

Hydration Modeling of Calcium Sulphates

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ABSTRACT

The CEMHYD3D model has been extended at the University of Twente in the last ten years [1,2]. At present the cement hydration model is extended for the use of gypsum. Although gypsum was present in the model already, the model was not suitable for high contents of gypsum and did not include the transitions between the different calcium sulphate phases (anhydrite, hemihydrate and gypsum). Besides that gypsum was seen as intermediate phase instead of a final phase. The presented model addresses these problems and has the possibility to simulate the microstructure development of gypsum, including reaction kinetics (dissolution, diffusion and precipitation) and the formation of gypsum needles. The model enables multi-time modelling which means the possibility to zoom in and out on the hydration process with respect to time. Multi-time modelling enables the user to study the hydration in more detail in both the early phase (hours) and on the long term (years). This modelling is needed, since the hydration of calcium sulphates is very short compared to that of cement.

Keywords: *computer simulation, hydration, calcium sulphates, multi-time.*

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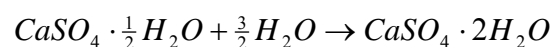
1. INTRODUCTION

In the nineties of last century the CEMHYD3D model has developed at National Institute of Standards and Technology (NIST) in United States. In the last ten years these model has been extended with pore water solution [1] and slag cement chemistry [2]. Recently a project has been started to extent the model with the hydration and fire behaviour of gypsum plasterboards. These plasterboards consist almost completely out of calcium sulphate phases. Although these calcium sulphate phases had been present in the original model, for application of the hydration of gypsum plasterboards the model was not suitable.

Firstly, the amount of calcium sulphates is much more than the amount present in cement hydration. The kinetics for calcium sulphate phases was therefore rather basically modelled, which was not sufficient for the present application. Secondly, the calcium sulphate phases were considered as source for reactions, while now calcium sulphate dihydrate (gypsum) is the final product. Thirdly, more specific properties of calcium sulphates, like needle shape growing and swelling, were not present.

2. THEORY

This section describes the reaction kinetics of the hydration of calcium sulphates. The main reaction is the reaction of calcium sulphate hemihydrate with water to form calcium sulphate dihydrate.



This main reaction consists in several variations. For instance, there are two forms of hemihydrate. The production-method of the hemihydrate is the main difference between both forms. These forms differ in reactivity, crystal shape and strength of the hydration products [3]. The form normally used for the production of gypsum plasterboards is the alpha-hemihydrate.

The model used for the modelling of the hydration is CEMHYD3D. CEMHYD3D is diffusion-based model. Three of the six reaction mechanism mentioned in [4] are used, namely dissolution, diffusion and precipitation.

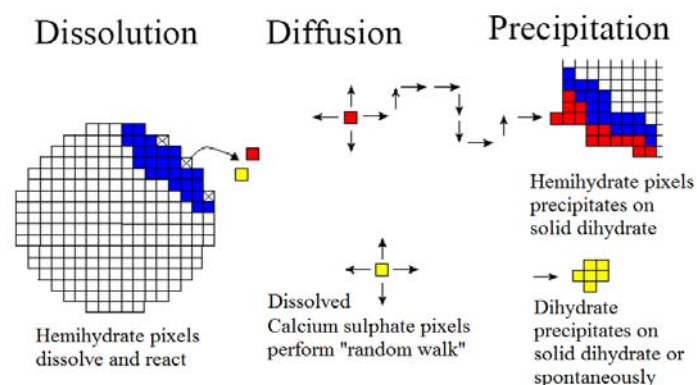


Figure 1: Main reaction mechanism CEMHYD3D (modified from Van Eijk [1])

2.1 Dissolution

Dissolution is the mechanism in which salts break into ions. The amount that will dissolve depends on the dissolution product of the salt (K_s). The amount of solid salt and dissolved salt in a solution is assumed to be in equilibrium. The solution product of alpha-hemihydrate is $10^{-3.73} \text{ mol}^{2.5} \text{ l}^{-2.5}$, while the solution product of gypsum is $10^{-4.52} \text{ mol}^4 \text{ l}^{-4}$. A solution saturated with respect to alpha-hemihydrate is always supersaturated with respect to gypsum. Owing to the supersaturation of gypsum, gypsum will precipitate. The rate of saturation of a solution depends on the concentrations of a salt dissolved in a liquid and the activity of the ions:

$$K_s = a\{\text{Ca}^{2+}\} \cdot a\{\text{SO}_4^{2-}\} \cdot a\{\text{H}_2\text{O}\}^{0.5} = 10^{-3.73} \quad (1)$$

In which K_s is the solution product of hemihydrate.

According to Amathieu and Boistelle [5] the dissolution of hemihydrate is extremely fast and not only results in free Ca^{2+} and SO_4^{2-} ions, but in soluble complexes such as CaOH^+ and HSO_4^- . The concentrations of CaOH^+ and HSO_4^- are negligible in comparison to the concentrations of CaSO_4 , Ca^{2+} and SO_4^{2-} . According to [6], there are more chemicals involved in a Ca- SO_4 -H $_2\text{O}$ system. [6] also includes the ions resulting from the dissolution of NaCl in the system.

The dissolution of hemihydrate is controlled by an interfacial process at low density replaced by a process controlled by volume diffusion at high density [5]. In case of the production of gypsum plasterboards, there is a system with high a density, so the process is volume diffusion controlled [7, 8].

2.2 Diffusion

Diffusion is a spontaneous process, which can be considered as the outcome of a random walk. The mechanism of diffusion is the Brownian motion, whereby a molecule makes a random walk about a central location since by kinetic theory the mean velocity of a pixel is zero when is not subject to any external forces. Due to collisions with neighbouring molecules the motion of the particle is characterized by a mean free path which tends to limit the pixel. But since there is no potential field acting to restore a pixel to its original position, it is free to move through the fluid, in which it is located.

Diffusion is closely related with the second law of thermodynamics, since it increase the entropy and decrease the Gibbs free energy of a mix. These random walks result in the net movement of pixels from an area of high concentration to an area of low concentration in a fluid (either liquid or gas). Therefore the net diffusion is proportional to the concentration gradient and is in the direction of the lowest concentration.

2.3 Precipitation

Precipitation involves many individual steps and kinetic processes [9]. The most important steps are primary nucleation, growth and secondary nucleation. These steps have a certain

overlap. The key variable within the precipitation process is the supersaturation [9]. The degree of supersaturation of gypsum can be calculated with Eq. (2).

$$\beta = \frac{a\{\text{Ca}^{2+}\} \cdot a\{\text{SO}_4^{2-}\} \cdot a\{\text{H}_2\text{O}\}^2}{K_s} \quad (2)$$

A solution saturated with respect to hemihydrate is supersaturated with respect to gypsum. But the condition of supersaturation is not sufficient cause for a system to begin crystallizing [10]. Before crystals can grow a number of minute solid objects must exist. These minute solid objects are called seeds, embryos or nuclei. A stable nuclei is necessary for the growth into crystals of visible size. A stable nuclei is a particle larger than the critical size formed in a supersaturated or supercooled system.

Different forms of nucleation exist [9]. The main difference between primary and secondary nucleation is the presence of any crystal from the chemical that is crystallizing. Two types of primary nucleation exist; homogeneous and heterogeneous. Homogeneous nucleation is the formation of the solid phase when no solid phase exists. At heterogeneous nucleation, only foreign solid phases exist. Secondary nucleation is a mechanism by which formation of the solid phase is initiated by the presence of the solid phase of the crystallizing material itself [9].

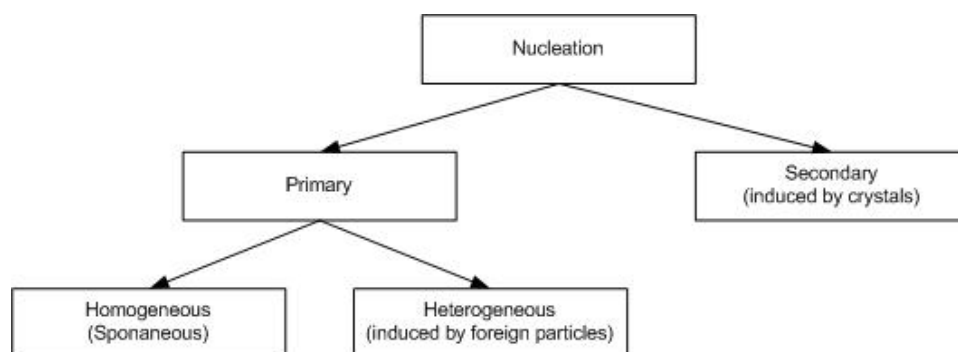


Figure 2: Different forms of nucleation

The hydration of hemihydrate to gypsum can be categorized as heterogeneous and secondary nucleation [5]. The gypsum is formed by heterogeneous nucleation onto hemihydrate particles. But in a later phase of the hydration the gypsum nucleates on the present gypsum particles, which is secondary nucleation. Unfortunately there are no general laws for heterogeneous and secondary nucleation available. Although the secondary nucleation rate will decrease with an increase in the seed size or in the number of seeds of a given size [10].

The crystal growth of gypsum has normally a needle form and can be described by spiral growth theory. This theory is based on a particular mode of dislocation of the crystalline, the screw dislocation. A screw dislocation forms when the atoms are displaced along a dislocation line, rather than at right angles to it as in the case of the edge dislocation. The attachment of growth units to the face of the dislocation results in the development of a spiral growth pattern over the crystal face [10]. This growth looks like it is growing up a spiral staircase'.

Complex spirals often develop, especially when several dislocations grow together. The curvature of the spiral cannot exceed a certain maximum value. This is determined by the critical radius for a two-dimensional nuclei's under conditions of supersaturation in the median in which the crystal is growing [10].

The crystal form of the gypsum crystal depends on the concentration of calcium sulphates present, but also on the presence of for instance citric acids. Plate-like crystals are formed at an initial CaSO₄ concentration of less than 270 mol/m³, while needles are formed at concentrations of more than 400 mol/m³. Citric acids can be used to change the crystal shape and delay the hydration of gypsum [9]. The citric acid can be used for crystal shape engineering.

3. MULTI-TIME MODELLING

In the newest version of CEMHYD3D, it is possible to use the option of multi-time modelling. Multi-time is comparable with multi-scale modelling. The idea behind multi-time is the variation of the length of the time steps in the model. In order to describe this variation, the multi-time factor k is introduced. A lower multi-time factor results in smaller time steps during hydration and therefore resulting in more cycles. This is necessary, because the hydration of gypsum is very fast compared with the hydration of cement. The complete hydration of gypsum takes place within half an hour, while cement takes a few days. Multi-time modelling introduces two major adaptations to the model: the modification of the reaction kinetics and a correction of the calculation of the reaction time.

In the CEMHYD3D model, the diffusion controlled cement hydration process is accounted for the formation of hydration product layers on the particles, which affects the dissolution probability. However this feature is not yet introduced in the model for hemi-hydrate dissolution, the dissolution probability is assumed to be constant for the moment.

Within CEMHYD3D the kinetics are mainly regulated by the dissolution and nucleation chances and the number of diffusion steps. Due to smaller time step at lower k -factor, the number of particles that dissolve, diffuse and nucleate is smaller. Therefore these probabilities need to be smaller. In this Section, the modification of the reaction kinetics are described.

3.1 Dissolution

The modification of the dissolution probability is done by multiplying by the standard dissolution probabilities ($P_{D,1}$) with the correction factor χ .

$$P_{D,k} = P_{D,1} \cdot \chi \quad (3)$$

The factor χ is the correction factor for dissolution, when taking in account conditional probability. Conditional probability is needed, because of interdependence between the cycles. Conditional probability takes in account that a pixel can only dissolve in the second cycle when it had not dissolved in the first cycle. Assume that n particles will dissolve in one complete cycle then in two times a half cycle in multi-time modelling also n particles need to dissolve. So the total chance that a particle dissolves in these two multi-time cycles needs to be equal to one complete normal cycle. Assume that probability in normal cycle is 0.1 then the

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probability in one multi-cycle is not 0.05 since this will result in total probability after two cycles of 0.0975. But the chance needs to be about 0.0513 in order to have 0.1 after two cycles. Hence, the χ depends on the probability. Therefore χ needs to be calculated for each probability separately. For the present derivation, it is convenient to use the probability that a pixel does not dissolve after 1 or $1/k$ cycles, which have to be equal, reading:

$$1 - P_{D,1} = (1 - \chi \cdot P_{D,1})^{\frac{1}{k}} \quad (4)$$

With $P_{D,1}$ is the dissolution probability and k is multi-time factor. This system can be rewritten to extract the factor χ . This factor is needed for the reduction of the chances.

$$\chi = \frac{1 - (1 - P_{D,1})^k}{P_{D,1}} \quad (5)$$

3.2 Diffusion

As described earlier in Section 2, diffusion can be considered as a series of random walks. In the present model 500 random diffusion steps (D_1) are undertaken. After every diffusion step, there is a possibility for nucleation. When it is assumed that a pixel can walk in 1 cycle over a distance x and multi-time modelling will not change the speed of a pixel then in multi-time situation after $1/k$ cycles the same distance x should be travelled. This is only possible when the distance for each multi-time cycle is equal to $k \cdot x$. Therefore the number of diffusion steps (D_k) reads;

$$D_k = k \cdot D_1 \quad (6)$$

3.3 Nucleation

Nucleation is the third reaction mechanism. If $P_{N,1}$ is the nucleation probability for $k=1$ and $P_{N,k}$ is the nucleation probability for 1 cycle in the situation of $1/k$ cycles. Then the probabilities $P_{N,1}$ and $P_{N,2}$ can be described as;

$$P_{N,k} = \omega P_{N,1} \Leftrightarrow \omega = \frac{P_{N,k}}{P_{N,1}} \quad (7)$$

With ω is the factor describing the ratio between $P_{N,1}$ and $P_{N,k}$. Similar to the dissolution chance, also the nucleation chance in multi-time could also be described by conditional probability. Again, it is convenient to use the probabilities that no nucleation has taken place after 1 or $1/k$ cycles;

$$1 - P_{N,1} = (1 - \omega P_{N,1})^{\frac{1}{k}}$$

$$\omega = \frac{1 - (1 - P_{N,1})^k}{P_{N,1}} \quad (8)$$

The nucleation chance is described in the CEMHYD3D-model [1,2] by;

$$P_{N,1} = P_{N,0} \cdot \left(1 - e^{-\frac{i_1}{\max}} \right) \quad (9)$$

With $P_{N,0}$ is basic nucleation chance, i is the number of available diffusing pixels and \max is the maximum number of diffusion pixels. The available diffusing pixels are determined by the dissolution. This number is therefore proportional to the dissolution chance.

$$i_k = P_{D,k} \cdot M \quad (10)$$

With $P_{D,1}$ is dissolution chance and M the available pixels for dissolution.

The dissolution chance differs for different multi-time factor k . We have introduced χ as factor to correct the dissolution probability for multi-time, which will be used again now.

$$\omega = \frac{P_{N,k}}{P_{N,1}} = \frac{P_{N,0} \cdot (1 - e^{-\frac{i_k}{\max}})}{P_{N,0} \cdot (1 - e^{-\frac{i_1}{\max}})} = \frac{(1 - e^{-\frac{i_k}{\max}})}{(1 - e^{-\frac{i_1}{\max}})} = \frac{(1 - e^{-\frac{P_{D,1} \cdot \chi \cdot M}{\max}})}{(1 - e^{-\frac{P_{D,1} \cdot M}{\max}})} = \frac{\left(1 - \left\{ e^{-\frac{P_{D,1} \cdot M}{\max}} \right\}^{\chi} \right)}{\left(1 - e^{-\frac{P_{D,1} \cdot M}{\max}} \right)} \quad (11)$$

So, ω depends on the dissolution chance, the available number of pixels for dissolution, the maximum number of nucleation pixels and the multi-time factor k .

3.4 Time Correction

The second modification is the calculation of the time associated to one cycle. The calculation of the time within CEMHYD3D is based on Knudsen model [2]. The calculation within the Knudsen model is based on maturity approach with parabolic kinetics [11]. The maturity approach is mathematical dispersion model, in which the reaction rate determines the reaction time. The reaction rate (α) is influenced by particle size distribution and chemical composition and has a close related to the shrinking-core model, except that it takes in account the differences in particle sizes. A smaller range of particle sizes will lead to the best results based on the mean particle size (r_0). The time can be described according to following equation;

$$t_0 + t_2 A^2 = t \quad \text{with } A = \frac{\alpha}{1 - \alpha}, \quad t_2 = \frac{r_0^2}{k_2} \quad (12)$$

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With t_0 the induction time, t the reaction time, α the reaction rate, t_2 the time constant, r_0 the mean particle size and k_2 the rate constant from the shrinking-core model. CEMHYD3D calculates the reaction time based on Eq. (14) 2.

$$\text{Time}(t) = \frac{\beta}{\gamma} \cdot \text{cycles}^2 \quad \text{With } \gamma = e^{\frac{E_{\text{act}}}{R} \left(\frac{1}{T_i} - \frac{1}{T_0} \right)} \quad (13)$$

This time-calculation depends on two kinetic parameters (β and γ). The γ is the reaction rate at time t , which depends on the activation energy and the temperature difference between starting temperature (T_0) and actual temperature (T_i).

The multi-time modification influences both the number of cycles and the reaction rate. Since the reaction rate depends on the temperature and the reactions (dissolution and nucleation) in the model direct influence the temperature. No modification is needed here. The number of cycles needs to be modified. The number of old cycles can be calculated from the number of new cycles. The correction consists of two parts. The first part is the correction for the time step. Instead of 1 cycle in the old situation, $1/k$ cycles are made in the new situation. The second correction is a correction for the starting point. Instead of starting with cycle 0, the new situation starts with cycle $2-2k$. So the calculation of cycles is according to the following equation;

$$\text{cycle}_{\text{old}} = \text{cycle}_{\text{new}} \cdot k + (2 - 2k) \quad (14)$$

The time for the multi-time model becomes;

$$\text{Time}(t) = \frac{\beta}{\gamma} \cdot (\text{cycle}_{\text{new}} \cdot k + (2 - 2k))^2 \quad (15)$$

4. MODEL/RESULTS

This section will describe the results of the modelling of the multi-time modelling and results versus experimental results.

4.1 Multi-time Modeling

Based on the modification described in the previous section, an analysis of the use of multi-time is assessed. For the parameters used for these simulations are shown in Table 1 and the particle size distribution is shown in Figure 3. Figure 4 shows the dissolution of calcium sulphate hemihydrate for several multi-time factors k . The simulation for $k = 2$ resulted in only 4 data-points during the first 25 minutes of hydration. This low number of data-points introduces a higher uncertainty, therefore no line is drawn. For $k \leq 1$, the difference between the dissolution lines is very small. The same conclusion is valid for the nucleation of dihydrate from diffusion hemihydrate pixels, as can be seen in Figure 5.

Table 1: Used parameters for simulation [2]

Parameter	Value	Unit
Water/solid factor	1.1	
β	0.0038	Hour/cycle ²
P_D	0.1	
P_N	0.01	
I_{max}	9000	
E_{act}	40	kJ/mol
Initial temperature	20	°C

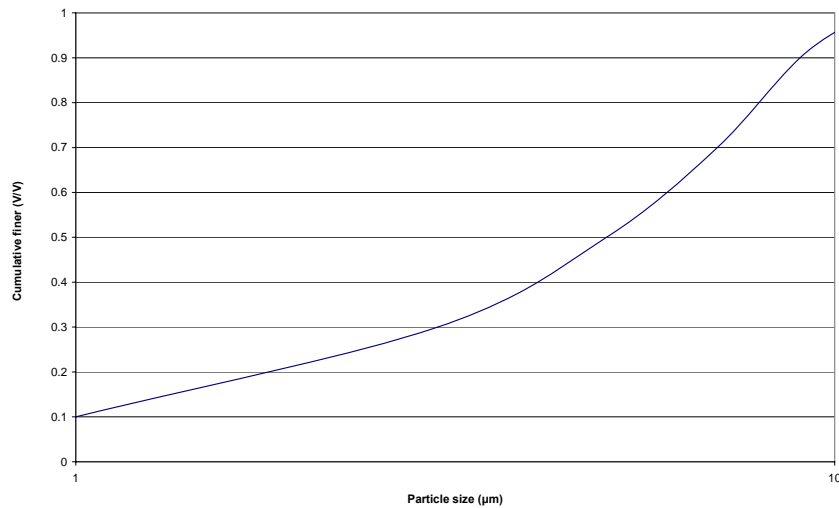


Figure 3: Particle size distribution of the used hemi-hydrate

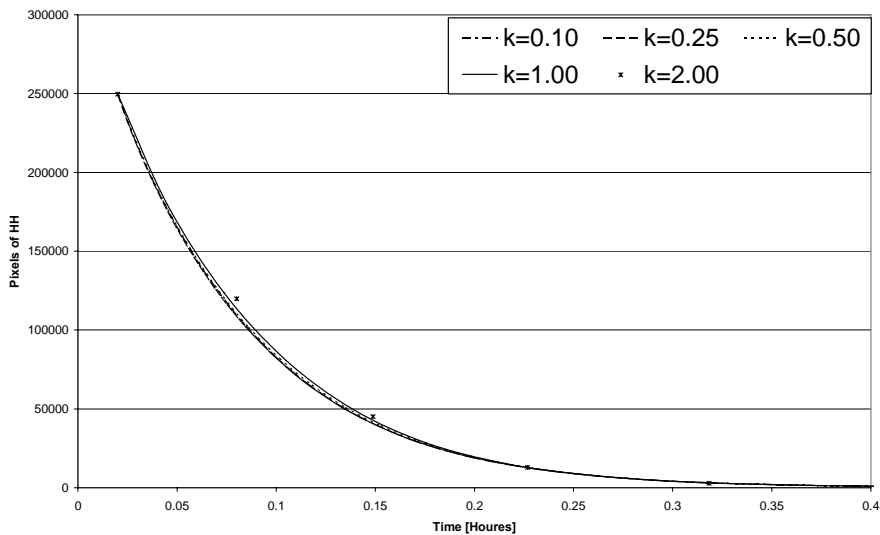


Figure 4: Dissolution of hemihydrate for different multi-time factors

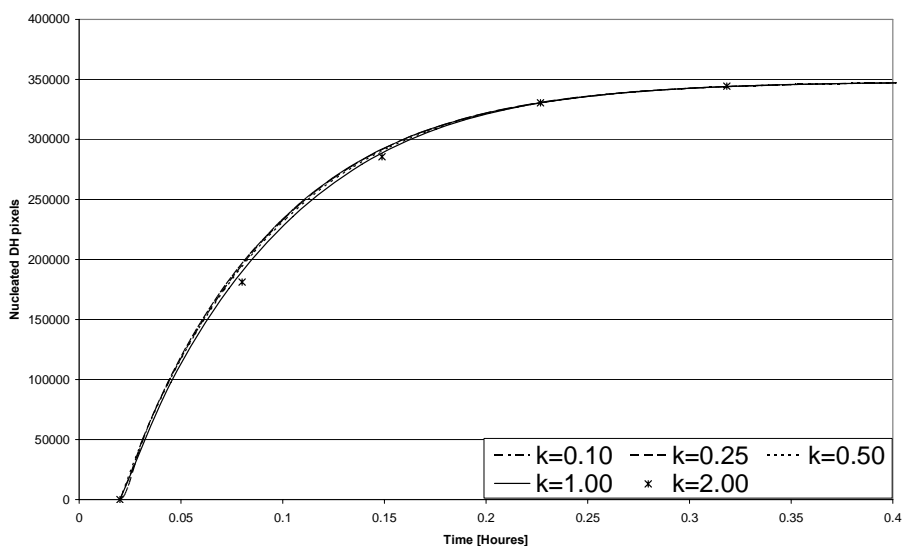


Figure 5: Nucleation of dihydrate for different multi-time factors

The close fit for dissolution and nucleation results in a close fit of the reaction degree for the different multi-time factors (Figure 6).

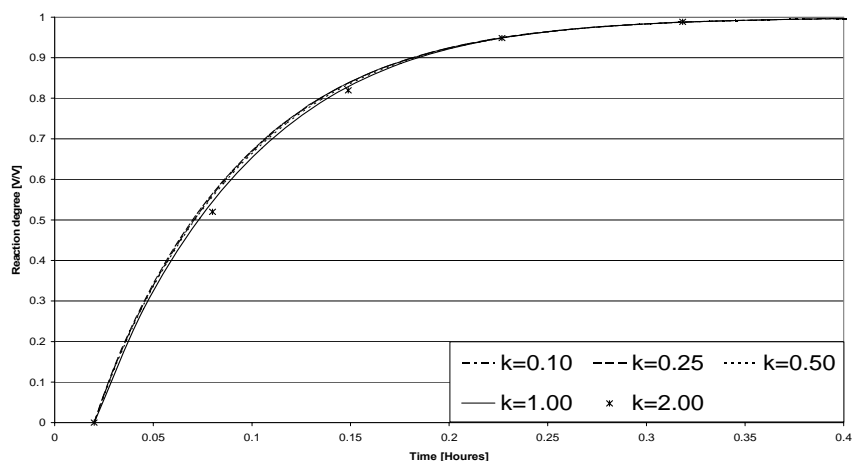


Figure 6: Reaction degree for different multi-time factors

4.2 Simulation

The simulation of the reaction degree is compared with the experimental results of Solberg and Hanssen [12]. For the simulation, the parameter for the simulation are shown in Table 2 and the PSD of hemihydrate is shown in Figure 3.

Table 2: Used parameters for simulation [2]

Parameter	Value	Unit
Water/solid factor	1.0	
β	0.0038	Hour/cycle ²
P_D	0.1	
P_N	0.01	
I_{max}	9000	
E_{act}	40	kJ/mol
Initial temperature	20	°C

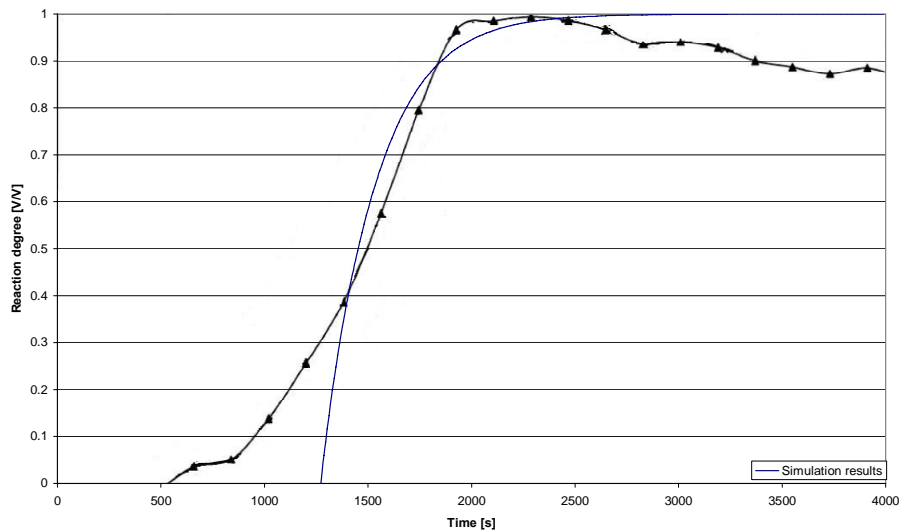


Figure 7: Simulated and real [12] reaction degree

The comparison between experimental data and simulation is shown in Figure 7 with the assumption that the induction time (t_0) was 1200 seconds. From Figure 6 it can be noticed that the slope of the real and simulated curves are comparable, but the smooth start of hydration in the simulation is still missing.

5. CONCLUSIONS

This article first focused on the possibility to perform multi-time modelling, needed for simulating the reaction of calcium sulphates. The results of the multi-time modification show that the hydration curves for different values of multi-time factor are almost the same. Furthermore, the simulated hemihydrate hydration shows a good agreement with the experimental data from literature, although the induction period can still be improved.

Acknowledgements

The authors wish to express their sincere thanks to the European Commission (I-SSB Project, Proposal No. 026661-2) and the following sponsors of the research group: Bouwdienst Rijkswaterstaat, Rokramix, Betoncentrale Twente, Betonmortelcentrale Flevoland, Graniet-Import Benelux, Kijlstra Beton, Struyk Verwo Groep, Hülskens, Insulinde, Dusseldorp Groep, Eerland Recycling, Enci, Provincie Overijssel, Rijkswaterstaat Directie Zeeland, A&G Maasvlakte (chronological order of joining).

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ABBREVIATIONS

Normal

Dk	Number of Diffusionsteps
Eact	Activation energy
ik	Number diffusion of pixels
k	Multi-time factor
max	Scale factor for nucleation
M	Number of pixels available for dissolution probability
PD,k	Dissolution probability for multi-time factor k
PN,k	Nucleation probability for multi-time factor k
t	Reaction time
t0	Induction time

Greek

α	Hydration degree
β	Kinetic parameter for calculation of reaction time
γ	Reaction rate at time t
χ	Correction factor for dissolution probability for multi-time factor k
ω	Correction factor for nucleation probability for multi-time factor k