

## **EFFECT OF ZnO ON THE HYDRATION OF PORTLAND CEMENT**

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ZnO added to the system Portland cement – water changes the kinetics of the hydration process substantially. Amorphous zinc hydroxide is formed and inhibits the reaction of tricalcium silicate with water, resulting in an induction period prolongation. This effect depends on the amount of ZnO added to the hydrated paste. The transformation of zinc hydroxide into calcium hydrozincate provokes the further hydration.

**Keywords:** cement mineral reactions, ZnO

### **Introduction**

Evaluation of the influence of ZnO on the hydration of Portland cement is of particular importance when the cement paste is used for the immobilization of detrimental industrial wastes [1–3]. Zinc is an amphoteric element active in the environment; it occurs in cement paste and exerts a strong influence on the hydration of cement minerals and on the microstructure of the hydration products [4–6]. Studies were carried out with the aim of determining the effect of ZnO on the kinetics of the reactions of cement and cement minerals with water, and the results are presented here.

### **Experimental**

The influence of ZnO on the kinetics of hydration of ordinary Portland cement (OPC) was investigated by recording heat evolution curves for the following samples:

1 – OPC

2 – OPC + 0.5% ZnO

3 – OPC + 1.0% ZnO

Standard ISO OPC-35 cement was used. ZnO was added as percentage by mass of the cement.

Microcalorimetric measurements were carried out with the isothermal, multi-chamber, differential calorimeter designed in the Institute of Building Technology in Warsaw, which allows the registration of  $10^{-6}$  W effects [7]. The heat evolution was followed at 293 K for 7 days on 8 g samples of cement mixed with water at a constant water to cement ratio of 0.5. The results were processed by the computer joined on-line with the calorimeter. It was found that ZnO added to the cement paste affects the heat evolved at the beginning of the reaction only slightly, but causes a significant elongation of the dormant period.

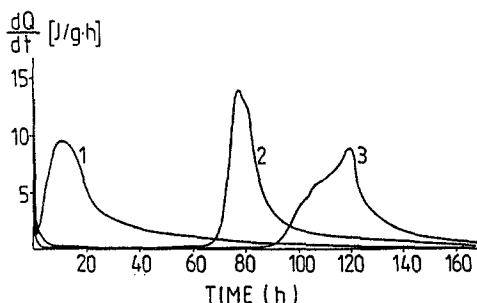


Fig. 1 Heat evolution curves of ZnO doped OPC samples. 1 – OPC-35, 2 – OPC-35+0.5% ZnO, 3 – OPC-35+1.0% ZnO

In the calorimetric curves of all the samples, the stages characteristic of cement hydration can be distinguished (Fig. 1). The two main components of cement controlling the hydration process in the early stages are tricalcium silicate,  $3\text{CaO}\cdot\text{SiO}_2$  ( $\text{C}_3\text{S}$ ), and tricalcium aluminate,  $3\text{CaO}\cdot\text{Al}_2\text{O}_3$  ( $\text{C}_3\text{A}$ ). These two clinker minerals were synthesized and ground to the specific surface required for OPC 35, i.e.  $3200\text{ cm}^2/\text{g}$ , as measured by the Blaine method. Mixtures with the compositions given in Table 1 were subjected to the hydration process at a water to solid ratio of 0.5, at 293 K. The hydration process was stopped after 3, 6, and 24 hours and after 3, 7 and 14 days. For this purpose, the hydrated pastes were crushed and washed with acetone. The dried samples were studied by XRD. The results are listed in Table 2. In the next series of experiments, samples of  $\text{C}_3\text{S}$  mixed with different amounts of ZnO were hydrated and the hydration products were identified by XRD. The hydration of  $\text{C}_3\text{S}$  with ZnO was followed at a water to solid ratio of 0.5, at 293 K, and stopped after 1, 3, 7, 14 and 28 days. The results are listed in Table 3.

**Table 1** Phase composition of initial mixtures

No of sample	Percentage of component			
	C <sub>3</sub> S	C <sub>3</sub> A	ZnO	SiO <sub>2</sub>
1	90	–	–	10
2	90	–	10	–
3	–	90	–	10
4	–	90	10	–
5	60	30	–	10
6	60	30	10	–

**Table 2** XRD data for C<sub>3</sub>S and C<sub>3</sub>A hydrated with Zn

Time	Crystalline hydration products					
	C <sub>3</sub> S		C <sub>3</sub> A		C <sub>3</sub> S + C <sub>3</sub> A	
	1	2	3	4	5	6
3 h	–	–	A, B	A	B	–
6 h	–	–	A, B	A	B	B
12 h	P	–	A, B	A, B	B, P	B
24 h	P	–	A, B	A, B, Z	B, P	B
3 d	P	–	A, B	A, B, Z	B, P	B
7 d	P	–	A, B	A, B, Z	B, P	B, P*, Z*
14 d	P	–	A, B	A, B, Z	B, P	B, P, Z

\* – traces. Sample code from 1 to 6 as Table 1: P-Ca(OH)<sub>2</sub>, A-2CaO·Al<sub>2</sub>O<sub>3</sub>·8H<sub>2</sub>O, B-4CaO·Al<sub>2</sub>O<sub>3</sub>·13H<sub>2</sub>O, Z-CaZn<sub>2</sub>(OH)<sub>6</sub>·2H<sub>2</sub>O

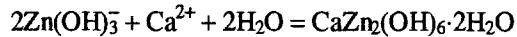
**Table 3** New crystalline phases formed in the system (C<sub>3</sub>S+ZnO)–H<sub>2</sub>O

ZnO content	New phases appeared in the ZnO doped samples as a function of time of hydration				
	1 day	3 days	7 days	14 days	28 days
–	P	P	P	P	P
0.5%	–	Z*	P	P	P
1.0%	–	–	Z	P	P
3.0%	–	–	–	Z	P
5.0%	–	–	–	–	Z
10.0%	–	–	–	–	–

Crystalline products denoted as in Table 2.

## Discussion

In a basic environment, zinc oxide turns to zinc hydroxide, which can occur as an amorphous or crystalline substance. A *pH* increase causes the formation of  $\text{Zn}(\text{OH})_3$  or  $\text{Zn}(\text{OH})_4^{2-}$ . The zincates are generally readily soluble, with the exception of calcium hydrozincate, which is formed according to the reaction [6]



Microcalorimetric measurements reveal that a ZnO admixture strongly decelerates OPC hydration. It should be underlined, however, that the inhibitory influence relates to  $\text{C}_3\text{S}$  hydration. The presence of zinc in the system  $\text{C}_3\text{S} - \text{H}_2\text{O}$  clearly disturbs calcium hydroxide formation. It seems that the influence of ZnO on  $\text{C}_3\text{S}$  hydration can be explained in terms of the protective coating theory [8, 9]. This theory assumes that in the early stages of hydration,  $\text{C}_3\text{S}$  grains are surrounded by an impermeable layer of highly disordered hydrate, the C-S-H phase, which hinders further reaction. The presence of ZnO brings about a tightening of this impermeable layer, resulting from zinc hydroxide precipitation. The zinc hydroxide thus formed is an amorphous substance undetectable by XRD. In the presence of the C-S-H layer impregnated with zinc hydroxide,  $\text{C}_3\text{S}$  hydration is hindered. Further reaction with water is possible after the transformation of amorphous zinc hydroxide into crystalline calcium hydrozincate. This reaction causes destruction of the impermeable layer, thereby promoting further  $\text{C}_3\text{S}$  hydration.

The hydration of the aluminate phase is not as affected by the presence of zinc as tricalcium silicate hydration. The calcium aluminate hydration products are well crystalline phases, such as  $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$  and  $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 13\text{H}_2\text{O}$ . The rate of growth of hydrated calcium aluminate crystals is so high that the impermeable amorphous zinc hydroxide layer cannot be formed and inhibit  $\text{C}_3\text{A}$  hydration. As a consequence of zinc hydroxide formation and its transformation to calcium hydrozincate, the calcium ion concentration in the liquid phase decreases. The prevailing  $\text{C}_3\text{A}$  hydration product is therefore the  $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$  phase. Finally, when  $\text{C}_3\text{A}$  is added to the system  $(\text{C}_3\text{S} + \text{ZnO}) - \text{H}_2\text{O}$ , the decelerating effect of ZnO is reduced. Additionally, the progressive  $\text{C}_3\text{A}$  reaction with water brings about increases in the  $\text{Ca}^{2+}$  and  $\text{OH}^-$  ion concentrations in the solution thereby facilitating the transformation of zinc hydroxide into calcium hydrozincate. This process promotes further tricalcium silicate hydration.

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**Zusammenfassung** — Durch den Zusatz von ZnO zum System Portlandzement-Wasser wird die Kinetik des Hydratationsprozesses grundlegend verändert. Amorphes Zinkhydroxid wird gebildet, was einen Inhibitor für die Tricalciumsilikatreaktion mit Wasser darstellt, wodurch die Induktionsperiode verlängert wird. Dieser Effekt hängt von der Menge ZnO ab, die dem Zementbrei zugesetzt wurde. Die Umwandlung von Zinkhydroxid zu Calciumhydrozinkat führt eine weitere Hydratation herbei.