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Negative effect of zinc compounds on hydration kinetics of ordinary Portland cement

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Abstract. Metals and metal containing compounds have significant effect on cement hydration mechanism and kinetics. The recycling of waste materials leads to increase of content of metals in various industrial products and visibly affects properties of the Portland cement. One of the metals that has been known to drastically increase the setting time is zinc. Zinc forms various hydroxyl species with calcium cations. Pore solution thus has lowered concentration of calcium which suppresses formation of portlandite. Due to insufficient concentration of calcium the formation of CSH gel and further hydration of clinker grains is inhibited. The aim of this study is to quantify the negative effects of zinc at different concentrations at ambient temperature at 20°C. Isothermal calorimetry was used to measure the negative effects of zinc on hydration kinetics of ordinary Portland cement. Zinc was added to the cement in the form of two soluble salts $\text{Zn}(\text{NO}_3)_2$ hydrate, ZnCl_2 and a poorly soluble compound ZnO . The concentration of zinc added was chosen between 0.1 and 1 wt. % of clinker. Significant retardation of cement hydration with increasing zinc content was proven.

1. Introduction

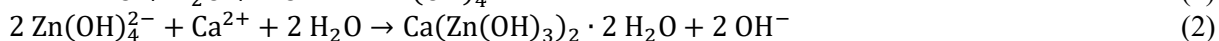
Portland cement is a hydraulic binder produced by burning of ground limestone, clay and other raw materials in rotary kiln. Created clinker is ground up and mixed with small amounts of gypsum. Produced clinker consists of many phases. The main clinker phases are tricalcium silicate (abbr. C_3S – $3\text{CaO}\cdot\text{SiO}_2$ or Ca_3SiO_5 , alite), dicalcium silicate (abbr. C_2S – $2\text{CaO}\cdot\text{SiO}_2$ or Ca_2SiO_4 , belite), tricalcium aluminate (abbr. C_3A – $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ or $\text{Ca}_3\text{Al}_2\text{O}_6$, celite) and calcium aluminoferrite (abbr. C_4AF – $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$ or $\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$, brownmillerite) [1].

Various metals can be introduced into cement in all stages of production or application. Limestone based on the specific deposit tends to contain other minerals such as sphalerite (ZnS). Ordinary Portland cement is also widely researched as a binder for solidification and immobilization of toxic waste containing metals. Solidification and immobilization of toxic elements encompasses reducing bioavailability, leachability, and mobility of hazardous elements [1–5].

Zinc can be present in admixtures, in its own separate phase in clinker or in solid solution with main clinker phases. Solid solution with C_3S seems to be preferred over C_2S [6]. Ions of zinc present in pore solution hydrolyse into various hydroxyl species. These compounds coat hydrating grains of cement clinker and react with calcium cations evolved into the pore solution during formation of CSH gel. The resulting insoluble $\text{Ca}(\text{Zn}(\text{OH})_3)_2\cdot 2\text{H}_2\text{O}$ depletes concentration of Ca^{2+} preventing the formation of portlandite and severely suppressing saturation of pore solution and further hydration of cement grains. Precipitation of portlandite and CSH gel is inhibited until all zinc has been converted into



insoluble $\text{Ca}(\text{Zn}(\text{OH})_3)_2 \cdot 2\text{H}_2\text{O}$. Once this process reaches completion hydration continues once more. Reactions leading to $\text{Ca}(\text{Zn}(\text{OH})_3)_2 \cdot 2\text{H}_2\text{O}$ are shown in equations (1) and (2) [7–10].



The purpose of this study is to show the effect of zinc compounds ZnCl_2 , $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and poorly soluble compound ZnO at different concentrations on the hydration induction period of ordinary Portland cement at lower ambient temperature than most studies and compare results with studies using higher ambient temperature. Exposure of zinc oxide to humidity affects both solubility and particle size distribution. Moisture present in chemicals can lead to misleading results by altering the concentration of zinc in the zinc source. These parameters can also affect reaction kinetics of zinc oxide in pore solution. Monitoring of these effects is done using isoperibolic calorimetry. It is apparent that ambient temperature has significant influence on both hydration of cement and mechanisms behind zinc induced prolonging of induction periods.

2. Experimental

2.1. Materials and Sample Preparations

All samples were prepared using cement CEM I 42,5 R produced by Mokrá—Českomoravský cement, a.s., Heidelberg Cement Czech Republic. Chemical composition of this cement is provided in technical documentation and is shown in table 1 [11]. Each cement sample contained a specific amount of zinc equal to weight % of cement (1, 0.5 and 0.1%) and 0.4 water to cement ration. Cement pastes were prepared using standard kitchen aid mixer according to the norm ČSN EN 196-1.

Table 1. Chemical composition of used cement [11].

Component	Cement (wt. %)
CaO	63.7
SiO ₂	19.6
Al ₂ O ₃	4.8
Fe ₂ O ₃	3.3
MgO	1.4
SO ₃	3.1
Cl ⁻	0.040
K ₂ O	0.75
Na ₂ O	0.19
Insoluble	0.7
LOI	3.4

Zinc was introduced into cement paste in a form of soluble salts ZnCl_2 and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and poorly soluble compound ZnO in concentrations 0.1; 0.5 and 1 wt. % of pure zinc in cement. The humidity of the oxide was determined with Kern MLS 50-D humidity analyser. Zinc oxide used as one of zinc sources contained on average 0.35 weight % of moisture. ZnO was used in stock and dried form. ZnO was dried at 80°C for 72 h. Zinc chloride and zinc nitrate hexahydrate were purchased from Lach-Ner, s.r.o. while zinc oxide was purchased from Lachema, s.r.o..

2.2. Isoperibolic Calorimetry

One of the best methods for evaluating hydration of cement is multicell isoperibolic calorimetry. This type of device allows monitoring of multiple samples and references allowing easy comparison of different cement mixtures. This method is widely used for the study of the effects of different admixtures such as superplasticizers, hardening accelerators and various secondary industrial products on setting of cement pastes [12].

Cement mixtures were weighted (300 g) into polystyrene cup with thermocouples and covered with thermo-insulating top. Calorimetric curves showing cement hydration and differences between various samples were obtained using isoperibolic calorimetry in a room with ambient temperature at 20°C.

3. Results and discussion

Mixtures of samples were prepared outside of the calorimeter thus the first peak on hydration curve was not measured in its entirety. Nevertheless, the early stages of cement hydration are not significant to this study and do not significantly contribute to any changes during hydration.

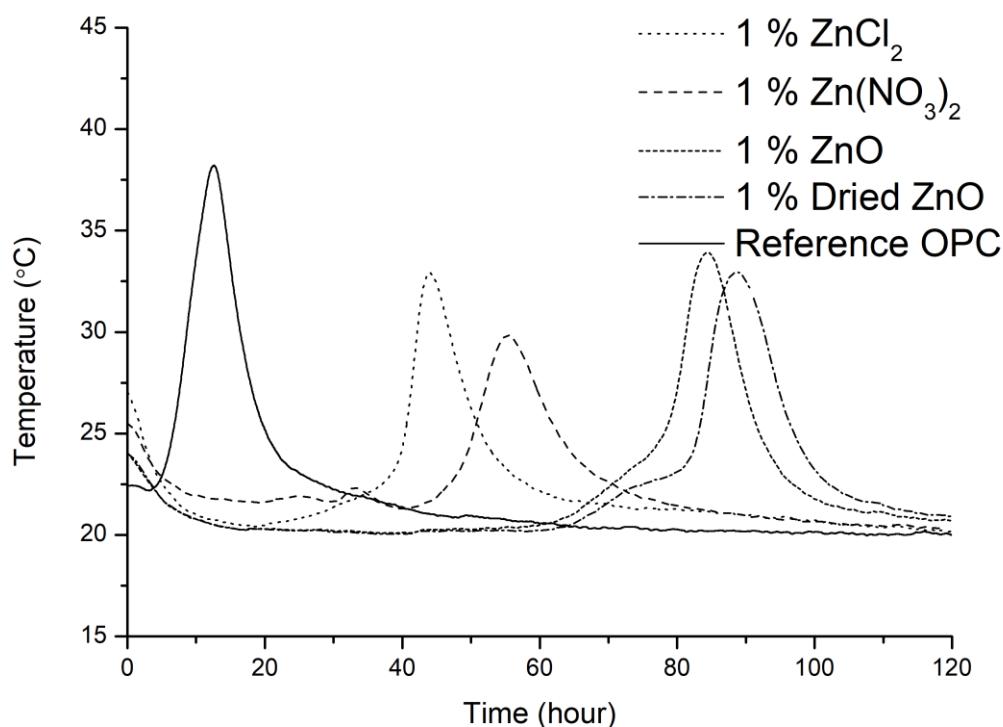


Figure 1. Isoperibolic calorimetry curves for samples with 1% weight concentration of zinc.

From calorimetric curves shown in figure 1 it is apparent that cement hydration of samples doped with zinc compounds was severely inhibited as peaks are shifted to the right of the reference peak. There also appears to be a small wide peak at around 25 h on a curve for sample with zinc nitrate. The heat evolution causing this peak was probably a result of dissolution of the zinc salt or crystallization on the surface of the cement grains as explained in works [13, 14].

Maximum temperatures reached by sample peaks were also lower than that of reference. Maximum temperatures reached by the samples were 32.9°C for cement with chloride, 29.9°C for nitrate, 34.0°C for untreated zinc oxide and 33.2°C for samples with dried zinc oxide. This is probably a result of zinc compounds slowing hydration of clinker grains.

At the same concentration of zinc, ZnCl_2 seems to show lower inhibitory ability than zinc nitrate. zinc oxide showed the highest inhibition of hydration. The difference in behaviour of samples doped with zinc oxide is due to lower solubility in water than zinc chloride and zinc nitrate. Smaller inhibition by chloride and nitrate is due to the ability of chloride and nitrate ions to accelerate cement hydration with chloride being more effective accelerator at this concentration [15].

When compared with similar studies done by Siler et al. [16, 17] who used 25°C (as opposed to 20°C in this study) as ambient temperature, first noticeable differences are wider hydration peaks with higher

maximum temperature when higher ambient temperature is used. This corresponds with accelerated hydration of cement and formation of hydration products. Samples containing chlorides show comparable induction period with samples in this study but had reached significantly higher maximum temperature at around 37 and in contrast with 32.9°C for our samples. Maximum temperatures of samples with zinc oxide are comparable with samples in this study but the length of induction period was different. This could be explained by lower solubility of dried zinc oxide, but the difference does not seem to be very significant. In study published by Kolářová et al. [18] these cement systems were studied using isothermal calorimetry. Induction period measured by this method was at around 80 h which is very similar to 77.8 h with dried zinc oxide and 73.3 h with untreated zinc oxide. Summary of determined induction periods is shown in table 2.

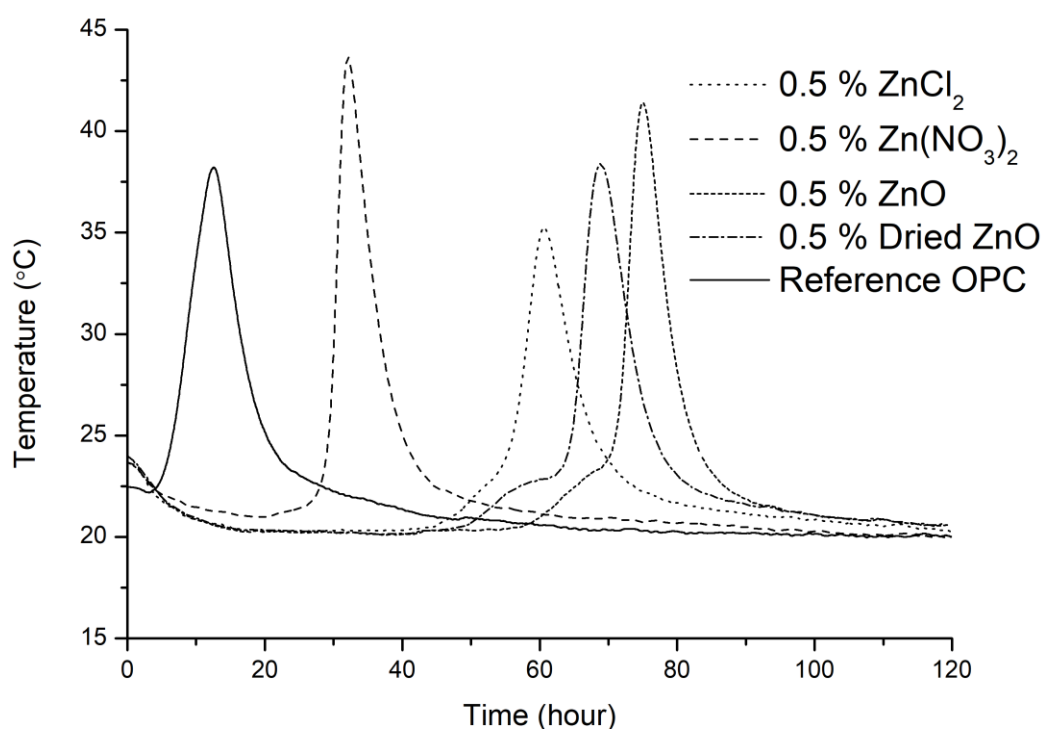


Figure 2. Iso-peribolic calorimetry curves for samples with 0.5% weight concentration of zinc.

Behaviour of samples with concentration of zinc equal to 0.5% of weight of the clinker visibly changed as is demonstrated in figure 2. Peaks belonging to the zinc oxide samples shifted to the left indicating shorter induction period. Both zinc oxide peaks were thinner than those of samples with concentration of 1%. This indicates faster hydration relative to the previous samples.

Peaks of chloride and nitrate samples were visibly thinner than those of previous samples. The maximum temperature reached by nitrate sample was higher than maximum temperature of the reference. This indicates accelerated hydration in comparison to the samples with higher concentration of zinc. Significant difference was observed in induction periods of nitrate and chloride samples. Overall lengths of induction periods of all samples are in table 2. While the induction period of nitrate sample dropped from 48.2 h to 29 h with decrease in concentration of zinc, the induction period of chloride sample increased from 38.9 h to 56 h with decrease in concentration of zinc. This could be result of chloride and nitrate anions accelerating hydration through different mechanisms. While chloride anions are said to affect hydration by incorporation into CSH gel, disrupting it, allowing more water to be available to hydration reactions, nitrates affect formation of ettringite and the hydration

of β -C₂S. Next parameter to consider is solubility of various ion species in pore solution with differing concentrations of chlorides and nitrates in such complicated systems [19, 20].

Results of Šiler [16, 17] measurements corresponding to 0.5% chloride show higher maximum temperature in comparison with 1% chloride, while the induction period was similar. In contrast with measurements in this study where induction period increased. This could be explained by loss of inhibitory effect with decreasing zinc ion concentration, loss of acceleration by chloride ions but with added acceleration caused by higher ambient temperature. Samples doped with nitrates measured by Šiler show significant increase in maximum temperature with decrease of concentration of nitrate. This correlates with presented results. Although sample of 0.5% nitrate measured at higher temperature showed shorter induction period than our results, the decrease in induction period with decreasing concentration was not as high as in our experiment. [16, 17].

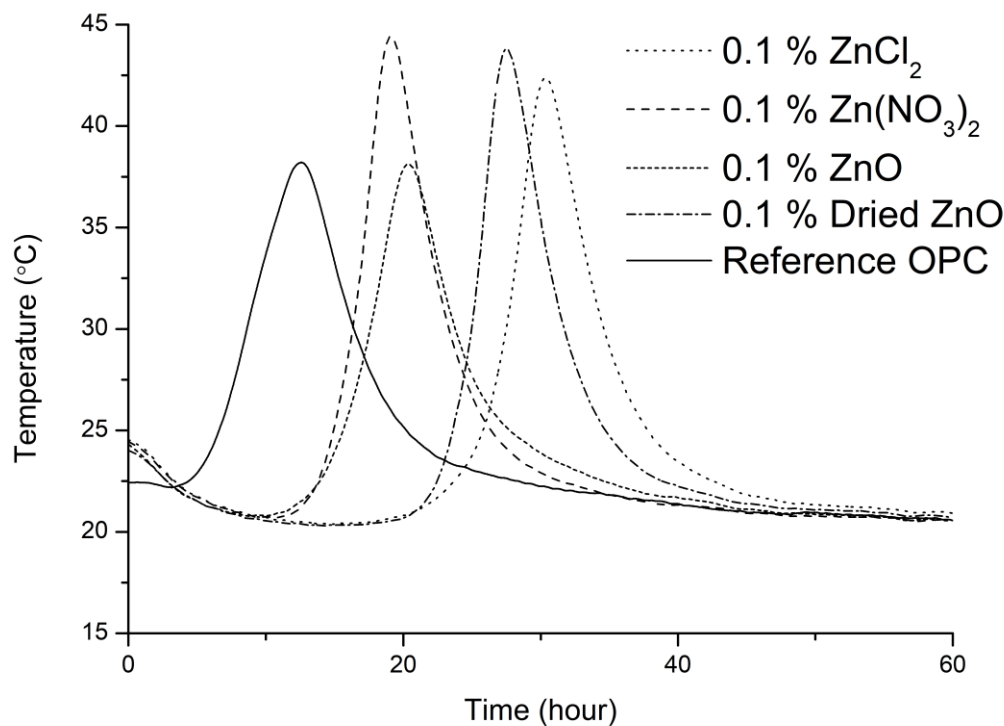


Figure 3. Isoperibolic calorimetry curves for samples with 0.1% weight concentration of zinc.

Table 2. Summary of induction periods measured based on isoperibolic curves.

Concentration of zinc (wt.%)	Induction period (hour)				
	ZnCl ₂	Zn(NO ₃) ₂	ZnO untreated	ZnO dried	Cement
0.0					4.9
0.1	27.1	13.7	14.9	22.6	
0.5	56.0	29.0	63.5	56.5	
1.0	38.9	48.2	73.3	77.8	

Differences between lengths of induction periods and maximum temperatures reached decrease with decreasing concentration of zinc. Peaks of all samples shifted to the left indicating shorter induction periods as seen in figure 3. Samples doped with zinc oxide reached higher maximum temperature than

the reference cement. Induction periods of all samples ranged between 13.7 h and 27.1 h. These are significantly longer induction periods than the induction period of reference sample. These results are comparable with literature [16, 17].

Induction periods measured by Kolářová [18] ranged between 10 and 20 h. Sample doped with zinc chloride had significantly longer induction period than those doped with zinc nitrate. This phenomenon correlates with results of Kolářová. Samples doped with zinc oxide had the longest induction period out of her measurements. These results are very similar to our measurement with untreated zinc oxide samples. Our samples of cement with dried zinc oxide show significantly longer induction period than samples with untreated oxide.

4. Conclusion

The aim of this study was to monitor the effects of various zinc compounds on induction period of cement hydration at 20°C ambient temperature as opposed to 25°C used in other studies [16–18]. Compounds used as zinc source in this study were soluble salts ZnCl_2 and $\text{Zn}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ and insoluble compound ZnO in dried and not dried form.

- The length of induction period was increasing with increasing concentration of specific zinc source except for sample with 1 weight % of zinc in a form of ZnCl_2 due to acceleration effect of chloride anions at this concentration.
- Ambient temperature of 20°C was used during measurements (as opposed to of 25°C as used in studies [16–18]) which resulted in significantly higher peak temperatures reached at high concentrations of zinc.
- Differences in the length of induction periods between zinc chloride and zinc nitrate samples are bigger at 20°C ambient temperature as opposed to 25°C used in studies [16–18].
- The difference between induction periods and maximum temperatures reached by cement samples with dried and untreated zinc oxide was relatively small. Induction period of both samples were similar with consistent difference between 5 to 7 h. Untreated zinc oxide contained 0.35 weight % of water. This is insignificant amount that probably would not influence the results. The difference in hydration induction periods was probably caused by different particle size distribution of heat treated and untreated zinc oxide and different level of homogenization of sample pastes.

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