

## MODELLING AND EXPERIMENTAL STUDY OF HYDRATION FOR ORDINARY PORTLAND CEMENT

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### Abstract

In this paper, the results of experimental study concerning the calorimetric measurements of heat of hydration of cement pastes with different  $w/c$  ratio and different hygral conditions are presented. The model of cement hydration proposed by Parrot and Killoh [1] is implemented in the model of concrete at early ages by Gawin et al. [2], which allows us to carry out simulations of the evolution of hydration degree in different conditions of maturing. The results of the simulations are compared with the experimental data, both obtained by the authors and published elsewhere.

### Streszczenie

W artykule zostały przedstawione wyniki badań kalorymetrycznych ciepła hydratacji dla zaczynów cementowych o różnym stosunku  $w/c$  dojrzewających w różnych warunkach wilgotnościowych. Implementacja opisu procesu hydratacji autorstwa Parrot and Killoh [1] do modelu numerycznego młodego betonu autorstwa Gawina i in. [2] pozwala na przeprowadzenie symulacji ewolucji stopnia hydratacji w różnych warunkach dojrzewania. Wyniki symulacji z użyciem wspomnianego modelu zostały porównane z wynikami badań eksperymentalnych.

Keywords: Early age concrete; Hydration; Numerical modelling of cementitious materials.

## 1. INTRODUCTION

During hydration of cement, a series of coupled thermo-chemo-hygral phenomena takes place in cement-based materials. It is generally agreed, that the conditions in which these phenomena take place have a great influence upon the final properties and performance of the material. Thus, it is especially important to properly predict and account for various phenomena accompanying the hydration process. On the one hand, the hydration process may be analyzed during laboratory tests, most commonly calorimetric measurements, that provide information on the amount of heat released during the process and are widely in use nowadays, both in research and engineering practice. On the other hand, the efforts of the research com-

munity are focused on providing the analytical or numerical models that would enable both the simulations of the hydration process, and further predicting the evolution of material properties.

In modelling of concrete maturing, the concepts of maturity (e.g. [3]), or equivalent time are often in use (e.g. [4]). These approaches meet, however, some serious difficulties, when it comes to modelling a strong non-linear process like hydration, as shown e.g. by Jensen and Hansen [5].

The concept of normalized hydration degree [6] is used in this work as the evolution variable describing the maturing of a cementitious material. Constitutive relationship governing the kinetics of hydration in the form proposed by Parrot and Killoh [1] is implemented in the model of concrete by Gawin et al. [2].

**Table 1.**  
**Mix composition**

	w/c = 0.3	w/c = 0.3 SAP	w/c = 0.25	w/c = 0.25 SAP
w/c basic	0.3	0.3	0.25	0.25
w/c entrained	-	0.05	-	0.045
Cement, g	100	100	100	100
Water, g	30	35	25	29.5
Super-plasticizer, g	0.4	0.4	0.9	0.9
SAP, g	-	0.4	-	0.36

The hydration model is briefly described and its main features are analyzed. The results of the simulations carried out with the applied hydration description are compared with the experimental data, both obtained by the authors and published by Lura [7]. The experimental tests carried out within the framework of this work concern the calorimetric measurements of hydration heat of cement pastes with different w/c ratio and with the application of internal curing method [8]. At the same time, the self-desiccation of the cement pastes was measured in order to determine the influence of RH on the evolution of hydration process.

## 2. EXPERIMENTAL MEASUREMENTS

The experimental work presented in this section was focused on determining the influence of different curing methods on the evolution of hydration process. It is commonly known, that the moisture state of cementitious material has a great impact on the kinetics of cement hydration and final material properties [9].

The hydration process evolution was analyzed by means of calorimetric measurements of hydration heat. The specimens were maturing in sealed or under-water condition, and with or without so-called internal curing [8]. Internal curing was obtained by means of the addition of super-absorbent polymers (SAP) to the mixture. SAP is the material with great absorption potential of water. SAP is added to the mixture along with some extra water, which it adsorbs during mixing, and then provides it during maturing, being uniformly distributed in the volume of material. Internal curing is used in order to prevent self-desiccation process (the drop of internal RH observed in sealed specimens) and to promote hydration process by providing extra water. The internal curing allows obtaining the material of greater strength (e.g. [10])

and more fine inner structure of porosity, and thus lower permeability (e.g. [11]).

Two mixtures with different w/c ratios were used: 0.25 and 0.30, both without and with SAP addition. All specimens were observed both in sealed conditions and under-water.

At the same time, the evolution of internal RH in hydrating pastes (self-desiccation) was determined for sealed mixtures, with and without internal curing.

### 2.1. Materials and Methods

Four types of cement pastes with the mixture proportions presented in Table 1 were investigated. The cement used was Portland cement CEM I 32.5 R produced by Cemex. The calculated Bogue's composition of cement was (by wt%): C<sub>3</sub>S: 57.1, C<sub>2</sub>S: 16.8, C<sub>3</sub>A: 9.1, C<sub>4</sub>AF: 7.9, and the specific surface area was equal to 365 m<sup>2</sup>/kg.

The pastes were mixed in vacuum mixer in order to avoid the influence of entrapped air bubbles.

The evolution of hydration heat was measured with the isothermal calorimeter TAM Air manufactured by Thermometric AB. The measurements were performed at constant temperature of 20°C. The mass of cement paste specimens was equal to a couple of grams.

The autogenous RH change was measured with the Rotronic hygrometer. The temperature in the measuring set was maintained during the measurements on the level equal to approximately 20°C.

### 2.2. Results and discussion

As can be seen in Fig. 1, the presence of water layer on the surface of hydrating specimen leads to a visibly higher heat of hydration released. On the contrary, when the RH in the pores of cement paste

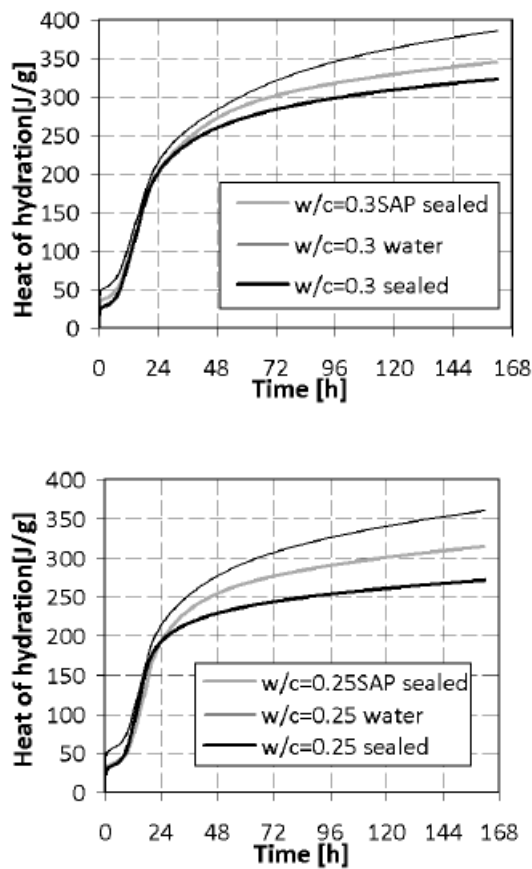


Figure 1. The heat of hydration compared for mixtures without and with SAP addition (“sealed”) and with water layer on top of specimen without internal curing (“water”)

decreases down to approximately 88-90% (see Fig. 2), the hydration kinetics is visibly decelerated. The influence of internal RH upon the decrease of rate of heat release starts to be pronounceable when the microstructure of cement paste is already formed, i.e. during the deceleration stage, and the access of cement to water-filled space controls the rate of the reaction (during the deceleration stage the kinetics is controlled mainly by diffusion process, and the hydration products may form only in water-filled spaces [12]).

In Fig. 1 also the influence of SAP addition on the hydration process is presented and compared to the influence of under-water curing, when no internal curing is provided. Maintaining full saturation by means of covering the material with water layer seems to be more efficient way of curing in this case. This is, however, due to very small dimensions of specimens (couple of grams). In real structures, covering with water will provide curing only for the

material within a layer very close to the surface, while addition of SAP will let maintain higher saturation and thus faster hydration uniformly in the whole volume of material. The effect of availability of “normal” mixing water (i.e. not the water absorbed by SAP), increasing with w/c ratio is also well visible, especially for sealed specimens (compare the curves for w/c = 0.23 and w/c = 0.3 in Fig. 1).

The results of the autogenous RH drop measurements are presented in Fig. 2. In case of SAP addition, the results were close to 100%RH (and even exceeding it). Due to this fact, the result may be considered erroneous for these pastes (the testing device usually meets some problems when measuring such high levels of RH, mainly due to the condensation on the sensor). Nevertheless, all the results are presented in Fig. 2. The RH curve for the paste w/c = 0.3SAP reaches the constant value of 99.8% and for paste the w/c = 0.25SAP the result should not be considered as a real value, since it is greater than 100%, thus obviously false. Hence, the result of self-desiccation measurement for this paste may be only found as an indicator of the trend. It is obvious based on these measurements, that self-desiccation may be retarded or even completely ceased due to internal curing application.

This explains the accelerated hydration evolution and greater heat release in the process visible in Fig.1 for SAP mixtures with respect to the “plain” mixtures.

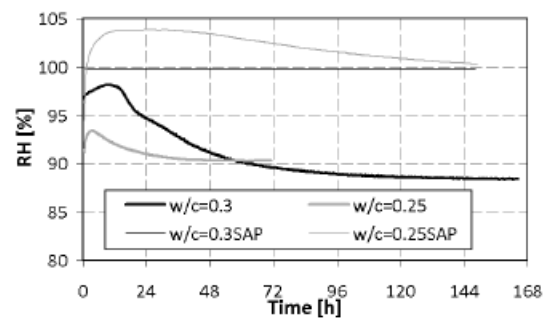


Figure 2. Autogenous RH evolution in the cement pastes. The curve for the cement paste w/c = 0.25 SAP is only for illustration, the correct value is probably close, but smaller than 100%

### 3. MODELLING THE CEMENT HYDRATION PROCESS

#### 3.1. Description of the model

In the structural modelling of concrete maturing, the concept of hydration degree is often used, e.g. [2, 6], as the evolution variable, governing the development of material properties, e.g. strength or porosity. In this work, the hygro-thermo-mechanical model of maturing concrete by Gawin et al. [2] was used, modified by implementing the description of hydration proposed by Parrot and Killoh [1].

The hydration degree  $\alpha_{hydr}$  may be defined as:

$$\alpha_{hydr} = \frac{m_{c,hydr}}{m_c} = \frac{m_{hydr}}{m_{hydr\infty}} \quad (1)$$

describing the ratio of mass of hydrated cement  $m_{c,hydr}$ , to the initial content of cement  $m_c$ , or the ratio of mass of non-evaporable water  $m_{hydr}$  to its mass at full hydration  $m_{hydr\infty}$ . In general, hydration degree is the variable quantitatively describing the progress of chemical reactions involved in cement hydration.

Dependent upon the purpose of modelling, this can be the overall degree of hydration  $\alpha_{hydr}$  of cement, where hydration is treated as a sum of reactions, or the degree of hydration of single cement constituent (defined analogically, as the ratio of mineral reacted to its initial content) modelled separately for each constituent. By definition, these quantities can be bound by means of weighted averaging (e.g. [1]):

$$\alpha_{hydr} = f_{C3S}\alpha_{C3S} + f_{C2S}\alpha_{C2S} + f_{C3A}\alpha_{C3A} + f_{C4AF}\alpha_{C4AF} \quad (2)$$

where  $f_x$  is the relative mass fraction of individual cement compound  $x$  ( $x = C_3S, C_2S, C_3A, C_4AF$ ) determined e.g. based on Bogue's formulas or quantitative analysis,  $\alpha_x$  is the degree of hydration of individual compound  $x$ . If the overall hydration degree concept e.g. [6] is used, the hydration is considered in a general manner as a reaction of cement with water instead of several reactions of its individual components.

If the hydration degree is used as a variable for modelling the evolution of material properties, it is convenient to apply the concept of normalized hydration degree  $\Gamma_{hydr}$ , [2]:

$$\Gamma_{hydr} = \frac{\alpha_{hydr}}{\alpha_{max}} \quad (3)$$

where  $\alpha_{max}$  is the final degree of hydration for the given concrete (or paste) mixture. This accounts for the fact, that in realistic conditions, the hydration degree  $\alpha_{max}$  is always smaller than one (i.e. not all of the cement is able to react). Thus, normalized hydration degree takes values from 0 to 1 at the end of the process in the mixture considered.

In the presented work, the model of hydration by Parrot and Killoh [1] is used, in which the hydration of four main clinker compounds (i.e.  $C_3S, C_2S, C_3A, C_4AF$ ) is described independently, and the overall hydration degree is calculated as the weighted average with equation (2).

In the model of concrete used, the estimation of the ultimate hydration degree is of importance, since normalized hydration degree is used as an internal variable of the model, eq. (3). To predict the ultimate degree of hydration, the empirical formula by Mills [13] is often used, e.g. [2, 4]. However, this kind of approach does not account for the composition of cement, which may be of key importance. In order to overcome these limitations, in this work the ultimate hydration degree is calculated *a priori*, to serve then for normalization according to equation (3). For that purpose, it is necessary to assume no influence of RH and isothermal conditions at the reference temperature of 20°C. In experimental work by Mills [13], the hydration was assumed to be completed at the age of 450 days. As shown by our simulations this period may seem to be too short. Thus, in the presented model, it is assumed that the ultimate degree of hydration is reached at the age of 1000 days. In Fig. 3, the dependence of the ultimate hydration degree for individual compounds of cement and for the cement upon the mixture composition ( $w/c$  ratio) is presented.

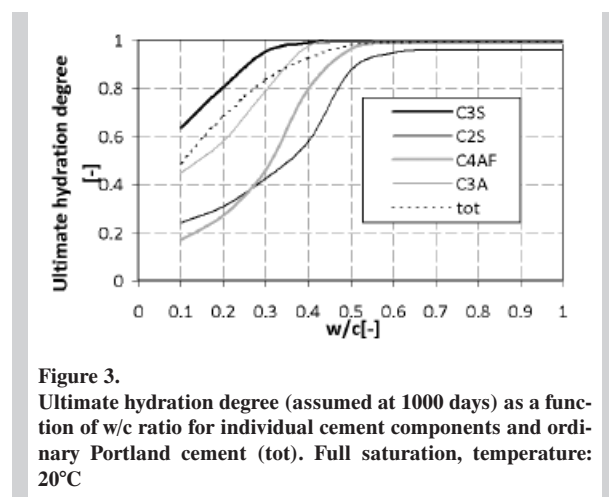


Figure 3. Ultimate hydration degree (assumed at 1000 days) as a function of  $w/c$  ratio for individual cement components and ordinary Portland cement (tot). Full saturation, temperature: 20°C

The kinetics of hydration process is strongly dependent upon the w/c ratio [13]. At later stages of hydration, the lack of larger pores available for hydration products to form leads to the cease of the process. Parrot and Killoh [1] related the point when lack of pores leads to the decrease of hydration rate with the w/c ratio by means of equation (10). According to this assumption, the effect of lack of pores is significant for mixtures with w/c < 0.65 (based on parameters determined by Lothenbach et al. [14]).

Parrot and Killoh [1] derived (based on quantitative X-Ray measurements) empirical expressions which describe the rate of hydration of a single clinker compound x as the minimum among the rates of the following processes:

*Nucleation and growth*

$$\dot{\alpha}_{1x} = \frac{K_{1x}}{N_{1x}}(1 - \alpha_x)(-\ln(1 - \alpha_x))^{(1-N_{1x})} \quad (4)$$

*Diffusion*

$$\dot{\alpha}_{2x} = \frac{K_{2x}(1 - \alpha_x)^{2/3}}{1 - (1 - \alpha_x)^{1/3}} \quad (5)$$

*Shell formation*

$$\dot{\alpha}_{3x} = K_{3x}(1 - \alpha_x)^{K_{3x}} \quad (6)$$

where the empirical parameters  $K_{ix}$  and  $N_{ix}$  are based on the work by Lothenbach et al. [14]. The final rate of hydration degree for a single clinker constituent x is calculated as [1]:

$$\dot{\alpha}_x = \min(\dot{\alpha}_{x1}, \dot{\alpha}_{x2}, \dot{\alpha}_{x3}) \cdot f_{w/c} \cdot \beta_{RH} \cdot \frac{A}{A_0} \exp\left(\frac{E_a}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right) \quad (7)$$

where  $A$  and  $A_0$  are the actual and reference surface area of cement, respectively, with the latter being 385 m<sup>2</sup>/kg,  $T$  is the absolute temperature,  $T_0$  is the reference temperature equal to 293.15K,  $\beta_{RH}$  is the empirical parameter taking into account the influence of relative humidity [1]:

$$\beta_{RH} = \left(\frac{\varphi - 0.55}{0.45}\right)^4 \quad (8)$$

Optionally, the relation proposed by Bazant and Najjar [15] may be used:

$$\beta_{RH} = (1 + (7.5 - 7.5\varphi)^4)^{-1} \quad (9)$$

Function  $f_{w/c}$  takes the influence of w/c ratio on the rate of hydration into account, according to the equation [1]:

$$f_{w/c} = (1 + 3.333(H_x \cdot w/c - \alpha_x))^4, \quad \text{if } \alpha_{hydr} \geq H_x \cdot w/c$$

$$f_{w/c} = 1, \quad \text{if } \alpha_{hydr} < H_x \cdot w/c \quad (10)$$

where  $H_x$  is the empirical constant. It should be underlined, that the influence of w/c on the hydration rate starts to be taken into account for each clinker constituent separately when certain level of the overall hydration degree  $\alpha_{hydr}$  is reached, which refers to the time instant, when the free space for hydration products to form is limited enough to decelerate the rate of the process.

The overall rate of cement hydration is calculated by means of weighted averaging, similarly as in equation (2):

$$\dot{\alpha}_{hydr} = f_{C3S}\dot{\alpha}_{C3S} + f_{C2S}\dot{\alpha}_{C2S} + f_{C3A}\dot{\alpha}_{C3A} + f_{C4AF}\dot{\alpha}_{C4AF} \quad (11)$$

In Fig. 4 the hydration degree evolutions and their rates are presented for individual cement compounds. The curves have been obtained by means of the Parrot and Killoh model [1], assuming full access to water (RH equal to 100% and no influence of w/c ratio) and isothermal conditions ( $T = 20^\circ\text{C}$ ).

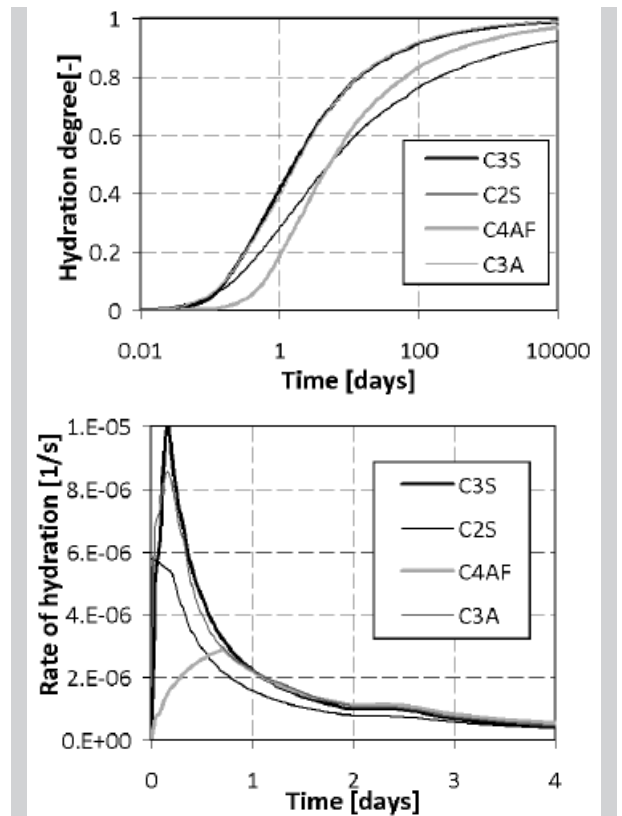


Figure 4. Hydration degree (up) and hydration rate (down) of individual cement components at full saturation, temperature: 20°C, w/c = 1.0



Hydration of cement is a strongly exothermic reaction. At the same time, as hydration proceeds, water is being chemically combined. In the presented model, these phenomena are considered as heat source and mass of water sink (negative source) terms, respectively. They enter the governing equations of the model written for mass and enthalpy conservation (for full description of the model equations see [2]) in the following form:

$$\frac{\partial Q_{hydr}}{\partial t} = f_{C3S} \frac{\partial \alpha_{C3S}}{\partial t} Q_{C3S} + f_{C2S} \frac{\partial \alpha_{C2S}}{\partial t} Q_{C2S} + f_{C3A} \frac{\partial \alpha_{C3A}}{\partial t} Q_{C3A} + f_{C4AF} \frac{\partial \alpha_{C4AF}}{\partial t} Q_{C4AF} \quad (12)$$

$$\frac{\partial m_{hydr}}{\partial t} = f_{C3S} \frac{\partial \alpha_{C3S}}{\partial t} m_{C3S} + f_{C2S} \frac{\partial \alpha_{C2S}}{\partial t} m_{C2S} + f_{C3A} \frac{\partial \alpha_{C3A}}{\partial t} m_{C3A} + f_{C4AF} \frac{\partial \alpha_{C4AF}}{\partial t} m_{C4AF} \quad (13)$$

where  $Q_x$  and  $m_x$  are the heat of hydration and mass of non-evaporable water of individual component, respectively. The relationships presented in equations (12) and (13) may be considered as describing the driving forces for self-heating and self-desiccation, respectively.

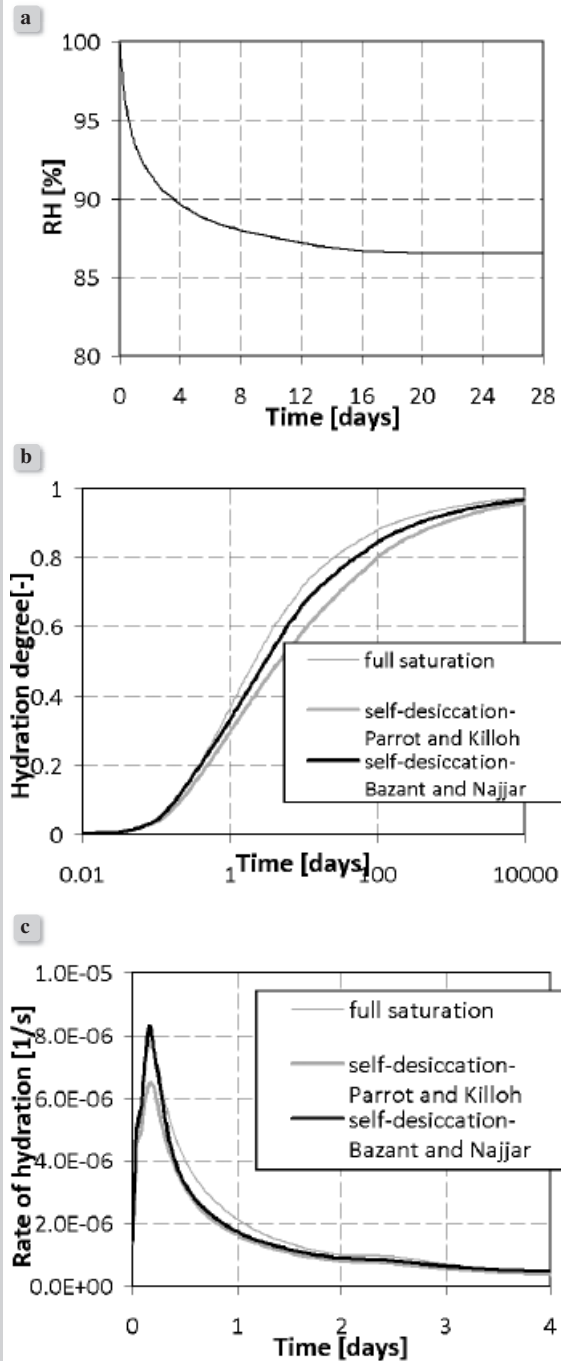
The assumed values of hydration heat and non-evaporable water contents for individual cement components are presented in Table 2.

**Table 2.**  
Hydration heat of cement compounds

Cement compound	C <sub>3</sub> S	C <sub>2</sub> S	C <sub>4</sub> AF	C <sub>3</sub> A
Q, J/g [12]	500	250	420	1340
m <sub>x</sub> , g/g [1]	0.235	0.20	0.25	0.55

As water is being consumed by the hydrating cement, and menisci form in the pores, the autogenous RH drop is observed [16], Fig. 2. In Fig. 5 the influence of this phenomenon on the hydration process is presented. The RH-drop down to 86.5% RH was assumed at full hydration, Fig. 5.

It should be noted, that due to self-desiccation, considerable retardation of the hydration process occurs (see also discussion on experimental observations, section 2.2). At the age of 28 days, the hydration degree reached is smaller with respect to the specimen where full saturation was maintained, by about 15% and 7% based on the formula by Parrot and Killoh [1] and Bazant and Najjar [15], respectively (and similar trend should thus occur for strength of the material).



**Figure 5.** Autogenous RH drop (down to 86.5% RH) (a), hydration degree (b), hydration rate (c) compared for the influence of RH-drop according to Parrot and Killoh [1] or Bazant and Najjar [15] and for full saturation (100% RH). Temperature: 20°C, w/c = 1.0

3.2. Experimental validation

3.2.1. Hydration in isothermal conditions at full saturation

The validation of the hydration model presented in this section concerns the material hydrating at constant temperature (isothermal conditions,  $T = 20^{\circ}\text{C}$ ) and fully saturated with water. In this way, the influence of heat release (i.e. self-heating) and RH-drop (self-desiccation) can be “subtracted” from the analysis.

The validation is based on the experimental work presented in section 2 of this paper. Only the mixtures without SAP addition were used, since the influence of SAP addition on the hydration process is not visible if full saturation is maintained. The initial hydration degree of each constituent of cement was assumed to be equal to 0.05 in all simulations. The comparison of simulation and experimental results,

concerning the rate of heat evolution and the heat released is presented in Fig. 6. As can be seen, the discrepancy between the simulations and experiment is especially visible during the deceleration stage of hydration. This involves further calibration of the empirical parameters in future. However, the agreement can be found as satisfactory for engineering purposes.

3.2.2. Hydration in isothermal conditions with auto-genous RH drop

The simulations of the heat evolution in Portland cement pastes maturing in sealed conditions (i.e. taking the RH-drop due to self-desiccation into account) have been compared to experimental data presented in section 2 of this paper and to experimental data by Lura [7].

First set of simulation concerns two types of Portland cement pastes:  $w/c = 0.30$  and  $w/c = 0.25$  (see section 2.1). The initial hydration degree of each phase constituent was assumed to be equal to 0.05 in all simulations. Having the parameters governing the evolution of RH (see [2]) agreed with the experimental observations presented in Fig. 2, it was possible to carry out the simulations of hydration process with RH influence taken into account. The results of the simulations are presented in Fig. 7. Although the simulations were carried out with the Parrot and Killoh model [1], two methods of taking the influence of RH into account were analyzed, i.e. according to equations (8) and (9). The simulations for mixtures with SAP have not been carried out, since the RH drop was not properly measured for this type of mixtures.

The results of simulations are in sufficient agreement with the experimental observations, only if the dependence of hydration rate upon RH is assumed after [15].

Lura [7] carried out the calorimetric measurements of hydration of moisture-sealed Portland cement pastes at different (constant) temperatures:  $20^{\circ}\text{C}$ ,  $30^{\circ}\text{C}$  and  $40^{\circ}\text{C}$ . Simultaneously, the RH drop was observed on the companion specimens in the temperature of  $20^{\circ}\text{C}$ . The  $w/c$  ratio was equal to 0.37. The ordinary Portland cement was used for the pastes. The composition of cement was (by %wt):  $\text{C}_3\text{S}$ : 53.6,  $\text{C}_2\text{S}$ : 20.1,  $\text{C}_4\text{AF}$ : 9.1,  $\text{C}_3\text{A}$ : 8.2, and the surface area was equal to  $530\text{m}^2/\text{kg}$ .

Similarly as in the previous example, the parameters of the model governing the sorption isotherms (see [2]) have been determined in order to fit to the RH experimental curve for  $20^{\circ}\text{C}$  (for other temperatures

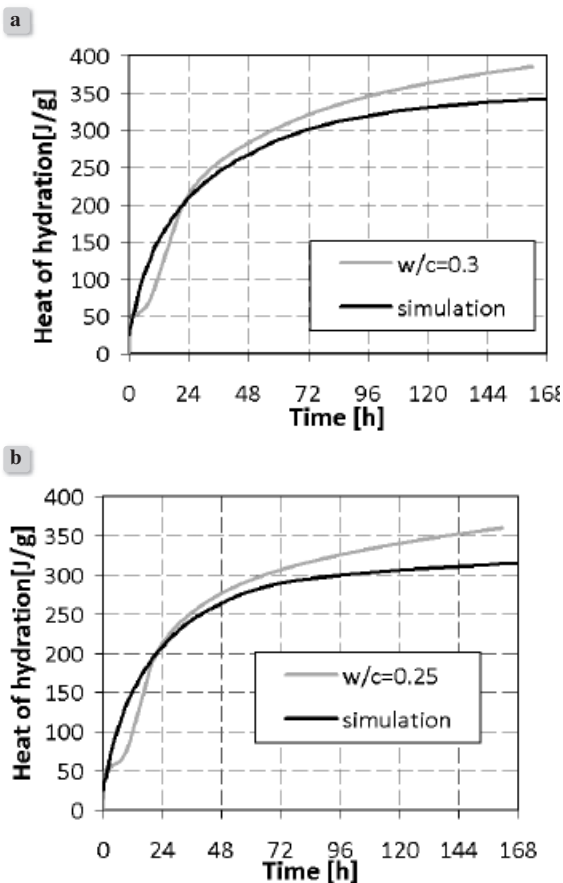


Figure 6. Comparison of the simulation and experimental (dashed line) results concerning heat of hydration for  $w/c = 0.3$  (a) and  $w/c = 0.25$  (b) cement pastes. The experimental results are presented also in section 2. Full saturation, temperature:  $20^{\circ}$

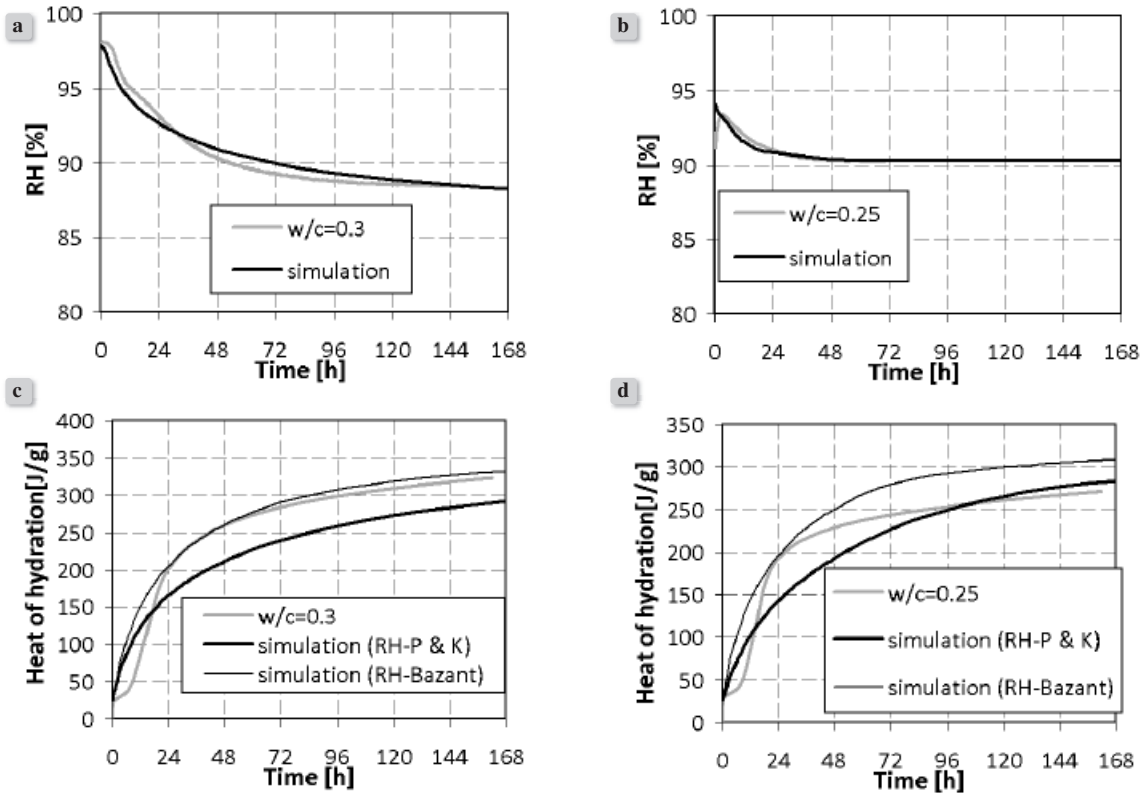


Figure 7. Comparison of the simulation and experimental results (gray line) concerning self-desiccation (top graphs) and heat of hydration (bottom graphs) for  $w/c = 0.3$  (left) and  $w/c = 0.25$  (right) cement pastes. The simulations carried out for two models of RH influence (P&K refers to eq. (8), Bazant refers to eq. (9)). Temperature: 20°

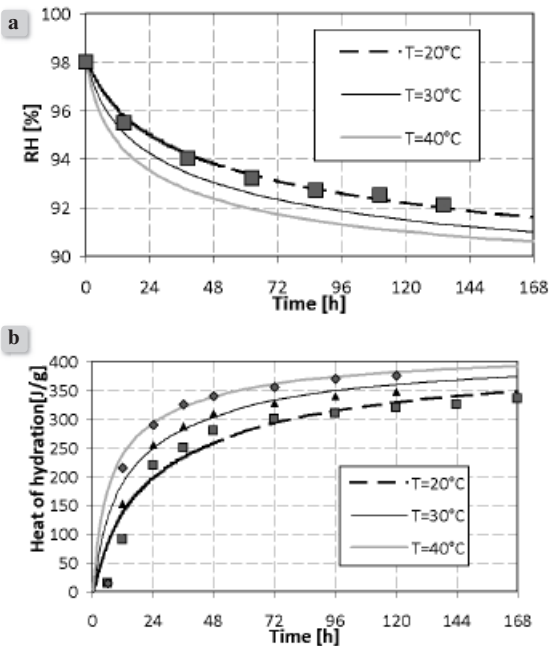


Figure 8. Comparison of the simulation and experimental results by Lura [7] concerning self-desiccation (top) and heat of hydration (bottom) for different temperatures

the RH evolution was not measured, thus comparison in Fig. 8 concerns only the 20°C curve). The initial hydration degree of each phase constituent was assumed to be equal to 0.05 in all simulations. The results of the simulations are compared against the experimental results in Fig. 8. In these simulations, the formula describing the dependence of hydration rate upon RH was assumed after [15], eq. (9), since this description gives the results in better agreement with the experiment.

As can be seen in Fig. 8, the results of the simulations are in a very good agreement with the experimental data. It is suggested, that the hydration of cement in sealed conditions (i.e. with self-desiccation) can be predicted with high accuracy, if the model by Parrot and Killoh [1] is slightly modified as far as the description of RH influence on the hydration process is concerned.



## 4. CONCLUSIONS

The experimental observations of cement hydration carried out by means of the calorimetric measurements have been presented. The attention has been paid to the influence of the curing conditions and moisture state on the kinetics and final values of the released heat of hydration.

Used description of hydration [1], implemented in the mathematical and numerical model of maturing concrete by Gawin et al. [2] let one simulate the evolution of hydration, taking into account the parameters of cement (its composition and surface area), as well as the influence of temperature,  $w/c$  ratio and relative humidity. Thanks to such an approach it is possible to use the model as a “predicting tool”. Even if the accuracy of the provisions may be limited in some cases, it is satisfying for engineering purposes, especially for applications when no experimental data on the mixture is provided. The validation of the model against experimental data shows, that a good agreement with the experiments can be achieved, however, some further calibrations of the model parameters seem to be necessary.

It is suggested by the authors, that the description of the RH influence on the hydration process, originally proposed by Parrot and Killoh [1], does not provide a sufficient accuracy. On the contrary, the modification of this description after Bazant and Najjar [15] let one obtain a good agreement of simulations with the experimental results.

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