The effect of zinc, water to binder ratio and silica fume on the hydration and mechanical properties of Portland cement mixtures

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Abstract. The amount of zinc in the clinker or in the secondary raw materials has been increasing in recent years mainly due to the processing of waste materials containing zinc. The aim of this work is to show the effect of zinc on hydration of Portland cement and mechanical properties. These effects were studied by isoperibol calorimetry and mechanical properties testing. Zinc was added to the cement in the form poorly soluble compound ZnO. The concentration of zinc added was chosen as 1 wt. percent. The newly formed compounds during hydration were identified by X-ray diffraction method (XRD). Another objective is to show the effect of silica fume (microsilica, SF) as the secondary raw material and water to binder ratio on hydration of cement in the presence of zinc.

1. Introduction

Concrete, usually Portland cement concrete is a composite material composed of fine and coarse aggregates bonded together with a Portland cement paste that hardens over time. The cement reacts chemically with the water and other ingredients to form a hard matrix that binds the materials together into a durable stone-like material that has many uses. Additives such as pozzolans are included in the mixture to improve the physical properties of the fresh mix or the finished material.

Portland cement is the most common type of cement in general use around the world as a basic ingredient of concrete, mortar, stucco, and non-specialty grout. It is a fine powder, produced by heating limestone and clay minerals in a kiln to form clinker, grinding the clinker, and adding small amount of supplementary ingredients.

The effect of zinc on the clinker properties was investigated in different works \citep{1-6}. The presence of zinc affected hydration of C\textsubscript{3}A and retards hydration of C\textsubscript{3}S \citep{2, 3}. Zn\textsubscript{2}(OH)\textsubscript{6}·2H\textsubscript{2}O was described in literature \citep{3} as product of hydration of Portland cement in the presence of zinc.

The zinc hydroxyl anions Zn(OH)\textsuperscript{−} and Zn(OH)\textsuperscript{2−} are found in the system between pH 12 and 13. Subsequently, they are transformed into insoluble CaZn\textsubscript{2}(OH)\textsubscript{6}·2H\textsubscript{2}O before portlandite. Thus, hydration can be inhibited until these reactions are complete, since both OH\textsuperscript{−} and Ca\textsuperscript{2+} are present in low concentrations \citep{4}.

\begin{equation}
\text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2
\end{equation}

\begin{equation}
\text{Zn(OH)}_2 + 2\text{OH}^- \rightarrow 2\text{H}_2\text{O} + \text{ZnO}_2^{2−}
\end{equation}
\[ 2\text{ZnO}^{2-} + \text{C}_3\text{S}/\text{O} - \text{Ca}^{2+} + 6\text{H}_2\text{O} \rightarrow \text{C}_3\text{S}/\text{O} - \text{CaZn}_2(\text{OH})_6 \cdot 2\text{H}_2\text{O} + 2\text{OH}^- \quad (3) \]

Dashes in equation 3 indicate bonding of Ca through oxygen.

The impact of ZnO on the properties of Portland cement was published in [5–7]. Due to zinc retardation, mechanical strengths after 3 days were less than for samples without zinc. After one week, the strength was increasing and after 28 days it was higher than for the control sample. This effect was attributed to the action of ZnO nanoparticles as filler. Decreasing porosity with an increasing amount of ZnO was also found [6]. According to information published in [7], the mechanism by which ZnO retards hydration reaction could be nucleation and/or growth poisoning of C-S-H.

Silica fume (SF), also known as microsilica is an amorphous silicon dioxide. It is an ultrafine powder collected as a by-product of the silicon and ferrosilicon alloy production and consists of spherical particles with very small diameter. The main field of application is as a pozzolanic material for high performance concrete [8]. According to [7], for the effectiveness of secondary materials, their specific surface area is most important.

The aim of this work is to show the effect of zinc on hydration of Portland cement, mechanical properties, influence of water to binder ratio and influence of the presence of microsilica. These effects were studied by isoperibol calorimetry and mechanical properties testing. Zinc was added to the cement in the form of poorly soluble compound ZnO. The concentration of zinc was 1wt. percent. The amount of microsilica was 15 wt. percent. The newly formed compounds during hydration were identified by X-ray diffraction method (XRD).

2. Sample preparation
The mixtures were prepared from the cement CEM I 42.5 R \( (x_{10} = 0.58 \, \mu m, x_{50} = 11.11 \, \mu m, x_{90} = 40.51 \, \mu m) \) and CEM I 52.5 N \( (x_{10} = 0.45 \, \mu m, x_{50} = 7.93 \, \mu m, x_{90} = 28.88 \, \mu m) \) Heidelberg Cement Group Českomoravský cement, a.s. Mokrá, Czech Republic. Zinc was added in the form of insoluble ZnO in the amount of 1 wt. % of the cement substitution (the percentages of the replacement were always calculated on pure zinc in the binder). The pastes were mixed with distilled water. Used microsilica was Elkem Grade 920U \( (x_{10} = 0.52 \, \mu m, x_{50} = 1.98 \, \mu m, x_{90} = 8.33 \, \mu m) \) Elkem Silicon Materials, Norway.

For measurements on isoperibol calorimeter, 300 g of the mixture was weighed into a polystyrene crucible equipped by a thermo-insulating jacket and a thermocouple. Calorimetric measurements and calorimetric curves were obtained.

The pastes for compressive strength determination were embedded into 100 × 20 × 20 mm moulds and stored in wet conditions for sample analysis.

3. Description of the methods used
3.1. XRD (X-ray diffraction)
X-ray diffraction (XRD) is usually used to obtain information about the structure of crystalline materials. A primary use of the technique is the identification and characterization of compounds based on their diffraction pattern. X-ray diffraction analysis was performed with X-Ray diffractometer Empyrean (Panalytical) with Bragg–Brentano parafocusing geometry and using CuKa radiation.

The measurements were done within the range from 5 to 120°2Θ with angular step 0.013°2Θ and 25 s duration using automatic divergence slits to maintain the constant irradiation of the sample area. The measurements were repeated four times and then summed.

3.2. Isoperibol calorimetry
The heat production is a result of the hardening processes in the cement paste. Very good representative values of the hydration process can be acquired using a multicell isoperibol calorimeter [9]. This simple method enables simultaneous monitoring of the progress of hydration of several samples and estimation of the beginning of the setting or hardening process. Unlike the isothermal calorimetry, the hydration curves show differences at constant ambient temperatures. By this way it is possible to simulate real
conditions of hydration. The data were collected using an isoperibol calorimeter constructed at the Faculty of Chemistry, Brno University of Technology (Brno, Czech Republic) and the resulting heat was obtained by numerical integration and multiplied by the integration constant of the calorimeter which was obtained from calibration. The calorimeter used was constructed based on the work published by Smrčková et al. [10]. This kind of calorimeter was primarily developed at the German Academy of Sciences (Halle, Germany). In this work, an upgraded version with 16 cells was used; its detailed description was reported by Brandštetr et al. [9].

4. Results and discussion

4.1. Influence of ZnO and microsilica

The effect of ZnO on the hydration of CEM I 42.5 R was investigated in literature [4]. There was found hydration retarding and maximum developed temperature decreasing thanks to a slower dissolution of ZnO. Further dissolution of ZnO leads to the incorporation of Zn$^{2+}$ ions into the amorphous phase. A slight decrease of temperature and evolved heat can also be attributed to the formation of a crystalline compound of Ca[Zn(H$_2$O)$_6$] or to the binding of zinc into amorphous compounds [4, 6]. According to [8] the effect of ZnO is mainly in nucleation and/or growth poisoning of C-S-H. The effect of SF as a secondary material depends mainly on the size of their particles.

Figure 1 shows the effect of ZnO and microsilica on hydration of CEM I 52.5 N.

![Figure 1. Isoperibolic calorimetry curves of cement CEM I 52.5 N.](image)

The difference in maximum temperature achieved with cement without admixtures and with microsilica is very small (0.5°C). This difference is due to the fact that microsilica is not as reactive as cement during hydration and thus does not develop as high temperatures as for hydration of pure cement. The decrease of temperature in the presence of zinc was observed. With replacing cement with microsilica or zinc, less heat is released. This is probably due to the slow hydration of cement and the emergence of new zinc products. The pure cement curve CEM I 52.5 N is the same as for CEM I 42.5 R [4], which is mainly due to the same mineralogical composition of cement. Only cement particle size is different. The different particle size in this case does not affect the rate of dissolution of the cement and the rate of hydration reactions.

Only slight hydration acceleration when using microsilica and finer cement CEM I 52.5 N was observed. At a 1% zinc dose, no acceleration of hydration was observed but almost no delay of hydration was observed unlike CEM I 42.5 R [4]. Microsilica, thanks to its high softness, acts as a component allowing the precipitation of hydration products and thus acceleration of hydration. However, this acceleration is only small because particle diameters are not small enough ($x_{50} = 1.98 \mu m$).
A decrease in total released heat was also observed using CEM I 52.5 N. Due to the effect of zinc, another reduction was found. This reduction is more significant than for coarse cement. It can be assumed that the heat will increase during the next stages of hydration. This result shows that the fineness of the cement is important for stability of zinc hydroxyl membrane which is formed during hydration in the presence of zinc.

4.2. Induction period length
To illustrate the effect of zinc and microsilica, the lengths of the induction periods were determined and plotted in relation to the amount of zinc in the samples by the same way as in literature [4].

| Induction period lengths (hours) | CEM I 52.5 N | CEM I 52.5 N+SF | CEM I 52.5 N+Zn | CEM I 52.5 N+SF+Zn |
|---------------------------------|-------------|----------------|----------------|------------------|
| Induction period lengths        | 3.3         | 2.8            | 97.4           | 97.4             |

Zinc and microsilica affect not only the maximum temperature but also the length of the induction period. Microsilica shortens the induction period (by 0.5 hours). It may be due to the fact that microsilica helps with nucleation due to its size (as shown in the literature [11]). Zinc, on the other hand, prolongs the induction period very significantly. As opposed to pure cement, the induction period was prolonged for zinc mixtures by 94 hours. This is probably due to gradual dissolution of zinc.

4.3. Influence of water to binder ratio
The influence of the water to binder ratio was tested on CEM I 42.5 R. Figures 2 and 3 shows this effect on the hydration of this cement. The addition of zinc was in the form of 1% ZnO.

![Figure 2. Influence of water to binder ratio on the pure CEM I 42.5 R.](image)
When the water to binder ratio is decreasing, the length of the induction period is also decreasing. At low water content, water is saturated with Ca\(^{2+}\) ions faster and hydration will be accelerated. With lower amount of water, it is not possible to hydrate all phases, thus reducing of the developed heat occur. It can be assumed that storage of concrete will result in the continuation of hydration and release of additional heat. In case of higher amounts of water than is needed for hydration, unreacted water becomes as inert, which draws off heat. It has to be heated and reduces the maximum developed temperature. With higher amount of water, the phase’s gets into better contact with water, the hydration is more complete and the developed heat increases slightly. Results also show retardation extending with increasing water content because of the greater distance of cement grains during hydration. These results are in line with the results published in the literature [12].

For zinc mixtures, retardation by zinc effect is indicated. With decreasing water to binder ratio, the rate of retardation is reduced due to the shortening of the induction period described for pure cement. Another reason is the less stable membrane from zinc hydroxyl anions of Zn(OH)_3\(^-\) and Zn(OH)_4\(^{2-}\) due to less water. Due to less amount of water, lower amount of these anions will form. It also leads to a faster transformation into insoluble CaZn\(_2\)(OH)\(_6\)·2H\(_2\)O.

### 4.4. Compressive strength measurement

The measured sample compressive strength values are shown in table 2.

| Days of hydration | Flexural strength [MPa] | Compressive strength [MPa] |
|------------------|-------------------------|----------------------------|
|                  |                         | CEM I 52.5 N               |
| 1                | 6.7 ±1.2                | 36.6 ±4.0                  |
| 7                | 4.0 ±0.9                | 68.0 ±3.5                  |
| 28               | 4.7 ±0.8                | 71.3 ±2.8                  |
|                  | 4.0 ±0.1                | 30.2 ±1.2                  |
|                  | CEM I 52.5 N+SF         |
| 7                | 3.6 ±0.4                | 59.0 ±2.6                  |
| 28               | 6.3 ±0.6                | 67.7 ±6.8                  |
|                  | 4.0 ±0.1                | 30.2 ±1.2                  |
|                  | CEM I 52.5 N+Zn         |
| 7                | 2.8 ±0.5                | 87.5 ±4.3                  |
| 28               | 3.6 ±0.3                | 87.2 ±3.6                  |
|                  | 3.6 ±0.9                | 82.1 ±7.7                  |
|                  | CEM 52.5 I N+SF+Zn      |
| 7                | 3.8 ±0.8                | 58.0 ±4.1                  |
| 28               | 3.6 ±0.9                | 82.1 ±7.7                  |
For cement with microsilica, both flexural and compressive strength are decreasing comparing with cement without admixture. This is probably due to the fact that the microsilica consumes a large amount of water due to its large surface, which is then missing when cement is hardened [13]. Another reason can be the loss of processability associated with the slowing of the hydration reactions. This effect would be avoided by using a superplasticizer. For samples with zinc, we can see a significant improvement in mechanical properties in later stage of hydration. This effect can be explained by the fact that zinc reduces the porosity of the structure and due to the filling effect of smaller nanoparticles of zinc oxide [6]. For samples with microsilica and zinc, the mechanical properties after 7 days are worse than that for cement without additives and almost comparable to sample only with microsilica, due to zinc retarding effects and water consumption by microsilica. The strengths after 28 days are again higher than those of zinc-free samples.

4.5. XRD results
Newly formed compounds during cement hydration in the presence of zinc were detected by X-ray diffraction analysis. The amount of these compounds is shown in table 3.

| Days of hydration | Ca(CO$_3$) | Calcite | C$_4$A$_3$H$_8$ | Etrange | Ca(OH)$_2$ | Portlandite | Ca$_2$(Fe$_2$O$_5$) | Brownmillerite | Ca$_3$(SO$_4$) | Lamite (belite) | Ca$_4$(SO$_4$) | Lamite (belite) | Ca$_4$Al$_2$(CO$_3$)[OH]$_2$ | Ca$_4$Al$_2$(CO$_3$)[OH]$_2$ | ZnAl$_2$CO$_3$(OH)$_5$ | ZnAl$_2$CO$_3$(OH)$_5$ |
|------------------|-----------|---------|----------------|---------|-----------|--------------|-------------------|----------------|---------------|----------------|----------------|---------------|-----------------------------|-----------------------------|--------------------------|--------------------------|
| CEM 52.5 N       | 1         | 5       | 4              | 23      | 7         | 10           | 50                |                |               |                |                |               | Ca$_4$Al$_2$(CO$_3$)[OH]$_2$ | Ca$_4$Al$_2$(CO$_3$)[OH]$_2$ | ZnAl$_2$CO$_3$(OH)$_5$ | ZnAl$_2$CO$_3$(OH)$_5$ |
|                  | 7         | 4       | 2              | 37      | 7         | 10           | 39                |                |               |                |                |               | Ca$_4$Al$_2$(CO$_3$)[OH]$_2$ | Ca$_4$Al$_2$(CO$_3$)[OH]$_2$ | ZnAl$_2$CO$_3$(OH)$_5$ | ZnAl$_2$CO$_3$(OH)$_5$ |
|                  | 28        | 12      | 3              | 32      | 4         | 14           | 31                | 3              |               |                |                |               | Ca$_4$Al$_2$(CO$_3$)[OH]$_2$ | Ca$_4$Al$_2$(CO$_3$)[OH]$_2$ | ZnAl$_2$CO$_3$(OH)$_5$ | ZnAl$_2$CO$_3$(OH)$_5$ |
|                  | 1         | 6       | 4              | 28      | 6         | 11           | 44                |                |               |                |                |               | Ca$_4$Al$_2$(CO$_3$)[OH]$_2$ | Ca$_4$Al$_2$(CO$_3$)[OH]$_2$ | ZnAl$_2$CO$_3$(OH)$_5$ | ZnAl$_2$CO$_3$(OH)$_5$ |
| CEM 52.5 N + SF  | 7         | 11      | 5              | 33      | 6         | 13           | 30                |                |               |                |                |               | Ca$_4$Al$_2$(CO$_3$)[OH]$_2$ | Ca$_4$Al$_2$(CO$_3$)[OH]$_2$ | ZnAl$_2$CO$_3$(OH)$_5$ | ZnAl$_2$CO$_3$(OH)$_5$ |
|                  | 28        | 8       | 5              | 32      | 6         | 12           | 36                |                |               |                |                |               | Ca$_4$Al$_2$(CO$_3$)[OH]$_2$ | Ca$_4$Al$_2$(CO$_3$)[OH]$_2$ | ZnAl$_2$CO$_3$(OH)$_5$ | ZnAl$_2$CO$_3$(OH)$_5$ |
| CEM 52.5 N + Zn  | 7         | 9       | 5              | 34      | 5         | 13           | 34                |                |               |                |                |               | Ca$_4$Al$_2$(CO$_3$)[OH]$_2$ | Ca$_4$Al$_2$(CO$_3$)[OH]$_2$ | ZnAl$_2$CO$_3$(OH)$_5$ | ZnAl$_2$CO$_3$(OH)$_5$ |
|                  | 28        | 11      | 2              | 39      | 4         | 10           | 30                | 4              |               |                |                |               | Ca$_4$Al$_2$(CO$_3$)[OH]$_2$ | Ca$_4$Al$_2$(CO$_3$)[OH]$_2$ | ZnAl$_2$CO$_3$(OH)$_5$ | ZnAl$_2$CO$_3$(OH)$_5$ |
| CEM 52.5 N + SF + Zn | 7   | 8       | 0              | 24      | 6         | 18           | 43                |                |               |                |                |               | Ca$_4$Al$_2$(CO$_3$)[OH]$_2$ | Ca$_4$Al$_2$(CO$_3$)[OH]$_2$ | ZnAl$_2$CO$_3$(OH)$_5$ | ZnAl$_2$CO$_3$(OH)$_5$ |
|                  | 28        | 7       | 8              | 24      | 4         | 11           | 41                | 2              |               |                |                |               | Ca$_4$Al$_2$(CO$_3$)[OH]$_2$ | Ca$_4$Al$_2$(CO$_3$)[OH]$_2$ | ZnAl$_2$CO$_3$(OH)$_5$ | ZnAl$_2$CO$_3$(OH)$_5$ |

In addition to the compound CaZn$_2$(OH)$_6$·2H$_2$O which is described in literature [4] but was not found in our samples, other compounds have been discovered. The mechanism of their formation is not yet described in the literature. New compounds affect hydration. Further prolongation of hydration can be attributed to the formation of these new compounds.

5. Conclusion
The aim of this work was to show the influence of zinc on the hydration and mechanical properties of mixtures with Portland cement. Another objective was to show the effect of microsilica as a commonly used pozzolanic material and the effect of water amount as an important factor during
hydration. By using of isoperibol calorimetry the effect of ZnO on the hydration of cement CEM I 52.5 N was investigated. The hydration retarding and maximum developed temperature decreasing thanks to a slower dissolution of ZnO was found. The different particle size of cement 42.5 and CEM I 52.5 N in this case does not affect the rate of dissolution of the cement and the rate of hydration reactions. Only slight hydration acceleration when using microsilica and finer cement CEM I 52.5 N was observed. The result shows that the fineness of the cement is important for stability of zinc hydroxyl membrane which is formed during hydration in the presence of zinc because there is more significant reduction of developed heat with the presence of zinc. When the water to binder ratio is decreasing, the length of the induction period is also decreasing thanks to faster saturation with Ca\(^{2+}\) ions. The same results were found for the presence of zinc. The reduction of hydration retardation in the presence of zinc was more significant thanks to lower stability of hydroxyl membrane with lower amount of water. Both compressive and flexural strength were decreasing especially during first 7 days of hydration thanks to presence of zinc but there were higher strengths then for zinc-free samples after 28 days due to filling effect of smaller nanoparticles of zinc oxide. The other reason can be thanks to formation of new surface for support of start of nucleation. Newly formed compounds during cement hydration in the presence of zinc were detected by X-ray diffraction analysis.

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