

## HYDRATION RATE EQUATION FOR CEMENTS

by

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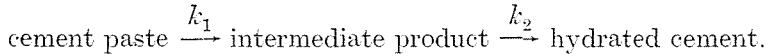
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Since long, there have been attempts to develop a formula, for the use of concrete designers, helping to predict the concrete strength, the heat generation during setting and hardening, or the degree of hydration. Some researchers [1,2,3,4,5] give empirical formulae based on own experiments, while others [6,7,8,9] deduce equations either from molecular setting processes or from general laws of diffusion rate. Without discussing in detail either precedent theories or the rate equation deduced recently by F. TAMÁS [10], let us notice that in theoretical studies the cement hydration process has either been treated as a single-stage reaction or as if cement setting would involve no other process than diffusion. And even if test results demonstrate two constants of hydration rates of Portland cement to exist, hydration stages are assumed to be independent [8].

It is generally known that the cement hydration is a rather complex process, not yet cleared to date [11,12,13,14,15]. The Powers structural model has been adopted world-wide, based on the assumption that the hardened cement paste is a solidified porous material of two components i.e. gel and crystalline phases. It is known, however, that tobermorite gel composition is far from being constant throughout the hydration. In fact, it changes. In the initial stage of hydration, most of the lamellae are of the thickness of an elementary layer, while in completely or almost completely hydrated cements the mean lamella thickness equals 2 or 3 elementary layer thicknesses. Thus, in fact, hydration of cement cannot be reasonably considered a simple diffusion-dependent process. Namely, crystal undergoing hydration and surrounding gel film are separated by a half ordered interface. If the prevailing osmotic pressure was not to be sustained by a process reducing somehow the supersaturation of the solution outside the gel film e.g. by nucleus formation or crystal growth, the diffusion would cease. In addition to the diffusion-dependent process, another process has to be assumed.

Thus, from the considerations above it can be stated that an expression

including a single transformation rate constant cannot describe perfectly the hydration process from the initial stage to completion. It seems to be justified to assume that the cement paste obtained by mixing cement and water passes through an intermediate state to reach the final state of hydration, just as usual for combined two-stage consecutive reactions:



Arrows indicate the direction of the reactions while  $k_1$  and  $k_2$  are the respective constants. Quantity of the hydration product as a function of time can be described by the well-known chemical equation [16]:

$$m = m_0 \left[ 1 - \frac{k_2 e^{-k_1 t} - k_1 e^{-k_2 t}}{k_2 - k_1} \right] \quad (1)$$

where  $m_0$  signifies the mass of the initial cement paste in case of a complete hydration, and that of the hydration product for time  $t = \infty$  in case of partial hydration.

There is no direct method to determine the quantity of hydrated cement, at most the reduction of non-hydrated components can be determined by X-ray diffraction. There is, however, some possibility, namely to examine the change of properties due to hydration, e.g. the development of compressive strength, or to determine hydration heat generation in function of time. The quantity of heat depends on the mass of hydrated material. If this assumption was correct, both strength development and heat generation ought to be described by an equation similar in form to Eq. (1):

$$A = A_0 \left[ 1 - \frac{k_2 e^{-k_1 t} - k_1 e^{-k_2 t}}{k_2 - k_1} \right]. \quad (2)$$

In these formulae  $A$  and  $A_0$  are compressive strengths at time  $t$  and after complete hydration, respectively, in the former case, and the respective heat generation in the latter case. Nevertheless, hardening and heat generation involve different  $k_1$  and  $k_2$  values each.

If it can be experimentally proved that these quantities vary according to Eq. (2) then this latter can be reasonably considered the hydration rate formula.

### Test measurements

Compressive strength has been tested on hardening cement paste cubes with 3 cm sides, made with a  $w/c$  ratio of 0,28, testing 4 cubes each at 12 different ages ranging from 6 hours to 7 days.

Chemical reaction rates being temperature-dependent, the hydration heat

measurements were to be made in isothermal conditions. These conditions could be considered to be met with calorimetric measurements where temperature rise did not exceed 2 to 4°C.

Testing apparatus is shown schematically in Fig. 1. Its essential part is a thermos with a closely fitting thermal insulating cork. The insulator supports a metal recipient, plastic coated outside, where the mortar can be filled in. Centrally in the sample there is embedded a 100 $\Omega$  nickel resistance thermo-

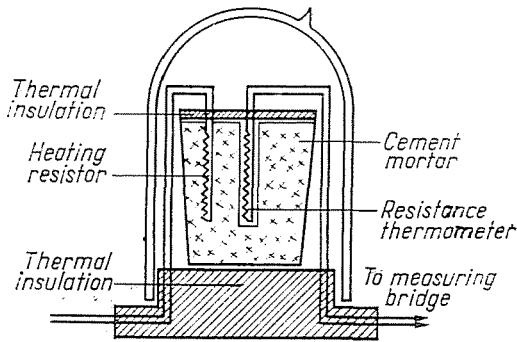


Fig. 1

meter, while about 200  $\Omega$  of heating resistance are evenly distributed at 6 spots. After having assembled the apparatus, the thermos was placed in a thermostat maintaining the temperature constant at an accuracy of  $\pm 0,1^\circ\text{C}$ . The nickel resistor was connected into a bridge circuit, potential differences due to changing temperature were recorded by a compensograph.

Test mortar was made of 1200 g normal sand, and 200 g cement, with a  $w/c$  ratio of 0,30, mixed for 3 minutes and mould, embedding of course thermometer and heating resistors. Mortar recipient was covered by a special plastic lid.

The calculation of the quantity of evolved heat required to determine the heat capacity of the calorimeter and the heat loss.

To this aim, after the mortar has set, and the specimen has cooled down, it was re-heated by means of the embedded heating resistors. From the power input and temperature rise, the heat capacity could be calculated. Again, recording the cooling down data of the calorimeter yielded the heat losses during measurements to be taken into account.

### Measurement results

Full line in Figure 2 shows the compressive strength diagram of Portland cement with a mineral composition of 45,0%  $C_3S$ , 24,5%  $C_2S$ , 12,9%  $C_3A$ , 7,1%  $C_4AF^*$ , indicating also strength and heat values calculated by Eq. (2) and by formula  $A = A_0(1 - e^{-k_1t})$ , respectively.

Fig. 3 shows calorimetry data of specimens made with cement grade *VDC 300*

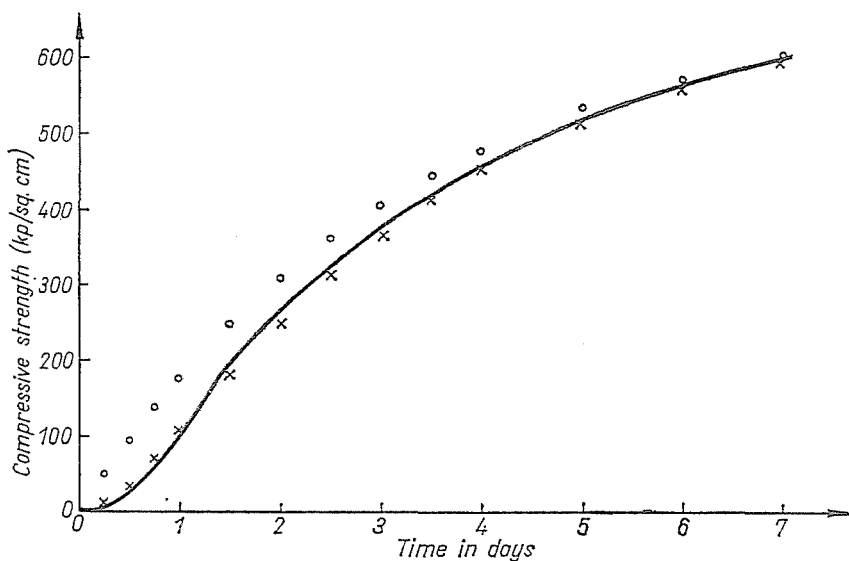


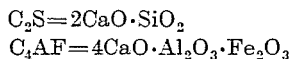
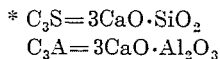
Fig. 2

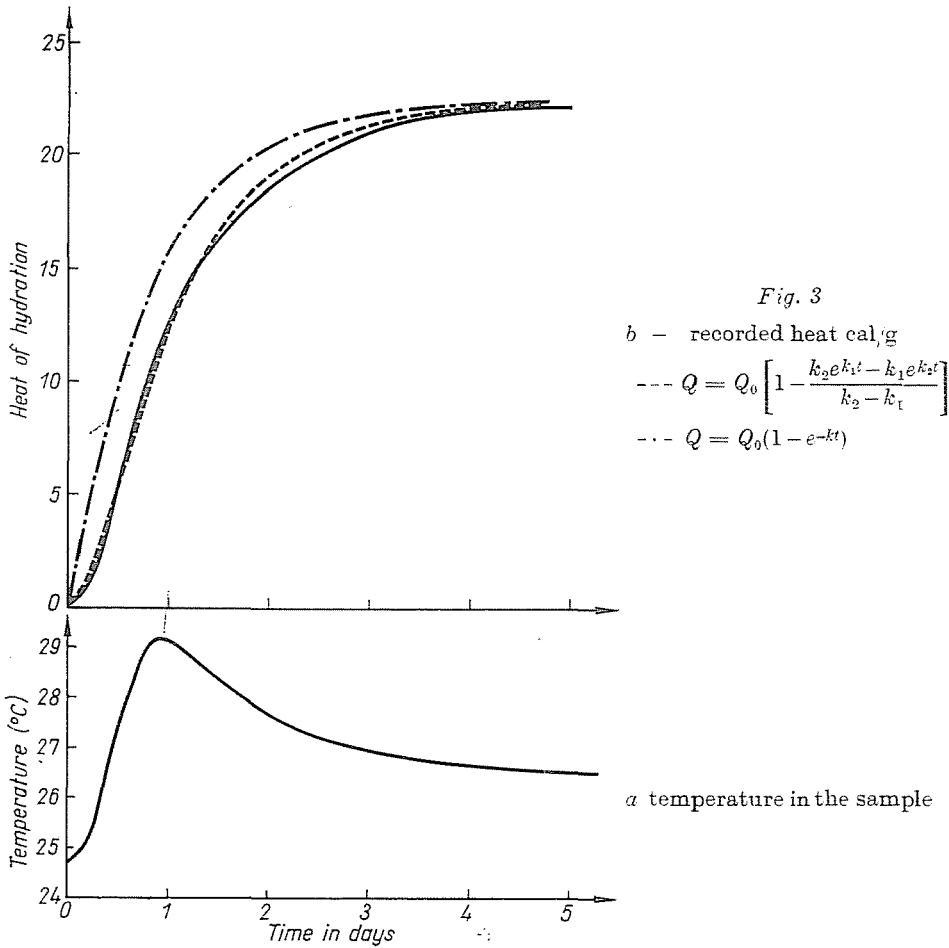
— recorded strengths:

$$xxx \quad \sigma = \sigma_0 \left[ 1 - \frac{k_2 e^{-k_1 t} - k_1 e^{-k_2 t}}{k_2 - k_1} \right]$$

$$ooo \quad \sigma = \sigma_0 (1 - e^{-kt})$$

containing 70 per cent of blast furnace slag and nearly 30 per cent of clinker. Curve *a* indicates temperatures in °C inside the specimen vs. time, and it is seen that the calorimeter temperature rose by 4,5 °C over the initial 24,7°C. Diagram *b* represents heat evolution during the set of cement mortar vs. time, omitting warming up during mixing. In this figure also heat volumes calculated by both Eq. (2) and formula  $Q = Q_0(1 - e^{-k_2t})$  have been plotted.





**Conclusions**

Comparing test results and values calculated by Eq. (2), it can be concluded that Eq. (2) suits well to describe cement setting and hardening as well as heat generation, provided the respective rate constants are known. These latter are:

for the compressive strength of Portland cement paste:	$k_1 = 0,3 \frac{1}{\text{days}},$	$k_2 = 2 \frac{1}{\text{days}}$
for the heat generation of blast furnace slag cement:	$k_1 = 1,2 \frac{1}{\text{days}},$	$k_2 = 3 \frac{1}{\text{days}}$

It is the problem now, how to interpret processes each rate constant pertains to. Available measurement results probabilize that processes of heat generation and of hardening are related to different reaction mechanisms.

Since initial heat generation during mixing cement with water had not been reckoned with in our calculations, it can be assumed that essentially the heat volume evolved during the  $C_3S$  hydration has been measured, which is a diffu-

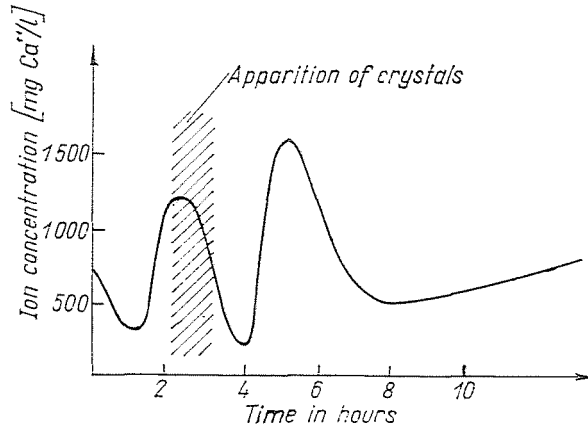


Fig. 4

sion dependent process, and can be characterized by the corresponding rate constant. Nevertheless physico-chemical conditions favouring this process have to develop around the cement grains. Heat evolution constant  $k_2$  is characteristic to exactly this process.

It is an accepted assumption that hydrates evolving during the  $C_3A$  hydration are decisive for the development of the induction stage, which, however, involves important processes rather than to be a rest period. According to complexometry tests on the solution pressed out of the cement paste (Fig.4) [17], during the induction stage the  $Ca^{++}$  ion concentration highly changes, while microscopy testing of thin spread samples shows beginning of the interstitial  $Ca(OH)_2$  crystallization, with a simultaneous reduction of ion concentration. From Fig.4 it appears that 6 to 7 hours are necessary for the important change of ion concentration to end. In the evolution of these processes the  $C_3A$  hydrates may have a decisive role and the free evolution of the diffusion-dependent process may be hindered by the process with rate constant  $k_2$ . Rate constant  $k_2$  of the strength diagram is related to the transformation processes in the tobermorite gel.

Test results lead to the conclusion that the presented formula suits better

than any other existing equation to describe processes in setting and hardening, and constants can clearly be evaluated. Its use will provide valuable help in studying development in time and mechanism of concrete-borne reactions.

### Summary

Investigations both into the compressive strength of Portland cements and the heat of hydration of blast furnace slag cements have led to the conclusion that their time-dependent development can be described by the same equation as the consecutive chemical reactions. Speed constants of the heat generation depend on the diffusion and on the physico-chemical processes responsible for the conditions of the main hydration stage. Constant  $k_2$  of the strength diagram is related to the transformation processes in the tobermorite gel.

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