Pergamon

Cement and Concrete Research 31 (2001) 641–646

CEMENT AND CONCRETE RESEARCH

Dissolution of $CaSO_4{\cdot}1/2H_2O$ and precipitation of $CaSO_4{\cdot}2H_2O$ A kinetic study by synchrotron X-ray powder diffraction

Cristell Solberg[a,b], Staffan Hansen[a,*]

[a]Inorganic Chemistry 2, Chemical Center, Lund University, P.O. Box 124, S-221 00 Lund, Sweden
[b]Gyproc AB, P.O. Box 153, S-746 24 Bålsta, Sweden

Received 9 September 2000; accepted 16 January 2001

Abstract

Time-resolved X-ray powder diffraction has been performed on hydrating samples of calcium sulfate hemihydrate with 0.50 wt.% dihydrate seeds added. Data were recorded in transmission mode using a position sensitive detector and synchrotron X-ray radiation of optimised intensity (wavelength 1.4 Å). The dissolution of the hemihydrate and the formation of the dihydrate were both monitored. Varying the water/solid weight ratio (w/s) from 0.50 to 1.50 did not affect the reaction rate significantly. Addition of 0.50 wt.% potassium sulfate to the water accelerates the reaction and 0.25 wt.% citric acid monohydrate causes retardation; times for complete reaction: 17 and 42 min, respectively, compared to 28–32 min without additive (w/s = 1.00). A comparison of the reaction curves shows (i) that hemihydrate dissolves and dihydrate precipitates at the same rate, and (ii) that preferred orientation effects are absent in the diffraction experiments. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Hydration; Kinetics; X-ray diffraction; Sulfate

1. Introduction

Calcium sulfates constitute a group of inorganic binders that has been utilised by man since ancient times [1]. The most commonly used cementitious reaction in the group is the reaction of calcium sulfate hemihydrate, $CaSO_4{\cdot}1/2H_2O$, with liquid water to form calcium sulfate dihydrate, $CaSO_4{\cdot}2H_2O$ (gypsum).

There is now common agreement that the hydration of the hemihydrate takes place via a through-solution route, i.e., the hemihydrate first dissolves and the dihydrate then precipitates from the aqueous solution because it is less soluble than the hemihydrate [2], as shown by Reactions (1) and (2) beneath. Addition of the two reactions gives the overall Reaction (3).

$$\mathrm{CaSO_4{\cdot}1/2H_2O(s)\rightarrow Ca^{2+}(aq)+SO_4^{2-}(aq)+1/2H_2O(l)},\quad \Delta H_1^o=-18\ \mathrm{kJ/mol} \tag{1}$$

$$\mathrm{Ca^{2}+(aq)+SO_4^{2-}(aq)+2H_2O(l)\rightarrow CaSO_4{\cdot}2H_2O(s)},\quad \Delta H_2^o=+1\ \mathrm{kJ/mol} \tag{2}$$

$$\mathrm{CaSO_4{\cdot}1/2H_2O(s)+3/2H_2O(l)\rightarrow CaSO_4{\cdot}2H_2O(s)},\quad \Delta H_3^o=-17\ \mathrm{kJ/mol} \tag{3}$$

Two of the most important properties of any inorganic binding agent are setting time and mechanical strength. There are several different methods [3] that can be used to monitor the setting time and some of these are summarised in Table 1. Knife cut closure and needle penetration depth are methods that most manufacturers employ to control the setting time because they are quick and easy to perform. These methods give information about the formation of gypsum as it monitors the physical setting of the slurry. By far the most common method of investigating the hydration of calcium sulfate hemihydrate is calorimetry. With the calorimeter it is possible to follow the dissolution of hemihydrate. As can be seen from Reactions (1) and (2), the standard enthalpy change associated with the dissolution of hemihydrate is quite large (– 18 kJ/mol). The enthalpy

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* Corresponding author. Tel.: +46-46-222-8117; fax: +46-46-222-4012.

E-mail address: staffan.hansen@oorg2.lth.se (S. Hansen).

0008-8846/01/$ – see front matter
PII: S0008-8846(01)00464-1

Table 1
Reaction steps probed by different techniques commonly used to follow the hydration of calcium sulfate hemihydrate

Experimental technique	Dissolution of $CaSO_4 \cdot 1/2H_2O$	Formation of $CaSO_4 \cdot 2H_2O$
Knife cut closure	No	Yes
Needle penetration depth	No	Yes
Calorimetry	Yes	No[a]
Differential thermal analysis[b]	Yes	Yes
Powder X-ray diffraction	Yes	Yes

[a] Only a small contribution to the overall heat evolution.

[b] Only performed on samples where the hydration has been stopped.

change associated with the formation of gypsum, on the other hand, is small (+1 kJ/mol) and does not contribute much to the enthalpy change of the total reaction. The heats of reaction were calculated from the standard formation enthalpies (1 bar, 25°C) in Ref. [4]. Hydration of hemihydrate does not take place at standard conditions and the exact values will vary depending on the specific surface area of the hemihydrate, but it is safe to conclude that the total heat of reaction is dominated by the dissolution step.

Differential thermal analysis can give information on both the dissolution of hemihydrate and the formation of gypsum, but it has the limitation that it can only be performed on samples where the hydration has been stopped. A method that can give information on both the dissolution of hemihydrate and the formation of gypsum on hydrating samples is powder X-ray diffraction, which is the method employed in this study, where the influence of different water/solid ratios on the crystallisation kinetics have been investigated as well as the possibility of optimising the experimental conditions to improve the quality of the results. The systems studied consisted of hemihydrate, water and different combinations of the accelerators, gypsum seeds and potassium sulfate, and the retarder citric acid.

2. Experimental

2.1. Preparation of hemihydrate

Thirty grams of $CaSO_4 \cdot 2H_2O$ (Merck, zur Analyse) was heated on a dish for 2 h in a heating cabinet at 150°C. The weight loss of the fresh sample indicated a total composition of $CaSO_4 \cdot 0.52H_2O$ after calcination, i.e., close to the ideal hemihydrate composition. The powder was conditioned in the ambient atmosphere at room temperature for 1 h 10 min. After conditioning, a weight gain of 0.51 wt.% was observed, corresponding to the composition $CaSO_4 \cdot 0.56H_2O$.

2.1.1. Series 1

A portion of the hemihydrate powder was shaken in a jar together with 0.50 wt.% of the original $CaSO_4 \cdot 2H_2O$. The seeded mixture was then stored in a closed container and was used after 1 day, in the experiments with varying water/solid weight ratio (w/s).

2.1.2. Series 2

Another portion of hemihydrate was stored in a closed container for 2 weeks before hydration was undertaken. The hemihydrate powder was shaken in a jar together with 0.50 wt.% of $CaSO_4 \cdot 2H_2O$. The seeded mixture was then used the same day in the experiments with various additives.

Secondary electron images recorded in a scanning electron microscope indicated that the $CaSO_4 \cdot 2H_2O$ powder, used in the preparation of hemihydrate and for seeding in the experiments above, contained flattened dihydrate crystals with a size of 10–50 μm, but also a powder fraction with a grain size of less than a few micrometers.

2.2. Preparation and mounting of paste

2.2.1. Series 1

Pastes were prepared by manually mixing 2.5 g of the seeded $CaSO_4 \cdot 1/2H_2O$ powder with deionised water, in a plastic cup for about 1 min. The amount of water added was varied so that the water/solid weight ratio assumed the values, w/s = 0.50, 0.75, 1.00, 1.25, 1.50.

2.2.2. Series 2

Pastes were prepared by manual mixing of 2.5 g of the seeded $CaSO_4 \cdot 1/2H_2O$ powder and 2.5 g aqueous solution, in a cup for about 1 min. The solutions utilized were pure deionised water, 0.25 wt.% citric acid monohydrate (Riedel-de Haën, >99.8 wt.%) and 0.50 wt.% K_2SO_4 (Mallinckrodt, analytical reagent), respectively.

Filling of the glass capillary (Glas, 0.70 mm outer diameter and 0.68 mm inner diameter) was achieved using a Codan 2-ml syringe fitted with a piece of silicone rubber tubing. The paste-filled capillary was mounted horizontally on the diffractometer. Surrounding the capillary was air at 20°C and 35–50% relative humidity, while the relative humidity inside the capillary was assumed to be 100%. During the X-ray diffraction experiment, the capillary was rotated to minimise orientation effects (approximately 1 rps). The time passing between the start of mixing of the paste and the initiation of the X-ray data collection was measured with a stopwatch.

2.3. X-ray data collection

Synchrotron X-ray powder diffraction data on the hydrating samples were collected on beamline I711 at MAX-lab in Lund using monochromatised radiation of wavelength 1.406 Å in Series 1 and 1.385 Å in Series 2. The dimension of the beam close to the capillary was adjusted by slits to 1 × 1 mm. The X-ray measurements were performed using an Inel CPS 120 position sensitive detector in the vertical position. The data were collected using the computer program *KINETIK för CPS 120, version 1.0* (Göran Svensson, personal communication) and new X-ray spectra were saved continuously after a collection time of 3 min. Each spectrum covered a scattering angle of about 120° divided into 4096 channels and the number of counts in each channel was registered.

In order to obtain smooth hydration curves with as little experimental noise as possible, it is necessary to optimise the intensity of the X-ray beam used in each experiment. This is achieved by placing the metal foils of different thickness in the path of the primary beam. An increase of the intensity in the utilised X-ray diffraction peaks improves the counting statistics, but the saturation level of the position sensitive detector puts a limit on the maximum count rate that can be tolerated.

2.4. X-ray data processing

A drop of about 5% in the electron beam current in the storage ring was observed during a typical experiment and no correction was performed on the resulting X-ray intensities. An intense and nonoverlapping diffraction peak was selected for each of the two phases. For hemihydrate, the peak corresponding to an interplanar distance of 6.0 Å was used, and for dihydrate the 7.6-Å peak. The integrated intensity of the diffraction peaks was evaluated according to the procedure reported in Ref. [5].

The relative intensity α was calculated by dividing with the maximum intensity observed for each phase and α was then used to follow the time-dependence of the degree of decomposition of hemihydrate α(HH) and degree of formation of dihydrate α(DH). A calculation routine that reads the files, integrates over the channels given by the operator and plots the relative intensity as a function of time has been developed using the software *Matlab version 5.1.0.421* (The MathWorks, Natick, MA, USA).

3. Results and discussion

A comparison of the reaction rates for the samples without additives and w/s = 1.0 in Series 1 (Figs. 1 and 2) and Series 2 (Fig. 3, curves marked *b*), indicates no aging effect resulting from the 2-week storing in a closed container of the hemihydrate in Series 2. In both series, the reaction has gone to completion within about 30 min.

3.1. Varying water/solid ratio

As the mixing and mounting of the samples were done manually, it was difficult to know whether or not the actual composition of the slurry in the capillary corresponded to the nominal mixing composition when a new experiment was initiated. To find out how deviations in the water/solid ratio would affect the results, five experiments were performed, where the ratio was varied over a wide range of values. The ratios tested were: w/s = 0.50, 0.75, 1.00, 1.25, 1.50; and 0.50 wt.% of dihydrate was included in all cases. As shown in Figs. 1 and 2, the reaction is almost independent of w/s. There is a slight tendency for more rapid reaction at low w/s, but the effect is too small to be significant.

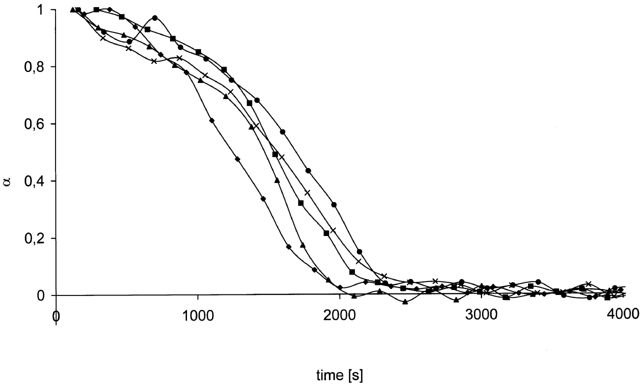

Fig. 1. Consumption of calcium sulfate hemihydrate in the experiments with 0.50 wt.% dihydrate seeds and varying water/solid weight ratio, w/s = 0.50 (◆), 0.75 (■), 1.00 (▲), 1.25 (×), 1.50 (●).

In conclusion, small variations in w/s due to inhomogeneous mixing or phase separation during the filling of the capillary will not influence the results. In the case of pastes of pure cement phases and water, the water/solid ratio sometimes has a strong influence on the rate of hydration. As an illustration, the second maximum in the heat evolution curve of C_4AF plus 20 wt.% $CaSO_4{\cdot}2H_2O$ is shifted from about 90 to 180 min following an increase in w/s from 0.37 to 1.00 [6].

3.2. Set modifying additives

A set of experiments were performed in order to investigate the influence of different set rate modifiers on the hydration of calcium sulfate hemihydrate. The systems studied consisted of different combinations of the accelerators potassium sulfate and dihydrate seed crystals and the retarder citric acid (see Fig. 3). Seven experiments were performed, in random order, where two were with 0.50 wt.% potassium sulfate and 0.50 wt.% dihydrate seeds (curves marked *a*); three were with 0.50 wt.% dihydrate seeds (curves marked *b*); and two were with 0.25 wt.% citric acid and 0.50 wt.% dihydrate seeds (curves marked *c*). As can be seen in Fig. 3, the results are reasonably reproducible and with potassium sulfate the reaction is completed in 17 min and with citric acid in about 42 min. This can be compared to the reference samples (b) that required 28–32 min for complete reaction.

The most likely rate-controlling processes in the different stages of hemihydrate hydration are: (i) nucleation of dihydrate; (ii) growth of dihydrate; and finally (iii) dissolution of hemihydrate [2]. Since seed crystals were included, we expect the acceleratory period to be controlled by dihydrate growth and the deceleratory period by the depletion of hemihydrate.

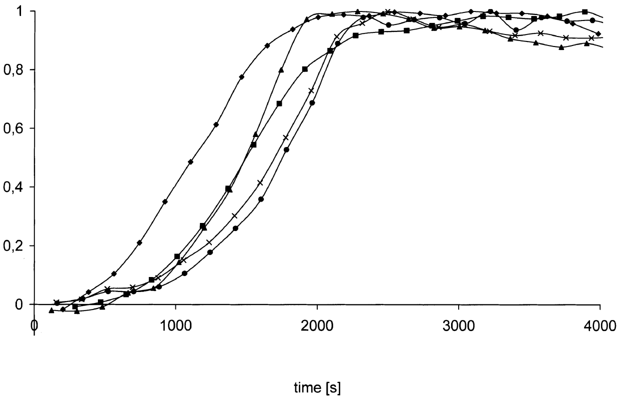

Fig. 2. Formation of calcium sulfate dihydrate in the experiments with 0.50 wt.% dihydrate seeds and varying water/solid weight ratio, w/s = 0.50 (◆), 0.75 (■), 1.00 (▲), 1.25 (×), 1.50 (●).

It has in general been observed that weak organic acids and their salts with strong bases act as retarders, while strong inorganic acids, as well as salts of strong acids and strong or weak bases are accelerators [7,8]. This type of acceleration has been referred to as a general ionic strength effect, which is due to the presence of noncomplexing ions [2]. In addition to this general effect, specific interactions occur since some salts are better accelerators than others. Potassium sulfate is known to be one of the better accelerators for the hemihydrate reaction [7,8].

The retarding effect of organic acids is likely to be related to the formation of calcium complexes in the aqueous solution or on the crystal surfaces. The citric acid molecule, H_4L, carries three carboxylic groups and one slightly acidic hydroxyl group. In aqueous solution, the following complexes are known to occur: CaH_3L^+, CaH_2L, $CaHL^-$, $Ca(H_2L)_2{}^{2-}$, $Ca(HL)_2{}^{4-}$ [9].

In the case of calcium-ion-complexing agents acting as retarders of the hydration of Portland cement, it has been argued that effective retardation is caused by surface adsorption of calcium complexes on the hydration products [10,11]. This results in blocked growth sites and slow addition of new ions to the surfaces of the hydration products. Returning to gypsum formation, a similar retarding mechanism is compatible with the observation that addition of organic acids, or their salts, can strongly alter the morphology of the gypsum crystals by binding to specific crystal faces [2].

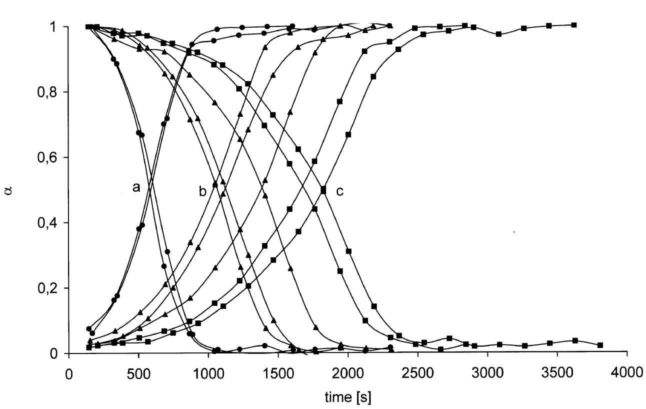

Fig. 3. Experiments with optimised beam intensity and set modifying additives, w/s = 1.00. (a) Two experiments with 0.50 wt.% potassium sulfate and 0.50 wt.% dihydrate seeds. (b) Three experiments with no additives except 0.50 wt.% dihydrate seeds. (c) Two experiments with 0.25 wt.% citric acid monohydrate and 0.50 wt.% dihydrate seeds.

Comparison with our earlier hydration experiments [5] indicates that 0.25 wt.% citric acid has a much stronger retarding effect on unseeded hemihydrate hydration than in experiments including gypsum seeds.

3.3. Rate of dissolution vs. precipitation

When the hydration of calcium sulfate hemihydrate is studied in detail, the most common method for performing the experiments is calorimetry. With the calorimeter, it is mainly the heat of dissolution of calcium sulfate hemihydrate that is measured. When experimental results of this kind are evaluated, it is customary to assume that the rate of growth of calcium sulfate dihydrate is equal to the rate of dissolution of calcium sulfate hemihydrate. When X-ray powder diffraction is used to study the hydration process, it is possible to follow both the dissolution of hemihydrate and the growth of dihydrate, simultaneously. By plotting the relative intensity of dihydrate α(DH) as a function of one minus the relative intensity of hemihydrate, $1-\alpha$(HH), it is possible to check whether the assumption of equal dissolution and growth rate holds. A linear relationship with a slope of unity implies that the assumption is correct. As seen in Fig. 4, the experimental curves are indeed almost straight, having a slope close to unity and a small positive intercept. The positive intercept is explained by the presence of dihydrate seed crystals and the time passing between mixing and starting of the data acquisition.

Preferred orientation of the crystals can sometimes cause problems when measuring X-ray powder diffraction intensities, but the linear relationship in Fig. 4 also demonstrates that this type of effect is absent. Scanning electron micro-

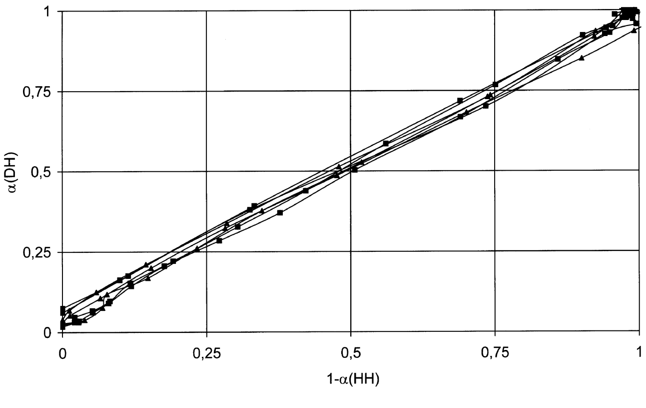

Fig. 4. Plot of α(DH) as a function of $1-\alpha$(HH) for the data in Fig. 3.

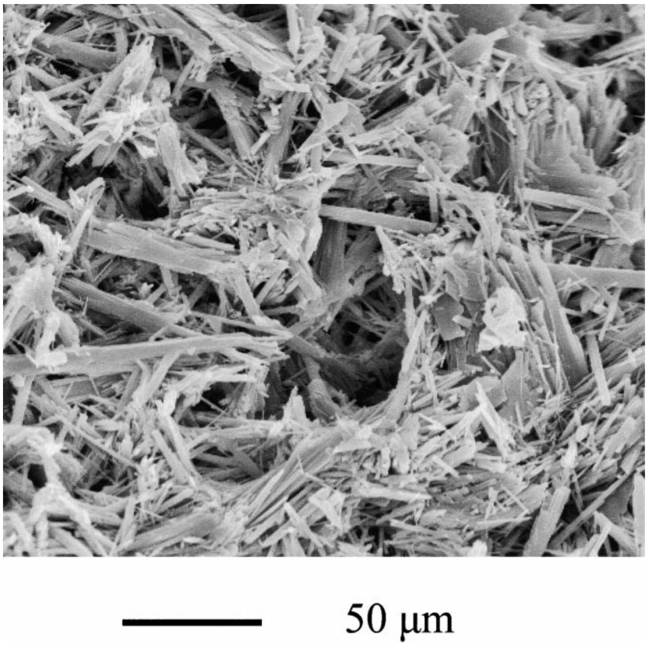

Fig. 5. Secondary electron image of calcium sulfate dihydrate crystals formed in a glass capillary used for the collection of in situ synchrotron X-ray diffraction data (hemihydrate with 0.50 wt.% dihydrate, no additives, w/s = 1.00).

scopy studies of the dihydrate formed in the glass capillaries showed intergrown crystals in random orientations. The dihydrate crystals were usually needle-shaped, with lengths of 20–80 μm (cf. Fig. 5).

3.4. Shape of hydration curve

In order to facilitate the comparison of the hydration curves, the time derivative of α(DH) vs. time is plotted in Fig. 6. The corresponding time-independent transformation curves are shown in Fig. 7. Different fundamental reaction steps can be expected to be rate limiting during each stage of the hydration of hemihydrate [2]. This is supported by the increasing scewness of the curves for the slower reactions in Fig. 6. In the present experiments, which included seed crystals, nucleation can be expected to be facile and it is mainly the stage limited by gypsum growth that is affected by the addition of potassium sulfate or citric acid. The slower reactions exhibit lower maximum reaction rates, as well as lower accelerations of growth (cf. Fig. 6). During the following stage, the deceleration is rather similar in the different experiments, which indicates a similar rate-limiting mechanism for all three types of paste, i.e., the reaction is running out of hemihydrate to dissolve.

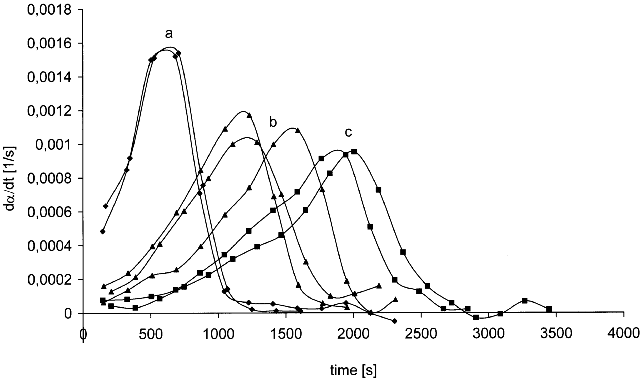

Fig. 6. Plot of dα(DH)/dt as a function of time for the same data as in Fig. 3. (a) Potassium sulfate, (b) no additives, (c) citric acid.

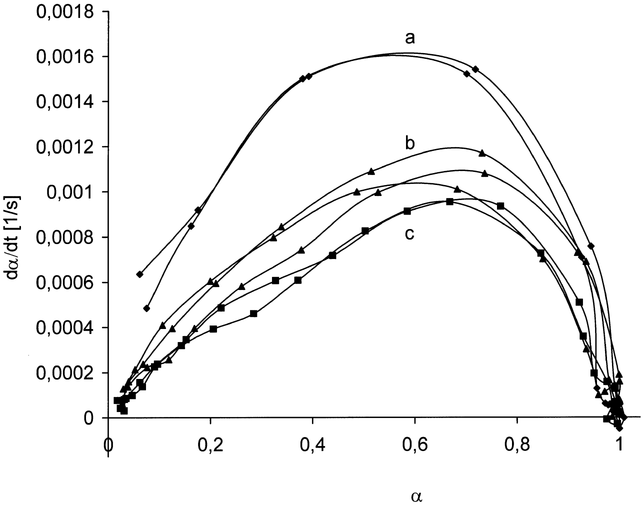

Fig. 7. Plot of dα(DH)/dt as a function of α(DH) for the same data as in Fig. 3. (a) Potassium sulfate, (b) no additives, (c) citric acid.

Some kinetic equations proposed in the literature for the hydration of calcium hemihydrate have been reviewed and evaluated in Ref. [12]. Two of the five equations discussed imply that the maximum reaction rate will occur at a constant value of α. Inspection of Fig. 7 indicates that the quality of the data does not allow any conclusion concerning this issue.

Acknowledgments

Financial support has been received from the Scancem Research and Development Fund and BPB Gypsum, as well as The Swedish Foundation for Strategic Research. The authors would like to thank Göran Svensson for supplying the program *KINETIK för CPS 120*, used in the data collection at MAX-lab, and Åke Oskarsson and Yngve Cerenius for their help in connection with the diffraction experiments.

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