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Cement and Concrete Research 36 (2006) 1016 – 1022

Hydration of tricalcium aluminate in the presence of various amounts of calcium sulphite hemihydrate: Conductivity tests

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Received 7 October 2005; accepted 12 January 2006

Abstract

Hydration of calcium aluminate C_3A ($3CaO{\cdot}Al_2O_3$) in the presence of calcium sulphite hemihydrate ($CaSO_3{\cdot}0.5H_2O$), with the molar ratio of substrates close to 1, produces the $C_3A{\cdot}CaSO_3{\cdot}11H_2O$ calcium monosulphite aluminate phase. Small amounts of calcium sulphite added to calcium aluminate (the ratio of $CaSO_3{\cdot}0.5H_2O/C_3A$ equalling 0 : 1) change the rate of C_3A hydration and influence the whole reaction. Reaction processes for various ratios of the C_3A–$CaSO_3{\cdot}0.5H_2O$ mixture were examined in pure distilled water with a considerable amount of liquid W/S = 38–50 (constant W/C_3A). Processes in the liquid phase were monitored with conductivity equipment, and the XRD analysis was used to identify the phases precipitated during the examined reactions.

Keywords: Hydration; Tricalcium aluminate; Calcium sulphite hemihydrate; Hydration products

1. Introduction

The number of publications discussing the reaction of tricalcium aluminate (the most reactive clinker mineral) with calcium sulphite is rather limited. They mostly focus on the properties and analytical data concerning the $C_3A{\cdot}CaSO_3{\cdot}11H_2O$ phase which results from the reaction between the two compounds (not ettringite-like phase as in the reaction between C_3A and gypsum) [1–9]. While it is possible to find information on different phases coexisting in the C_3A–$CaSO_3$–$Ca(OH)_2$–H_2O system after a long time of hydration [10], the results of tests involving all products of the reaction are extremely difficult to obtain. Their importance stems from the fact that the formation of a phase at the beginning of the reaction usually influences the rate and course of all processes within the system. The authors decided to investigate hydration processes of C_3A in pure water containing various amounts of calcium sulphite hemihydrate (with various molar ratios between the two phases). The study resulted from the need to find methods of disposing certain industrial wastes (by-products obtained in semi-dry installations of the desulphurization process). The tests were based on two methods: electrical conductivity of the solution, which depends on varying ion concentrations in the liquid phase, and the XRD analysis, while the aim was to determine the mineral composition of solid products formed in the reacting systems.

2. Materials and method

The tests involved the following material: tricalcium aluminate (C_3A) and calcium sulphite hemihydrate ($CaSO_3{\cdot}0.5H_2O$), both obtained under laboratory conditions. Calcium sulphite hemihydrate was produced in the reaction between Na_2SO_3 and $CaCl_2$, based on practical organic chemistry [11]. The pure deposit was dried at the temperature of 100 °C until the mass decrement disappeared, which was caused by the

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doi:10.1016/j.cemconres.2006.01.006

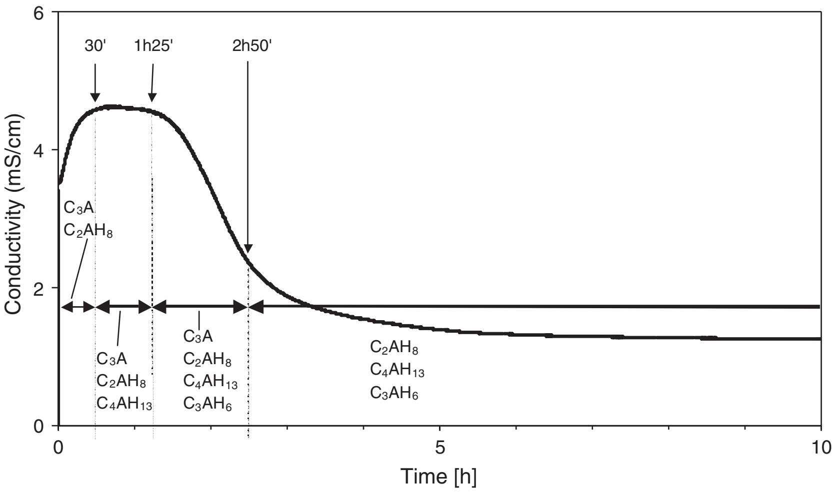

Fig. 1. Variation of conductivity during hydration of C_3A in water at 25 °C, with water/C_3A = 50. The times for X-ray analysis and the phases are indicated.

evaporation of water, possibly by the dehydration of the more hydrated sulphites [12]. Quantitative analysis carried out by the XRD method revealed a small proportion (less than 5%) of $C_{12}A_7$ in C_3A, while $CaSO_3 \cdot 0.5H_2O$ was pure in its mineralogical composition. The specific area of C_3A designated by Blaine's method equalled 330 m^2/kg.

Samples taken for conductometric tests were mixtures of C_3A and $CaSO_3 \cdot 0.5H_2O$, with 0, 0.2, 0.4, 0.8 and 1.0 molar proportions of $CaSO_3 \cdot 0.5H_2O/C_3A$. Reaction processes were carried out with the water/C_3A = 50, in containers where the hydrating suspension could be kept in motion at the constant temperature of 25 °C. To eliminate the influence of CO_2 present in the air, the process was conducted under the nitrogen shield. The oxidising effect of oxygen present in the air on the calcium sulphite was eliminated by the same method. The analysis involved samples of approx. 5 ml; the solid deposit was separated from the liquid, dried with ethyl alcohol, and analyzed by the X-ray diffraction with an Inel CPS 120 detector ($\lambda_{K\alpha 1}Cu = 1.54056$ Å).

3. Results

In the description of the results, one of the phases attested by the XRD method was the C_4AH_{13} phase, which indirectly proved the presence of the C_4AH_{19} phase in contact with the liquid phase. However, the method of preparing samples for the XRD analysis led to their partial dehydration resulting in C_4AH_{13}. The presence of C_4AH_{19} in contact with the liquid phase might have been confirmed by applying the XRD analysis to non-dried samples; however, such test was not carried out for organizational reasons. In the subsequent stages of the study, therefore, the C_4AH_{13} phase was listed as an attested kind of hydrated calcium aluminate which could be analyzed by the chosen methods.

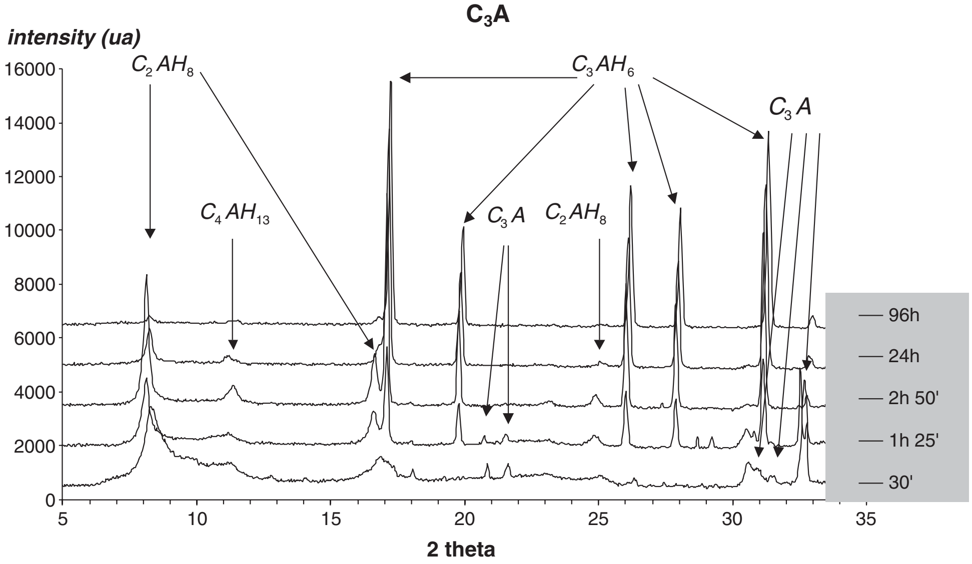

Fig. 2. X-ray diagrams showing phase compositions at different times of hydration of C_3A in water.

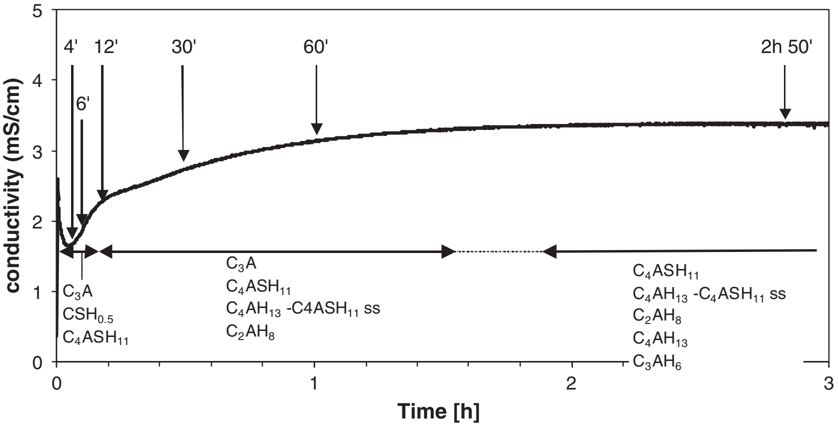

Fig. 3. Variation of conductivity during hydration of C_3A with calcium sulphite in water, $CaSO_3/C_3A$ molar ratio equalling 0.2. The times for X-ray analysis and the phases are indicated.

3.1. Hydration of C_3A in water

As regards C_3A hydration in water, the conductivity curve (Fig. 1) shows an initial increase, coinciding with the formation of the C_2AH_8 calcium hydroaluminate phase (Fig. 2). This increase in conductivity can be explained by the fact that the formation of C_2AH_8 consumes less than 3 mol of calcium produced by the dissolution of 1 mol of C_3A. The constant value of conductivity in the period between the 30th and 85th minutes of the test is caused the simultaneous formation of C_2AH_8 and C_4AH_{13}, which may consume 6 mol of calcium produced by the dissolution of 2 mol of C_3A. The decrease in conductivity following this plateau is related to the formation of C_3AH_6, and it corresponds to the complete dissolution of C_3A at the time indicated in Fig. 1.

The only process occurring in the subsequent hours is the formation of C_3AH_6 from ions produced by the dissolution of C_2AH_8 and C_4AH_{13}. These hexagonal minerals are unstable after the conductivity plateau, so that after 96 h of hydration they produce barely visible peaks on the diffraction pattern.

3.2. Hydration of C_3A with calcium sulphite, with the molar ratio of $CaSO_3 \cdot 0.5H_2O/C_3A$ smaller than 1

The conductivity curves for 0.2, 0.4 and 0.8 molar ratios are presented in Figs. 3, 4 and 5; phases indicated in the graph, obtained in the XRD analysis, are presented in Figs. 6, 7 and 8, respectively. Hydration tests for C_3A with calcium sulphite hemihydrate, the molar ratio of $CaSO_3 \cdot 0.5H_2O/C_3A$ smaller than 1, show an initial decrease in liquid conductivity, followed by a plateau which ends at the complete consumption of calcium sulphite ($CaSO_3 \cdot 0.5H_2O$).

During the initial decrease typical of the three conductivity curves, the only observed processes are the formation of the calcium monosulphite aluminate phase ($C_3A \cdot CaSO_3 \cdot 11H_2O$) from C_3A and calcium sulphite.

With the molar ratio equalling 0.8, however, the decrease in conductivity stops in the third hour of the experiment, followed by a long period of stability. Over that period, the formation of C_3AH_6 is revealed by the XRD analysis (Fig. 8).

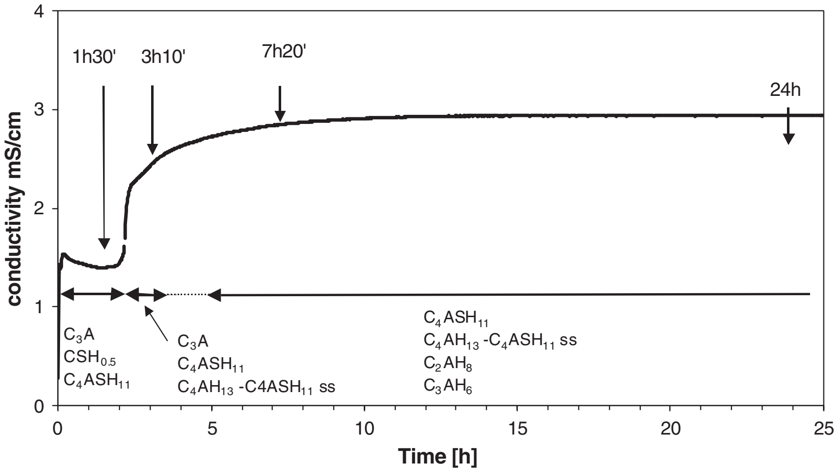

Fig. 4. Variation of conductivity during hydration of C_3A with calcium sulphite in water, $CaSO_3/C_3A$ molar ratio equalling 0.4. The times for X-ray analysis and the phases are indicated.

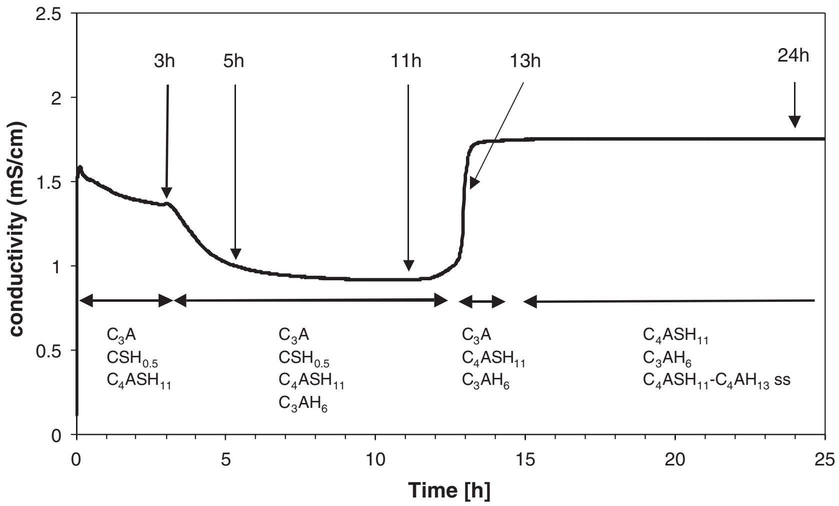

Fig. 5. Variation of conductivity during hydration of C_3A with calcium sulphite in water, $CaSO_3/C_3A$ molar ratio equalling 0.8. The times for X-ray analysis and the phases are indicated.

Total consumption of $CaSO_3·0.5H_2O$ in samples with 0.2 and 0.4 ratio of $CaSO_3·0.5H_2O/C_3A$ is followed by the formation of the solid solution C_4AH_{13}–$C_3A·CaSO_3·11H_2O$ ss; the presence of C_2AH_8 is also attested. In two cases, C_3AH_6 forms with other calcium aluminate hydrates after a longer period of time (C_2AH_8, C_4AH_{13} for 0.2 molar ratio; C_2AH_8 for 0.4 molar ratio). With a small amount of sulphite in the mixture at the end of the reaction, C_4AH_{13} is also obtained as a separate phase. The formation of this phase in the sample with 0.2 molar ratio is related to the presence of the solid solution with a limited range [10].

The solid solution (C_4AH_{13}–$C_3A·CaSO_3·11H_2O$ ss) is also attested for 0.8 molar ratio after the disappearance of calcium sulphite, but the only noted calcium aluminate hydrate is C_3AH_6, already precipitated before the total consumption of calcium sulphite. C_4AH_{13} and C_2AH_8 cannot be precipitated since they lose their stability in the presence of C_3AH_6.

The results also show that a higher ratio of $CaSO_3·0.5H_2O/C_3A$ causes a decrease in the rate of C_3A consumption during the reaction. In samples containing a large addition of sulphite (as in those with 0.8 ratio), C_3A is attested even after 11 h, while in samples with smaller additions of this mineral, calcium aluminate is not attested after 3 h (the sample with the molar ratio of 0.2).

3.3. Hydration of C_3A with calcium sulphite, with the molar ratio of $CaSO_3·0.5H_2O/C_3A$ equalling 1

With the $CaSO_3/C_3A$ ratio equalling 1, the decrease in conductivity is noted at the beginning only (Fig. 9), while the

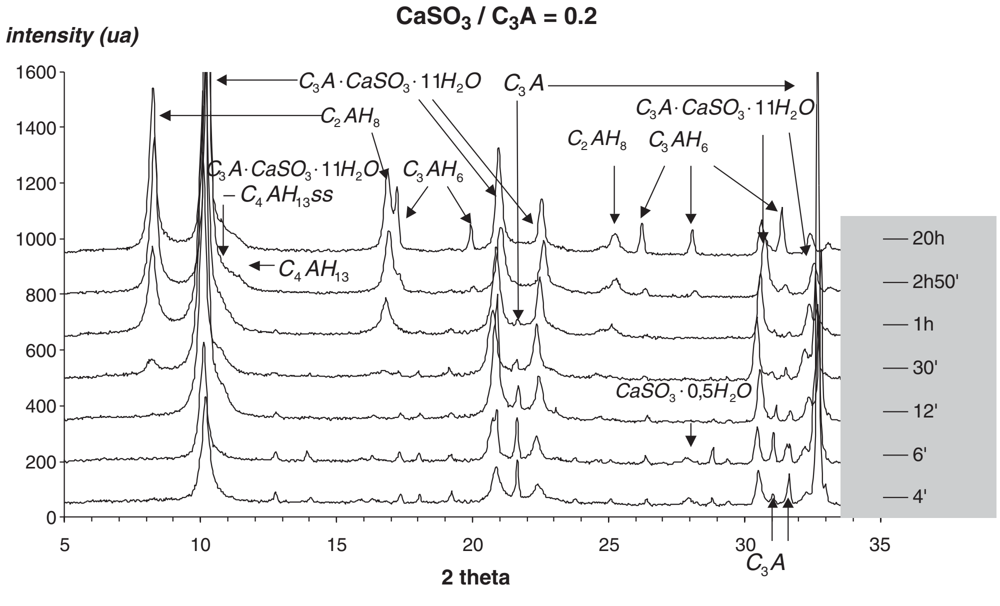

Fig. 6. X-ray diagrams showing phase compositions at different times of hydration; sample with the molar ratio of $CaSO_3/C_3A$ equalling 0.2.

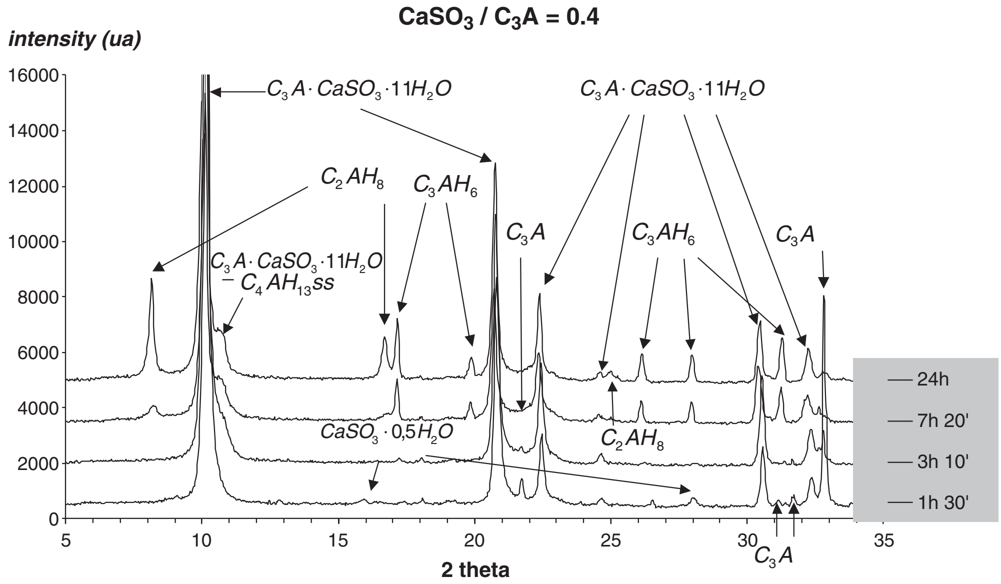

Fig. 7. X-ray diagrams showing phase compositions at different times of hydration; sample with the molar ratio of $CaSO_3/C_3A$ equalling 0.4.

analysis of solid products performed after two days reveals, as expected, precipitation of the calcium monosulphite aluminate phase ($C_3A{\cdot}CaSO_3{\cdot}11H_2O$). As the XRD analysis indicates (Fig. 10), C_3AH_6 is formed between the 1st and 3rd hours of hydration, but it fails to show on the conductivity curve, probably owing to the small amount of the phase. The authors relate the C_3AH_6 formation to the partial granulation of C_3A added to the suspension (containing calcium sulphite), and to the insufficient amount of sulphite ions in granulated C_3A. No precipitation of C_4AH_{13} and C_2AH_8 calcium aluminate hydrates or of C_4AH_{13}–$C_3A{\cdot}CaSO_3{\cdot}11H_2O$ ss is observed.

4. Conclusions

The experiments show that the addition of calcium sulphite to C_3A hydrated in water results in the monosulphite aluminate phase at the beginning of the reaction, independently of the low solubility of sulphite. If the amount of calcium sulphite is sufficiently high (molar ratio of calcium sulphite to calcium aluminate equalling 1), the obtainment phase remains stable. A smaller addition of calcium sulphite (molar ratio of calcium sulphite to calcium aluminate equalling 0.8) initially produces calcium sulphite aluminate hydrate. Hydration of the remaining calcium aluminate results in the solid solution of C_4AH_{13}

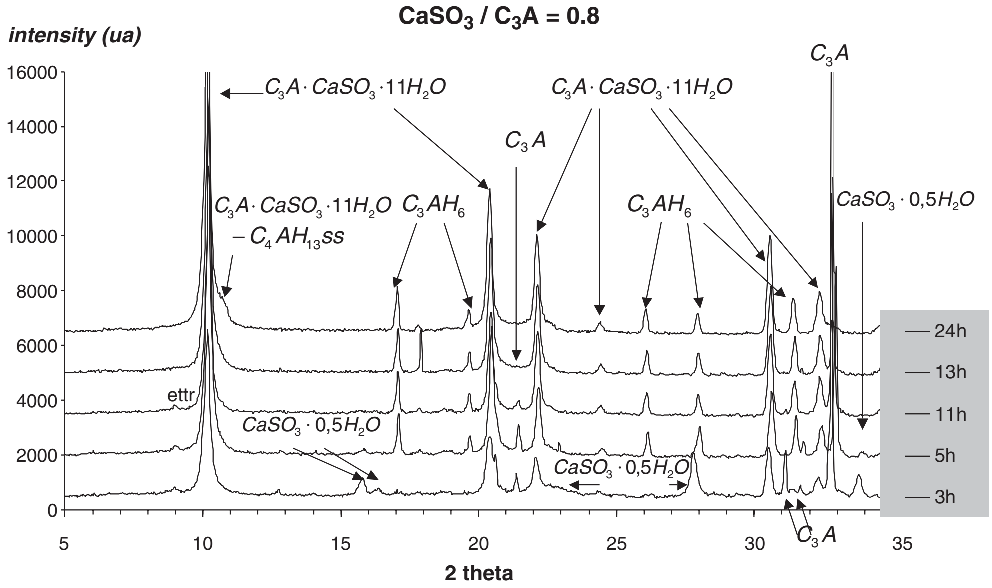

Fig. 8. X-ray diagrams showing phase compositions at different times of hydration; sample with the molar ratio of $CaSO_3/C_3A$ equalling 0.8.

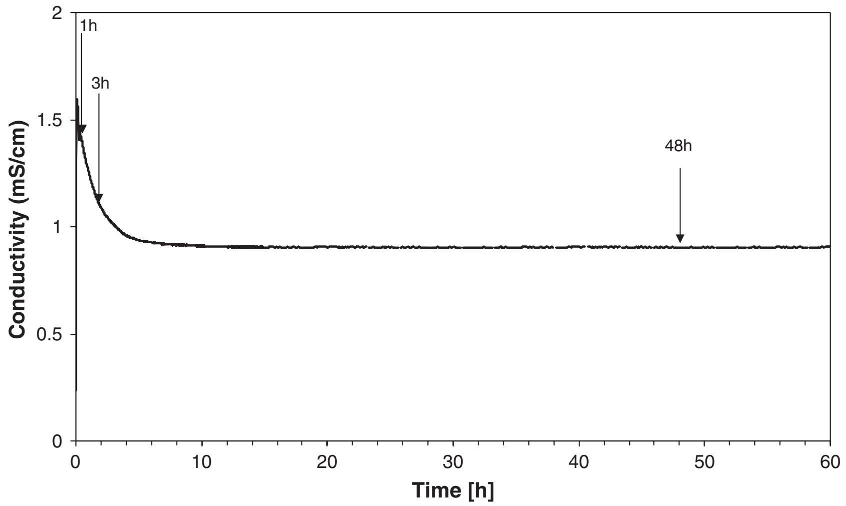

Fig. 9. Variation of conductivity during hydration of C_3A with calcium sulphite $CaSO_3/C_3A$, molar ratio equalling 1.0, in water at 25 °C, with water/C_3A = 50. The times of X-ray analysis and the phases are indicated.

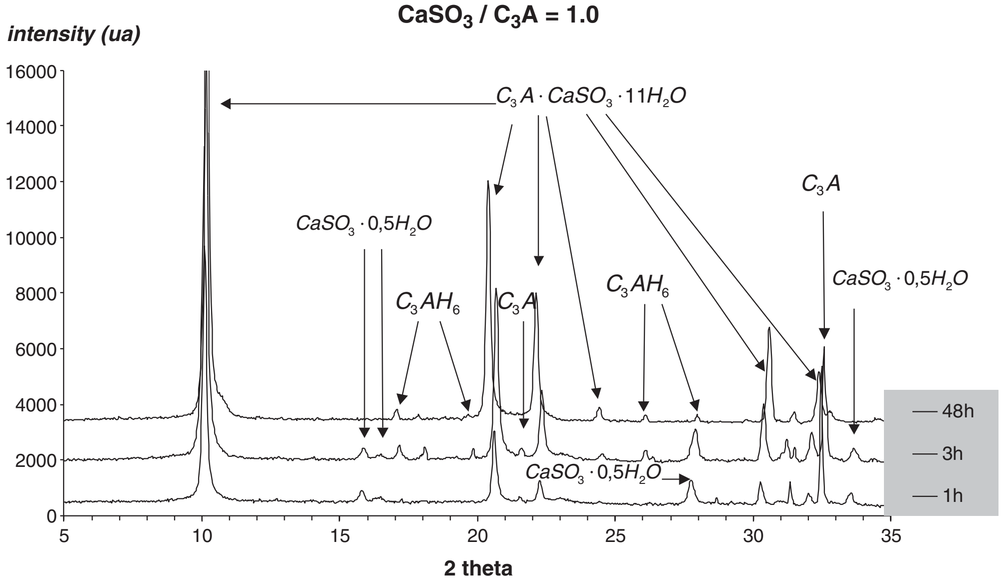

Fig. 10. X-ray diagrams showing phase compositions at different times of hydration; sample with the molar ratio of $CaSO_3/C_3A$ equalling 1.0.

with $C_3A·CaSO_3·11H_2O$. The additional reduction of sulphite also produces the C_2AH_8 phase, resembling the solid solution mentioned above. When the mixture contains a small amount of sulphite, C_4AH_{13} is obtained as a separate phase at the end of the reaction. Its formation is related to the presence of the solid solution with a limited range. The C_3AH_6 phase is obtained in each of the tests, especially after the first few hours of the reaction. This may be due to fact that, despite intensive stirring, C_3A prepared for the tests tends to form small granules in water. Furthermore, the experiments indicate that a larger amount of calcium sulphite decreases the rate of C_3A consumption during the reaction.

Acknowledgements

The authors wish to express their thanks to Andre Nonat for kindly permitting them access to the laboratory equipment in Dijon, and to other persons who helped them in the experimental work.

This work has been sponsored by the Polish Scientific Committee (grant No. 7 T08D 048 21).

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