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## Effect of cooling rates on the properties of Portland cement clinkers in the presence of Mg

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### ABSTRACT

In order to enhance the performance of Portland cement clinker, this study investigates the effect of cooling rates on the mineralogical composition of cement clinkers containing magnesium (Mg), which is the most common minor element in raw materials (e.g., limestone). Three cooling regimes were considered to simulate industrial kiln processing conditions. MgO contents of 0, 3, and 6 wt.% were considered in this study. After synthesis of the clinkers, quantitative X-ray diffraction is used to investigate the mineralogical composition, as well, the phase amounts using the Rietveld method. The results show that rapid cooling and Mg doping can promote the formation of alite, and monoclinic alite can be stabilized via Mg ions. Slow cooling and Mg incorporation can stabilize  $\gamma$ -C<sub>2</sub>S, but a rapid cooling rate is still effective to restrain the transformation from  $\beta$ -C<sub>2</sub>S to  $\gamma$ -C<sub>2</sub>S in MgO-doped clinker. The cooling rates do not influence the content of ferrite and C<sub>3</sub>A obviously, but the MgO incorporation can enhance the ferrite formation and reduce the C<sub>3</sub>A content. At a slow cooling rate, little Mg can dissolve in clinker phases, but the retention of MgO in clinker phases can be increased by a fast cooling rate. Therefore, the effect of MgO on the mineralization and the solubility of MgO is a function of cooling rates.

**KEYWORDS:** *Portland cement; clinker, magnesium; cooling rate.*

### 1. Introduction

With a decrease in the availability of high-purity raw materials and the need for emission reduction and material circularisation to achieve sustainability, the utilization of alternative raw materials and fuels in clinker production is unavoidable in various parts of the world. These alternative raw materials will introduce minor elements into the cement clinker, which can affect the formation and mineralogical composition of this clinker. Notably, magnesium is the most common guest element in raw meals for cement clinker manufacture. Additionally, the fate of magnesium oxide (MgO) in the clinker can be influenced by cooling rates

A MgO content in cement as high as 18.5% is still possible in some countries (Song et al (2021)). However, excess magnesium would form periclase (f-MgO), which would cause a 118% volume increase after hydration to form Mg(OH)<sub>2</sub> (Mo et al (2014)) and damage the concrete. Therefore, it is better to limit the formation of periclase. Conversely, the proper amount of MgO can reduce the burnability of raw meals (Zhao et al (2021)), since MgO can lower the liquidus temperature of cement clinker manufacture, which has a positive effect on reducing the consumption of fuels and the carbon dioxide footprint. Additionally, the solid solubility of MgO in clinker can be affected by cooling rates. Therefore, this study investigates the fate of Mg in cement clinker with different dosages and cooling regimes.

### 2. Materials and methods

## 2.1 Raw mixtures

The clinker composition is designed with fixed values of lime saturation factor (LSF), silica modulus (SM) and alumina modulus (AM) of 0.94, 2.5 and 1.4 respectively, and 0, 3, and 6 wt.% MgO was mixed into the raw materials. The synthesis of clinker involves the utilization of high-purity natural limestone ( $\text{CaCO}_3$ ) and silica flour ( $\text{SiO}_2$ ), combined with chemical grades such as aluminium oxide ( $\text{Al}_2\text{O}_3$ ), iron oxide ( $\text{Fe}_2\text{O}_3$ ) and magnesium oxide (MgO).

**Table 1. Information on the raw materials used in this study.**

Chemicals	Purity (%)	Supplier
Limestone	99.3	Glassworks Services
Silica flour	99.7	Industrial Mineral Services Ltd
Aluminium oxide	99	Acros Organics
Iron oxide	96	Sigma Aldrich
Magnesium oxide	99.95	Thermo Scientific

## 2.2 Clinkering and cooling regimes

The raw materials were mixed for 10 min with a grinding speed of 300 rpm in a ball mill (Planetary Ball Mill PM100) which is equipped with an 80 ml jar and 5mm balls made of zirconia. The raw mix was compressed into pellets using a hydraulic press. The pellets were heated from 1000°C to 1450°C at a heating rate of 10 K/min, followed by an isothermal hold for 30 min at 1450°C in the elevator furnace (BLF 17/3, Carbolite Gero).

Following the heating process, the hot clinkers were cooled through three cooling rates respectively. 1) Slowly cool in the furnace at a cooling rate of 1 K/min; 2) Quench in the air with fan assistance; 3) Quench in water via a platinum crucible which holds the clinkers. The name of the samples is shown in Table 2.

**Table 2. The Mg doped content and cooling regimes of the clinker.**

Name	Mg doping (%)	Cooling regimes
0MgO-S	0	1 K/min
0MgO-A		Air
0MgO-W		Water
3MgO-S	3	1 K/min
3MgO-A		Air
3MgO-W		Water
6MgO-S	6	1 K/min
6MgO-A		Air
6MgO-W		Water

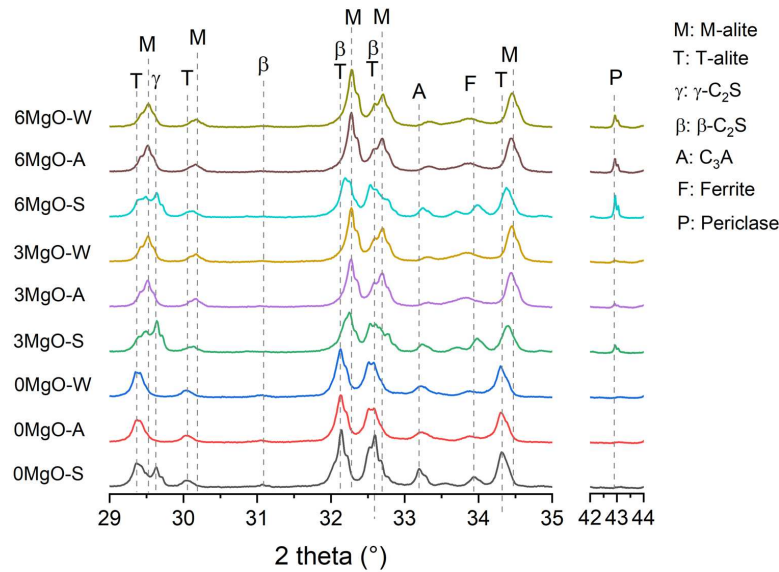
## 2.3 X-ray diffraction (XRD)

The resulting clinkers were characterized through XRD using a PANalytical X'Pert<sup>3</sup> powder diffractometer operating at 45kV and 40 mA. The data were collected under a rotating mode, with a scanning range of 10-80° (2 $\theta$ ) and a step size of 0.013° (160 s per step). The powders were sieved to -63  $\mu\text{m}$ . Topas v6 was used to execute Rietveld quantitative analysis.

## 3. Results and discussions

Figure 1 shows the XRD patterns of cement clinker doped with 0, 3, and 6 wt.% MgO and cooled at different cooling rates. The incorporation of MgO into the clinkers leads to a shift in the peak positions of alite, because Mg ions can promote the formation of high-temperature alite (monoclinic alite (M-alite))

which has higher peak positions than triclinic alite (T-alite). Whereas, a higher MgO content cannot widen the peak shift. In addition, slow cooling promotes the formation of  $\gamma$ -C<sub>2</sub>S, and MgO cannot restrain the  $\gamma$ -C<sub>2</sub>S formation.



**Figure 1. The XRD patterns of cement clinkers doped with 0, 3, and 6 wt.% MgO cooled at three cooling rates.**

Figure 2 shows the phase contents of cement clinkers calculated through the Rietveld method; all the  $R_{wp}$  values are below 5% which indicates the reliability of the fittings. No significant difference in phase content can be observed between cooling in air and water, probably because the clinker cooled in water mainly dissipate the heat through air. The water just cooled the platinum crucible and just a small area of clinker touched the crucible. Therefore, in the following content, both cooling in air and water are called rapid cooling. The alite content decreased under a slow cooling rate, and Mg can increase the alite ratio. More Mg ions can retain in alite phase at a rapid cooling rate and Mg ions preferably substitute the Ca atoms in tricalcium silicate (C<sub>3</sub>S), leading to the detachment of Ca ions. The released Ca ions combine with belite to form more alite, leading to the decrease of belite, shown in Figure 2. Whereas, the alite content does not show a noticeable difference in clinkers doped with 3 wt.% MgO and 6 wt.% MgO, because of the low solubility of Mg in clinker. Cooling rates also have a vital impact on the formation of belite.  $\gamma$ -C<sub>2</sub>S can form in 0MgO-S clinker, and more  $\gamma$ -C<sub>2</sub>S was observed in MgO-doping clinkers, which indicates the Mg ions can stabilize  $\gamma$ -C<sub>2</sub>S under slow cooling, which conforms to the results of Feng and Long (Feng and Long (1986)). Normally,  $\gamma$ -C<sub>2</sub>S is not a desirable form in a Portland cement clinker because of its low hydration reactivity. Although Mg ions can stabilize  $\gamma$ -type C<sub>2</sub>S, a rapid cooling rate is also effective to inhibit the formation of  $\gamma$ -C<sub>2</sub>S, even in high-Mg concentration clinkers.

The cooling rates do not have an evident influence on the formation of tricalcium aluminate (C<sub>3</sub>A). Additionally, MgO doping can reduce the C<sub>3</sub>A content and increase ferrite content. The Fe and/or Al atoms in ferrite can be occupied by Mg ions (Zhao et al (2021)), and the escaped Fe and/or Al ions combine with C<sub>3</sub>A to form more ferrite leading to a decrease in C<sub>3</sub>A. A rapid cooling rate is also effective to increase the ferrite content, because Mg ions preserve in ferrite phase. However, increasing the content of MgO to 6 wt.% cannot further increase the ferrite content due to the low solution limit of MgO.

2.9 wt.% of MgO was observed in the 3MgO-S clinker, which indicates only a small amount of Mg was found to dissolve in the cement clinker phases, but the solubility can be increased by fast cooling. In this study, the solubility limit of MgO in cement clinker is about 1.1 - 1.5 wt.% which is in line with the published limit of 1.3 wt.% reported by Zhao (Zhao et al (2021)). And, the solid solution limit of MgO also relates to the AM value (Zhang et al (2022)). The calculated MgO value in 6MgO-S clinker is higher than the additive amount, probably because some amorphous in this group of clinker cannot be calculated

by XRD method. So, an internal standard is required to calculate a precise MgO content. All the clinkers have little lime, which means the good burnability of raw materials in this project. This agrees with the results (Zhang et al (2015)), who concluded that with a low doping level, MgO can decrease the content of free lime. Or, some lime is amorphous in the clinkers, and cannot be observed by XRD technique, so a solution rapid testing method is required to further determine the content of free lime.

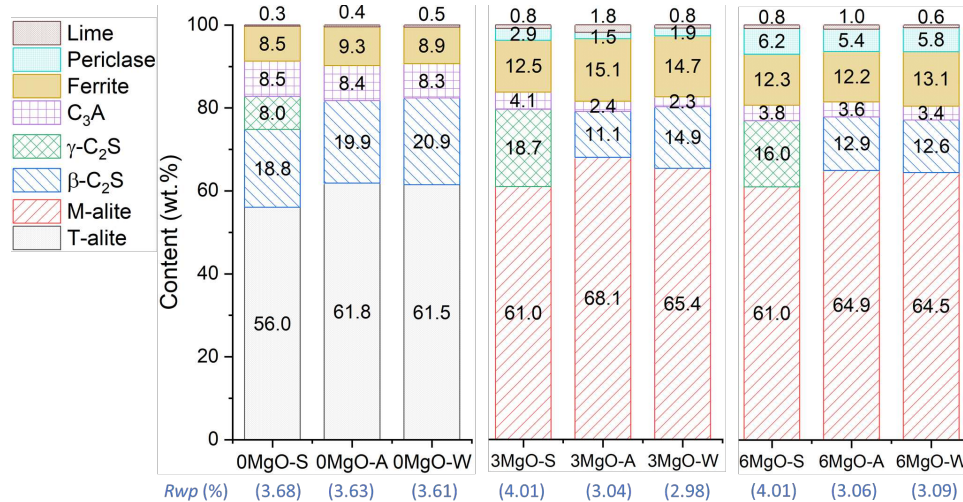


Figure 2. The phase content of clinkers doped with 0, 3, and 6 wt.% MgO at different cooling rates.

#### 4. Conclusion

In summary, the MgO can influence the crystal forms of alite and belite, and the fate of MgO in cement clinker can be influenced by cooling regimes. MgO can enhance the formation of high-temperature alite (M-alite), while stabilize low-temperature belite ( $\gamma$ -C<sub>2</sub>S). However, a rapid cooling rate can restrain the transformation of  $\beta$ -C<sub>2</sub>S to  $\gamma$ -C<sub>2</sub>S even in a high MgO-doped clinker. A high cooling rate is also beneficial to improve the retention of Mg in clinker phases.

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