

## Impact of ZnO on clinker composition and reactivity – Coupling with MgO

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### Abstract

The possible increase of incorporation of zinc-bearing by-products such as tires or non ferrous slags in cement production may lead to an increase of the zinc concentration in clinker. The mechanism of interaction between zinc and cement depends on its way of introduction (strong retarder when added to cement, more controversial effect when added to raw-mix). In this study, the impact of zinc addition to raw-mix on clinker composition and reactivity was studied. The results enlighten the interaction of zinc and magnesium oxide in the clinker. The presence of MgO in the raw-mix leads to a lower sensitivity of the clinker to ZnO addition. A possible mechanism is that MgO incorporates ZnO under the form of a periclase solid-solution. The release of zinc ions in solution is then slower, and the delay due to zinc is reduced. The interaction of zinc with MgO could explain the scattering of the results obtained previously.

### 1. Introduction

It is well known that zinc added to cement strongly delays cement hydration [1]. The impact of zinc in the raw-mix on clinker reactivity has also been studied [2, 3, 4], but the effective impact and threshold level of ZnO addition inducing delay in hydration depends on the author.

Most authors [2, 4, 5, 6, 7, 8] report a delay in cement hydration when ZnO is added to the raw-mix. According to Akatsu, the setting time seems to increase proportionally to CaO substitution by ZnO (+ 45 minutes for 1.0% ZnO). Bolio-Arceo and Glasser [3] find no negative (sometimes positive) effect on the setting time, even for high intakes of ZnO (up to 1.5%).

The retarding effect of zinc in cement systems has to be considered if one wants to understand why different results are found in literature. According to Arliguië [1, 9, 10, 11, 12, 13], who mainly studied the effect of zinc added to cement, the delay induced by zinc in cement systems is due to Zn<sup>2+</sup> ions in solution. Arliguië proposes the following mechanism: Zn<sup>2+</sup> ions in solution react with hydroxyl ions to form an amorphous layer of Zn(OH)<sub>2</sub> around cement grains, resulting in a slower dissolution of clinker phases. When calcium concentration in solution reaches a sufficient level,

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hydrated calcium hydroxizincate  $\text{Ca}(\text{Zn}_2(\text{OH})_6) \cdot 2\text{H}_2\text{O}$  precipitates, thus dissolving the previous  $\text{Zn}(\text{OH})_2$  layer, and hydration can resume.

The mechanism inducing a delay when ZnO is added to the raw-mix is probably the same, the main difference being that the  $\text{Zn}^{2+}$  concentration in solution will depend on the release of zinc from the dissolution of the zinc-bearing phases of clinker. Zinc has been reported to enter alite structure up to 2.5% [14]. However, in a Portland cement clinker, zinc is mainly present in the interstitial phase, the concentrations in alite and belite being closer to 0.1% than 1% [3]. Apart from what is found in the melt, more zinc is found in alite than in belite [15]. Zinc is also frequently found in periclase (MgO) [15]. When a large amount of ZnO (>1%) is added to the raw-mix, the X-ray diffraction peaks of aluminate ( $\text{C}_3\text{A}$ ) are reduced while those of ferrite ( $\text{C}_4\text{AF}$ ) are increased [5, 16]. Bolio-Arceo and Glasser showed that this corresponds to the apparition of a new phase,  $(\text{CaO})_6(\text{ZnO})_3(\text{Al}_2\text{O}_3)_2$  (shorthand  $\text{C}_6\text{Z}_3\text{A}_2$ ). This phase was previously described as  $\text{C}_{14}\text{Z}_6\text{A}_5$  [17]. The zinc aluminate phase  $\text{C}_6\text{Z}_3\text{A}_2$  is reactive within a few hours or days and is considered as a cementitious material [3]. MgO can substitute ZnO in  $\text{C}_6\text{Z}_3\text{A}_2$ , giving the  $\text{C}_6(\text{Z}_{1-x}\text{M}_x)_3\text{A}_2$  solid-solution [3]. Some authors find ZnO by SEM+EDS observations [7].

Bolio-Arceo and Glasser [3] report that synthetic  $\text{C}_6\text{Z}_3\text{A}_2$  added to cement delays the setting time by a factor  $\sim 2$ . When the equivalent quantity of ZnO was added to the raw-mix, no delay was observed. There may thus be a difference of reactivity (and a difference of zinc release into solution) between synthetic  $\text{C}_6\text{Z}_3\text{A}_2$  and the phase obtained during clinker sintering. This difference could come from MgO substitution: ZnO substitution in periclase has been reported by Andrade [15], and ZnO substitution in  $\text{C}_6(\text{Z}_{1-x}\text{M}_x)_3\text{A}_2$  by Bolio-Arceo [3]. No result discussing the impact of this MgO-ZnO substitution could be found in literature.

The present study aimed at evaluating how MgO in the raw-mix could limit the negative effects of zinc addition. The impact of ZnO addition to clinker raw-mix composition and reactivity was studied, with a specific focus on a possible coupling between MgO and ZnO. It appears that high MgO raw-mixes seem less sensitive to ZnO addition. A combination of ZnO and MgO under the form of a solid-solution could explain this result.

## 2. Experimental protocols

The study was lead with clinkers synthesized from pure  $\text{CaCO}_3$ ,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ . The synthetic clinkers were made with the following composition: 80.1%  $\text{CaCO}_3$ , 15.1%  $\text{SiO}_2$ , 3.0%  $\text{Al}_2\text{O}_3$  and 1.7%  $\text{Fe}_2\text{O}_3$  in order to give a potential Bogue composition of 65%  $\text{C}_3\text{S}$ , 18%  $\text{C}_2\text{S}$ , 8%  $\text{C}_3\text{A}$ , 8%  $\text{C}_4\text{AF}$  and 1% free lime.

Zinc and magnesium were respectively introduced in the raw-mix under the form of ZnO and MgO. In the remainder of the document, clinkers will be named after the percentage of ZnO (or MgO) in the raw-mix. The raw-mixes were homogenized for two hours, then dried at 110°C and pressed into pellets. The raw-mixes were decarbonated at 1000°C for one hour before being burnt at 1450°C for 30 minutes and quenched. The free-lime was 0.9% for the clinker free from ZnO and MgO (reference clinker). It was chosen to keep the basic raw-mix and burning protocol constant despite the different free-lime values obtained and the potential impact of cement performance, as setting for instance.

Pure gypsum was added to clinkers in order to reach 3% SO<sub>3</sub>. The mix was ground in order to reach a Blaine specific surface of 3800 cm<sup>2</sup>/g.

The clinker compositions were checked by X-ray fluorescence. The mineralogy of the clinkers was studied by X-ray diffraction. The composition of the clinker phases was investigated by scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS). The reactivity of the cements was evaluated through conductivity measurements in suspension (liquid / solid ratio = 20) and calorimetry measurements (liquid / solid ratio = 0.4). In some specific cases the ionic concentrations in solution were measured by induced coupled plasma (ICP).

### **3 Impact of ZnO addition**

This first section focuses on MgO-free systems. The localization of ZnO and the impact of ZnO addition to MgO-free raw-mixes or MgO-free clinkers are studied.

#### **3.1 Delay of hydration due to ZnO addition**

As shown in Fig. (1) and Fig. (2), ZnO addition (1%) to the raw-mix delays cement hydration. However the effect is much less detrimental than when ZnO is added to cement. As discussed in the introduction, this can be attributed to the fact that zinc is much more readily available when added to cement under the form of ZnO than when it is incorporated in the clinker phases.

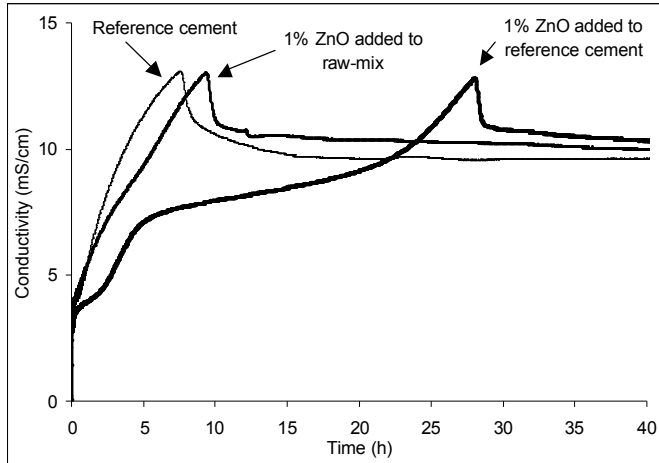


Figure 1: conductivity measurements on synthetic cements: impact of the way of introduction of ZnO.

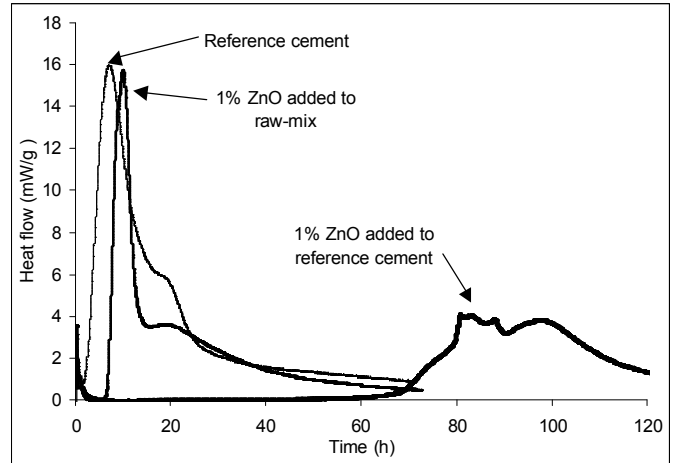


Figure 2: calorimetric measurements on synthetic cement: impact of the way of introduction of ZnO.

### 3.2 Localization of ZnO in clinker

As reported by other authors, zinc is mainly found in the interstitial phase of clinker ( $C_3A$  and  $C_4AF$ , cf. Table 1). ZnO is also detected by SEM + EDS as “white spots” at the interface between alite or belite and the interstitial phase (Fig. 3). The exact composition of the “white spots” could not be determined since the dimension of these spots is too small ( $\sim 1\mu\text{m}$ ), but EDS measurements showed a high level of zinc. As reported by Bolio-Arceo and Glasser [16], at high ZnO levels (2 and 5% ZnO), the  $C_6Z_3A_2$  phase is observed by SEM in the interstitial phase (Fig. 4) and detected by XRD.

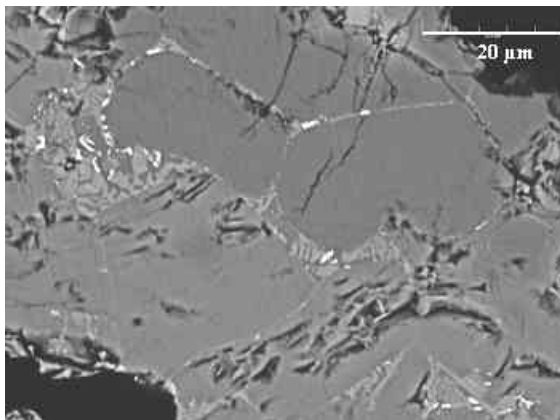


Figure 3: zinc-bearing “white spots” detected on clinker with 1.5% ZnO added to raw-mix.

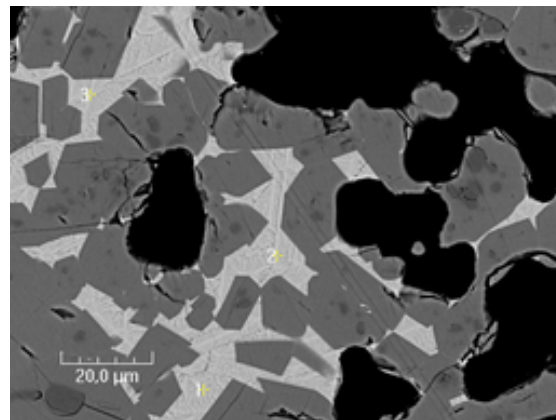


Figure 4: SEM image showing the interstitial phase made of finely intermixed  $C_4AF$  and  $C_6Z_3A_2$  in a clinker synthesized with 5% ZnO.

Table 1 : zinc localization in clinker phases, as determined by EDS (1% ZnO added to raw-mix).

Clinker phase	% Zn in clinker phases (at. wt.)
C <sub>3</sub> S	0.25
C <sub>2</sub> S	0.55
C <sub>3</sub> A	1.8
C <sub>4</sub> AF	1.6

#### 4 Impact of ZnO in presence of MgO

##### 4.1 Effect of MgO added to raw-mix

The presence of MgO in the raw-mix strongly reduces the negative impact of ZnO during hydration. For instance the comparison between the calorimetric curves of Fig. (5) (raw-mix without MgO) and Fig. (6) (raw-mix with 2% MgO) shows that the delay induced by the presence of ZnO is reduced from ~5 hours to ~2 hours. Moreover, the integrated area of the curves (heat of hydration) before 24h or 40h is much less reduced when MgO is present in the raw-mix.

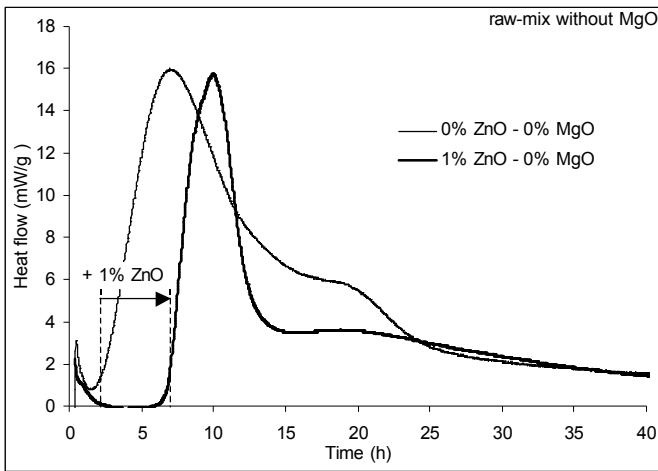


Figure 5: calorimetric measurements with ZnO and no MgO in the raw-mix.

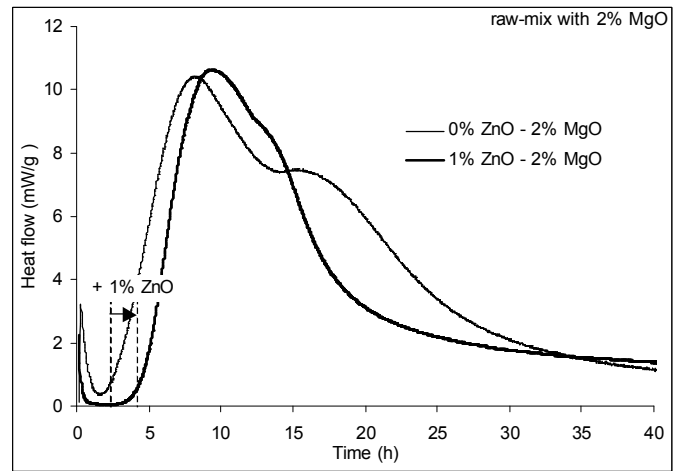


Figure 6: calorimetric measurements with ZnO and MgO in the raw-mix.

##### 4.2 Impact of MgO added to cement

The conductivity curves (Fig. 7) show that MgO addition is effective only if MgO is added to the raw-mix. MgO addition to cement has no effect. Thus MgO interferes with ZnO during clinkering.

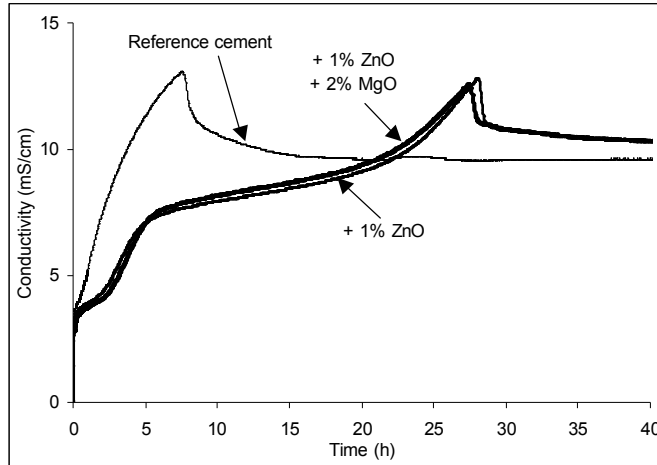


Figure 7: effect of ZnO and MgO addition to cement (conductivity measurements).

#### 4.3. Impact of MgO on ZnO distribution in clinker

Since MgO is effective only if present in the raw-mix, it should have an impact on clinker mineralogy or clinker phases composition. X-ray diffraction studies showed no detectable modification of the mineralogy when 2% MgO was added to the raw-mix, apart from periclase. The impact of MgO present in the raw-mix was thus studied for both the zinc-bearing “white spots” and zinc distribution in clinker phases.

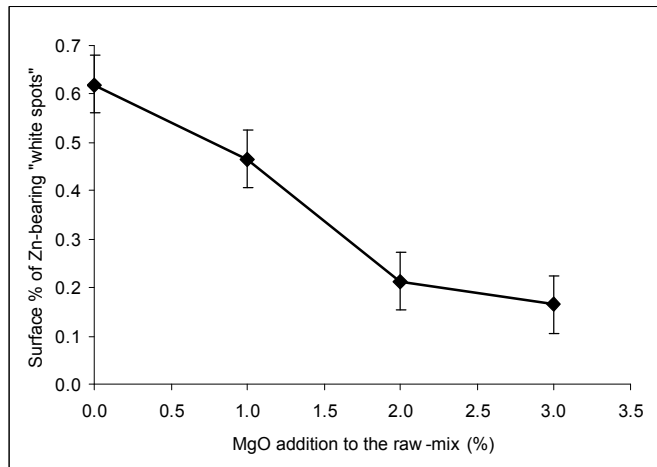


Figure 8: impact of MgO addition on the quantity of zinc-bearing “white spots” as determined by image analysis (1% ZnO added to raw-mix; error bars= $\pm$  1 standard deviation).

Image analysis of SEM results show that the quantity of zinc-bearing “white spots” (surface of white spots determined on 10 pictures  $80 \mu\text{m} \times 60 \mu\text{m}$ , thresholding made with Aphelion software [18]) strongly decreases when MgO is added to the raw-mix (Fig. 8). If the “white spots” are believed to be the main zinc-bearing phase, thus MgO addition clearly

modifies the ZnO distribution in clinker. In order to determine the new distribution of zinc, SEM-EDS results have been analyzed in order to determine the zinc content of each clinker phase as a function of MgO addition to the raw-mix (Fig. 9Figure ). As can be seen, the zinc content in the silicate phases is around 0.2-0.3% and is unaffected by the MgO content in the raw-mix. On the contrary, MgO addition to the raw-mix strongly modifies the zinc content of the aluminate phases, which increases until an optimum for C<sub>3</sub>A and a plateau for C<sub>4</sub>AF around 2% MgO, which probably corresponds to periclase (MgO) formation. This hypothesis is enforced by the strong diminution of the magnesium content in the C<sub>3</sub>A above 2% MgO. Zinc incorporation in the aluminate phases could explain the diminution of the surface of zinc-bearing “white spots”.

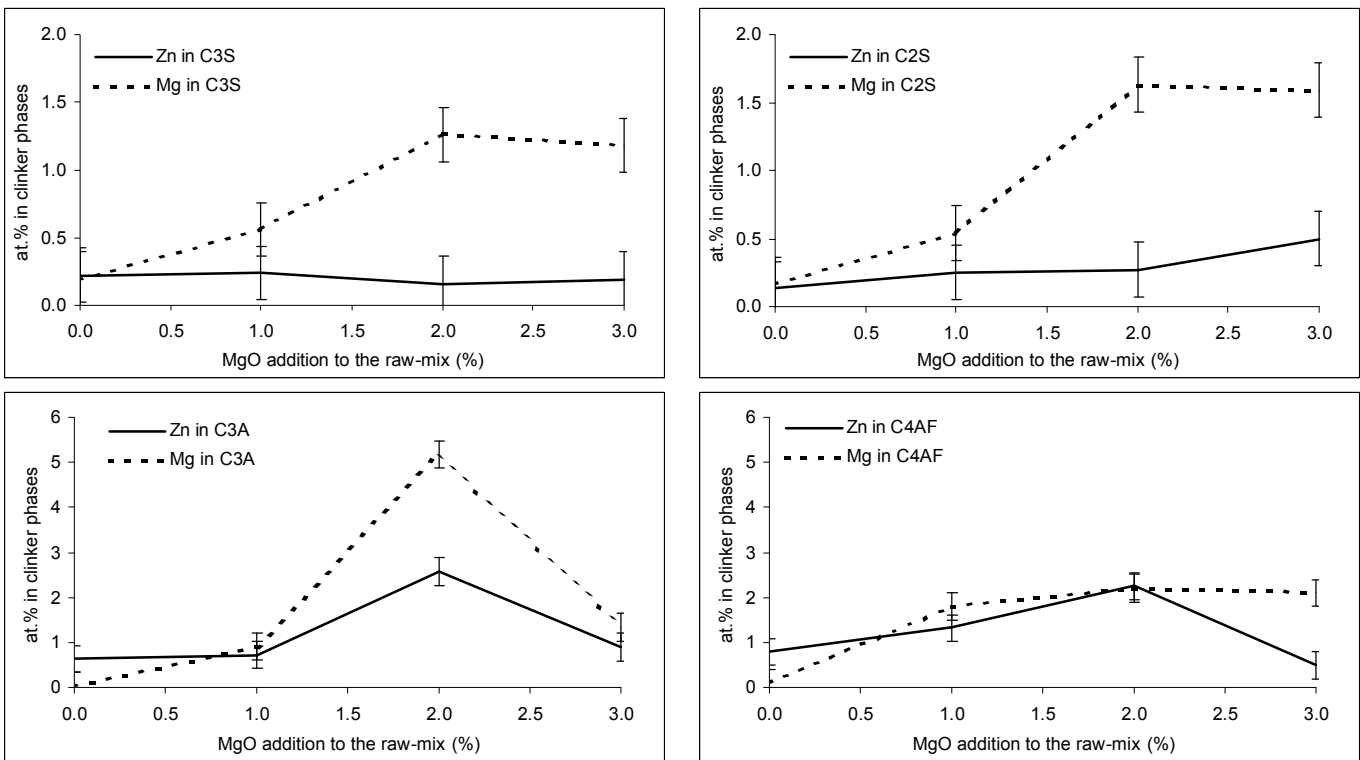


Figure 9: impact of MgO addition on the MgO and ZnO distribution in clinker phases, as determined by EDS.

#### 4.4 Impact of MgO-ZnO solid-solution on hydration

In order to validate that the action of MgO is to trap ZnO under the form of a MgO-ZnO solid-solution, thus reducing the negative impact of zinc during hydration, a MgO-ZnO solid-solution was synthesized and added to the cement. According to the phase diagram for MgO-ZnO [19], a 70% MgO–30% ZnO solid-solution was synthesized at 1450°C (Fig. 10). X-ray diffraction confirmed that this compound had the same diffraction pattern as periclase.

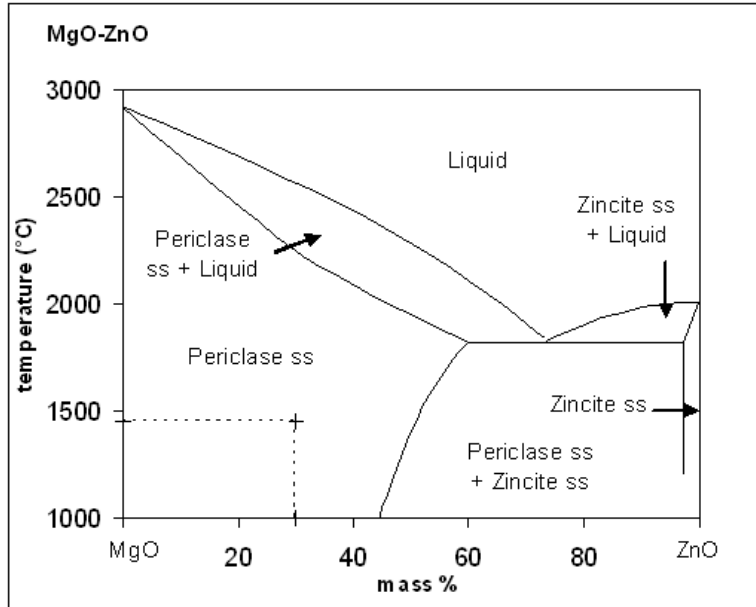


Figure 10: schematic representation of the MgO-ZnO phase diagram, after to [18]. The MgO-ZnO solid-solution synthesized in this work is represented by symbol “+”.

It is clear from conductivity measurements (Fig. 11) that the addition of a MgO-ZnO solid-solution to cement is much less detrimental than pure ZnO addition to the raw-mix. Zinc incorporated in periclase is probably less readily available than zinc under the form of zincite or in the aluminate phases, and thus is more slowly released in solution where it can act as a retarder of cement hydration.

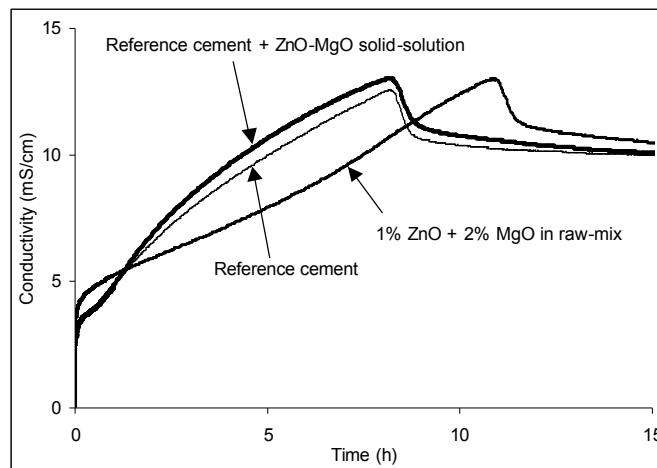


Figure 11: conductivity measurements: effect of the way of introduction of ZnO and MgO.

This mechanism is observable by measuring the concentration of zinc in solution during hydration (Fig. 12). When a clinker has been made from a raw-mix containing 2% MgO, the zinc concentration in solution is much



lower (by up to a factor  $\sim 4$ ) than when the raw-mix is free from MgO. The release of zinc is slower when MgO is present, probably due to the combination between MgO and ZnO under the form of a solid-solution. This lower zinc concentration limits the retarding effect of zinc present in the raw-mix.

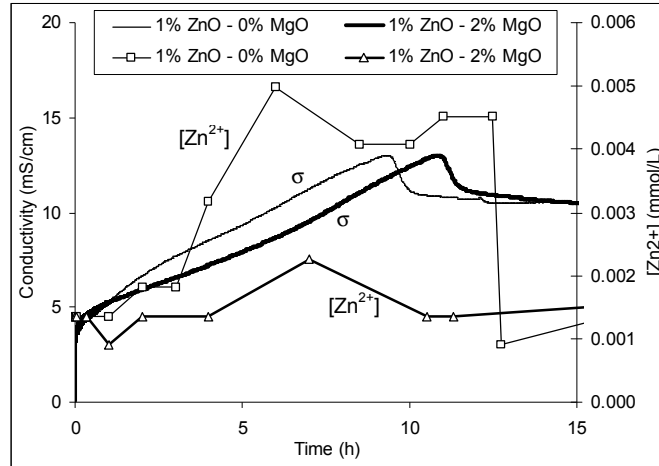


Figure 12: zinc concentration in solution during cement hydration (clinker with 1% ZnO, with 0 or 1% MgO), and correlation with portlandite precipitation as observed by conductimetry ( $\sigma$  curves).

## 5 Conclusions

Zinc appears to enter the clinker phases up to a value between 0.5 and 1% ZnO / raw-mix. At higher levels of ZnO, zincite or the calcium-zinc-aluminum phase ( $C_6Z_3A_2$ ) are observed. The delay in hydration due to ZnO can be attributed to the presence of zinc ions in solution. In this respect, ZnO addition to cement has a much more negative effect than ZnO added to the raw meal (more slowly released from clinker).

The presence of MgO in the raw-mix leads to a lower sensitivity of the clinker to ZnO addition. In other words, a raw-mix with a significant MgO content seems less affected by ZnO addition than a low MgO raw-mix. A proposed mechanism is that MgO incorporates ZnO under the form of a periclase solid-solution. The release of zinc ions in solution is then slower, and the delay due to zinc is reduced. Further research should focus on proving the formation of the MgO-ZnO solid solution in the clinkers.

These results have been obtained on synthetic clinkers. For industrial purposes, the way of introduction of zinc and the presence of other elements such as alkali and sulfate may modify the incorporation of zinc in clinker. The effect of MgO may thus be modified.

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