Ca(OH)_2$).

Table 2
Composition of mixtures for morphology examinations (tested after 30 min of hydration)

Sample code	Component (wt.%)			
	C_3A	$CaSO_4 \cdot 2H_2O$	$CaSO_3 \cdot 0.5H_2O$	$Ca(OH)_2$
CGC	80	15	–	5
CSC	80	–	15	5
CC	95	–	–	5

product, $C_3A \cdot CaSO_3 \cdot 11H_2O$, does not undergo a reaction similar to the reaction of ettringite in the mixtures containing gypsum.

The thermal analysis–TG curve (Fig. 3) made it possible to calculate the content of phase $C_3A \cdot CaSO_3 \cdot 11H_2O$ (including the phase C_4AH_{13} in the samples with the addition of calcium hydroxide). For calculation purposes, it was assumed that $C_3A \cdot CaSO_3 \cdot 11H_2O$ contains 11 molecules of water [8], as it is shown in the molecular formula. At 350 °C the complete dehydration process takes place. On the basis of this assumption, the weight loss caused by dehydration was measured. The results thus obtained (shown in Fig. 3b) confirmed the conclusions drawn from the XRD analyses. An increase in the content of hydration products is observed, that is, the increase in the degree of hydration of the components in the sample containing calcium hydroxide after 1 and 28 days of reaction.

3.2.2. Scanning microscope analysis

The tests of the morphology of hydration products C_3A with $CaSO_3 \cdot 0.5H_2O$ and C_3A with $CaSO_3 \cdot 0.5H_2O$ and the addition of $Ca(OH)_2$ (which were conducted with the use of scanning microscope) did not reveal any significant differences between the forms of $C_3A \cdot CaSO_3 \cdot 11H_2O$. It seems that the hexagonal plates of this phase observed after 1 day are slightly smaller in the presence of $Ca(OH)_2$ (Figs. 4 and 5).

Despite the fact that the processes of reaction between C_3A and gypsum with $Ca(OH)_2$ lead to the formation of impermeable ettringite layer after a few minutes, the degree of hydration of the components after 1 day or more is relatively high ([9], Fig. 1). In this case, the ettringite is not gelatinous but crystalline, as the $C_3A + CaSO_3 \cdot 0.5H_2O$ hydration products formed in the presence of $Ca(OH)_2$ after 24 h (Fig. 5). In order to verify the potential retarding influence of the calcium sulfite hemihydrate on C_3A in the presence of $Ca(OH)_2$, the morphology tests and EDS analysis of the products after 30 min of hydration were carried out. The samples for this study are given in Table 2. In comparison to the samples presented in Table 1, the samples for this study were specially prepared as the mixtures of components, but only with the 15% content of calcium sulfite or gypsum. The hydration processes were carried out at w/s = 1 and were stopped by means of acetone.

Fig. 6 shows the gel-like form of the CGC sample hydration products (C_3A, gypsum, $Ca(OH)_2$). This form is responsible for the retardation of tricalcium aluminate particularly within the first hours.

Fig. 7, instead, shows the surface of C_3A grains covered with the CSC sample reaction products (C_3A, $CaSO_3 \cdot 0.5H_2O$, $Ca(OH)_2$) with water. They are poorly crystallised, practically gel-like. They are not identical as in the CGC sample but they seem to form an impermeable coating, adjacent to C_3A grains, different from well-crystallised hexagonal monosulfite aluminate plates observed after a longer reaction time.

In the sample CC without sulfate or sulfite, the C_3A hydration leads to the formation of cubic or poorly crystallised hexagonal forms of hydrated calcium aluminate. The hexagonal crystalline forms were also observed in the 30th minute of the C_3A hydration in saturated $CaSO_3$ solution without $Ca(OH)_2$ (at w/s = 400).

The results thus obtained indicate that within the first hour of hydration, calcium sulfite hemihydrate, in the

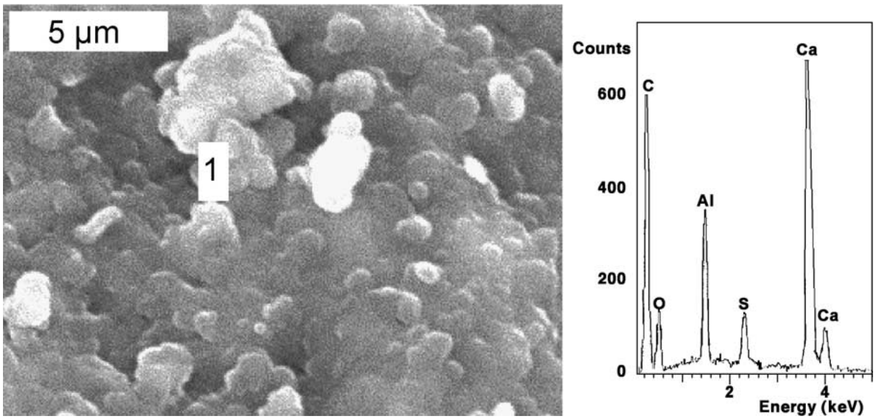

Fig. 6. Gel-like form of ettringite on the C_3A surface in the CGC sample (Table 2); EDS plots for point 1.

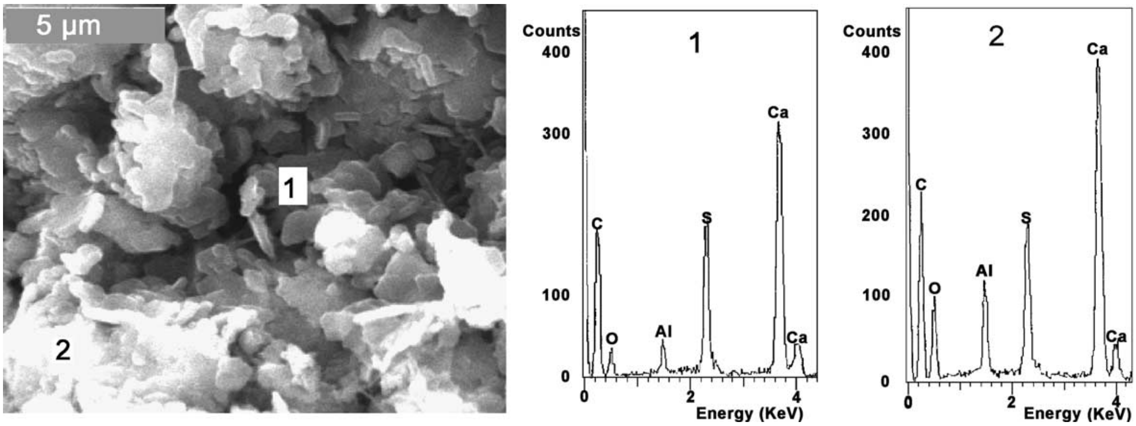

Fig. 7. Gel-like hydration products of the CSC sample (Table 2); EDS plots for points 1 and 2.

presence of $Ca(OH)_2$, plays a role of C_3A hydration retarder although to a lesser extent than gypsum in the similar system. Retardation can be seen in relation to hydration of pure C_3A in water.

3.2.3. Liquid phase chemical composition

The samples from Table 1 were subjected to the studies of the liquid phase chemical composition. After mixing, the samples with water at w/s = 10, the containers with suspensions were shaken. After a fixed time (3, 7, 15, 30 and 60 min), the suspensions were filtered using a glass porous funnel and then the liquid phase was analysed. The results obtained for the CS1 sample (C_3A and $CaSO_3 \cdot 0.5H_2O$) are given in Fig. 8. They show the relatively high concentration of $Al(OH)_4^-$ ions, SO_3^{2-} ions concentration which is practically constant, and Ca^{2+} concentration which is on the decrease. This concentration relationship indicates that the reaction between the components takes place practically undisturbed and it is difficult to find any reaction rate-limiting agent.

In the mixture of C_3A with $CaSO_3 \cdot 0.5H_2O$ and $Ca(OH)_2$ addition (the CS1C sample), SO_3^{2-} concentration in the liquid phase is lower by half in comparison to the CS1 sample (the common ion effect), whereas $Al(OH)_4{}^-$ concentration is low and hardly reaches 0.007 mmol/l (Fig. 9). It can be seen that the hydration rate in this system is basically limited by the migration rate of aluminate ions in the solution, which results from the high reaction rate or the slow migration of aluminate ions into the liquid phase, due to the probable formation of the reaction products layer on the C_3A surface (which is shown in Fig. 7). The decrease in the concentration of aluminate ions can be connected with common-ion effect which is associated with the addition of $Ca(OH)_2$, the solubility of which is relatively high.

The high hydration rate between the components in the presence of high Ca^{2+} ion concentration does not exclude C_3A hydration rate decrease, as the hydration products come into being near the slowest migration rate and, as a result, may block its surface.

A similar situation can be observed in the case of C_3A mixed with gypsum and $Ca(OH)_2$. The ettringite formation rate is so high that the products do not come into being in the crystalline form but the gel-like one, which covers the C_3A grains and blocks, at least for some time, the hydration of this phase.

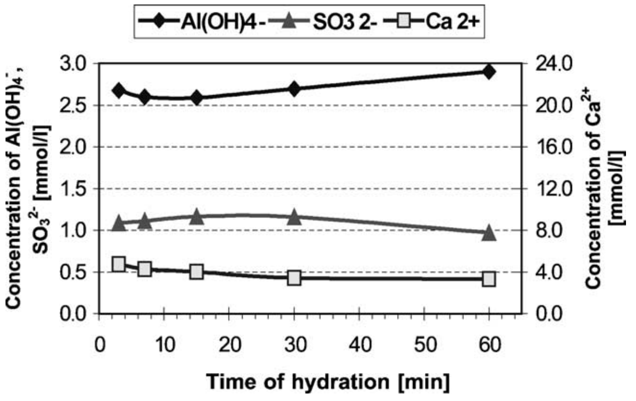

Fig. 8. Chemical analysis of the liquid phase in the CS1 sample.

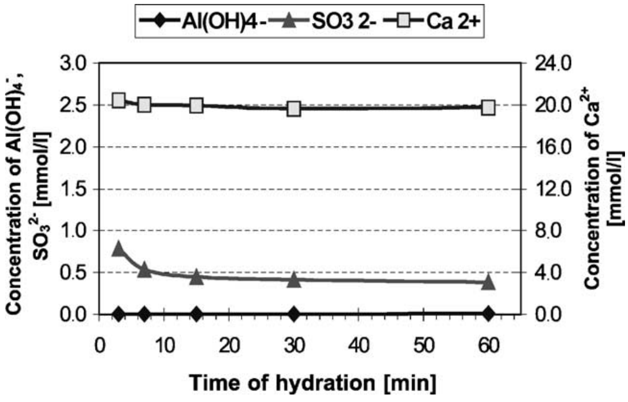

Fig. 9. Chemical analysis of the liquid phase in the CS1C sample.

4. Conclusions

(1) C_3A in the mixture with $CaSO_3 \cdot 0.5H_2O$ undergoes a fast reaction immediately after being mixed with water and calcium monosulfite-aluminate is produced, which crystallises in the form of hexagonal plates.

(2) Addition of $Ca(OH)_2$ to the mixture $C_3A-CaSO_3 \cdot 0.5H_2O$ lowers the rate of reaction in water due to the poorly crystallised form of the reaction products, which leads to the formation of a practically impermeable coating on the C_3A grains.

(3) The effectiveness of the C_3A reaction retardation in the presence of calcium sulfite and the addition of calcium hydroxide is not so high when gypsum, instead of sulfite, is used.

(4) After 24 h or 28 days, the hydration degree of C_3A in the mixtures with $CaSO_3 \cdot 0.5H_2O$ is higher in the case of the sample containing $Ca(OH)_2$ addition. Apart from the main reaction product, i.e. $C_3A \cdot CaSO_3 \cdot 11H_2O$ phase, one can also observe the presence of C_4AH_{13} phase, which may form solid solutions with monosulfite-aluminate phase.

(5) The reaction product of the C_3A phase and $CaSO_3 \cdot 0.5H_2O$ is not analogous to the ettringite phase, thus the monosulfite-aluminate form of $C_3A \cdot CaSO_3 \cdot 11H_2O$ does not undergo the ettringite → monosulfate reaction.

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