

EFFECT OF CALCIUM CHLORIDE ADDITION ON THE HYDRATION BEHAVIOR OF CALCIUM MAGNESIUM ALUMINATE CEMENT

QINGFENG WANG*

School of Materials Science and Engineering, Luoyang Institute of Science and Technology, 90, Wangcheng Avenue, Luoyang 471023, Henan, China

The calcium magnesium aluminate cement often presents a longer setting time than the conventional calcium aluminate cement containing 70wt. % Al_2O_3 , owing to the presence of the $MgAl_2O_4$ spinel in the cement clinker. In this paper, calcium chloride was used to control the hydration rate of the cement containing $MgAl_2O_4$ spinel. The temperature development of cement pastes was employed to characterize the hydration and setting behavior of the cement. The electrical conductivity measurement was utilized to evaluate the dissolution-precipitation rate of the cement. X-ray diffraction was conducted to identify the hydrates after halting cement hydration by vacuum freeze drying at a certain curing time. And scanning electron microscopy was used to observe the microstructure development during the cement hydration. These results reveal that calcium chloride addition intensifies the hydration of the calcium magnesium aluminate cement.

Keywords: calcium chloride, calcium magnesium aluminate cement, hydration, dissolution-precipitation rate, microstructure

1. Introduction

It is known that the increasing application and demand in refractories technology has been the use of monolithic refractory materials as a substitute for conventional bricks, resulting from the ready availability, faster, easier, and cheaper installation, and fewer corrosion-susceptible lining joints of refractory castables than the ones of shaped bricks [1]. And these refractory castables are commonly based on the hydraulic binders, which contain anhydrous mineralogical compounds that can react with water to form hydrated phases. And these hydrates can interlock or bind each other to give green mechanical strength of castables after demolding. Among these hydraulic binders, calcium aluminate cement (CAC) has been widely used as binder agent for refractory castables in industrial application, due to the fast setting and low cost as well as high strength and resistance to the aggressive environments.

Meanwhile, magnesium aluminate spinel (MA) is a technologically important material with very attractive properties, such as high melting point (2135°C), low thermal expansion coefficient, considerable hardness and high resistance to chemical attack [2]. Consequently, the addition of spinel to refractories for secondary metallurgy has been extensively applied to reduce the intensive

wear imposed by the steel ladle harsh environment [3]. However, there are different spinel incorporation route (in situ reaction or pre-formed grains addition), which plays a relevant role in the properties of refractories, such as thermal shock resistance, volumetric stability and mainly basic slag corrosion resistance. Usually, in-situ spinel can be produced by the reaction of fine alumina and magnesia in alumina-magnesia castables at high temperature. But the reaction of in-situ spinel formation is associated with a severe volume expansion of $\Delta V/V = 8.1\%$, which might hinder the formation of dense microstructure and causes the damage of castables in service at elevated temperatures [4, 5]. In order to overcome the volume expansion of in-situ spinel formation, the preformed spinel grains can be chosen as an alternative raw material in the manufacture of castables [6]. And it has been found that a dense microstructure associated with small crystal sizes of preformed spinel grains should be responsible for the higher corrosion resistance of castables at high temperatures [6].

Considering these advantages of preformed spinel with small crystal sizes, a new type of aluminous cement with microcrystalline magnesium aluminate spinel phase in the calcium aluminate cement clinker has been manufactured either by grinding a mixture of pre-prepared high alumina cement (>70% alumina) and prefabricated MA

* Autor corespondent/Corresponding author,
E-mail: qingfengwang_1@163.com

spinel, or the use of appropriate mixtures of raw dolomite (source of CaO and MgO) and active alumina as raw materials [7]. And the refractory castables bonded by the cement containing $MgAl_2O_4$ spinel have shown the increased thermal shock resistance [8] and slag attack resistance [7]. Therefore, calcium magnesium aluminate cement is gaining the interest for bonding refractory castables over the last few years [4, 9].

Nevertheless, the substitution of CaO by MgO in the cement clinker leads to the increased contents of hydraulically inert spinel and decreased contents of hydraulic phases, such as monocalciumaluminate ($CaO \cdot Al_2O_3$, CA) and calcium dialuminate ($CaO \cdot 2Al_2O_3$, CA₂), which brings to the deteriorated hydration and setting behavior of calcium magnesium aluminate cement. Consequently, the hydration behavior of calcium magnesium aluminate cement has been promoted as an important technological issue to enhance installation performance of castables.

Considering the fast rate of calcium aluminate cement hydration and hardening, some small quantities of retarders are frequently used to modify the hydration rate, in order to control the productivity of castable installation. It is generally agreed that retarders influence the kinetics of hydration by slowing down the dissolution of the anhydrous cement particles. On the other hand, accelerators can be used to influence mainly the dormant period of hydration [1]. For example, Li_2CO_3 has been proved to be the one of effective additives to accelerate the hydration of calcium magnesium aluminate cement [8]. The reason for this action is that Li^+ ions in solution lead to the formation of insoluble hydrates, such as $LiAl(OH)_4$, which can withdraw $Al(OH)_4^-$ ions from the solution. As a result, the Ca^{2+} ions concentration in solution increases, which favors the formation of calcium aluminate hydrates richer in calcium, accelerating the precipitation stage [10]. Apart from lithium

salts, however, some other salts which contain calcium cation can also be used as accelerators to improve the setting behavior of CAC [11]. And these compounds containing calcium can also lead to the improved properties of corundum-based castables at elevated temperatures due to the formation of calcium aluminates ($CaO \cdot 2Al_2O_3$ and $CaO \cdot 6Al_2O_3$) [12]. Although the hydration of CAC in the presence of calcium chloride has been studied, the effect of calcium chloride addition on the hydration and setting behavior of the calcium magnesium aluminate cement is not completely investigated yet. Therefore, calcium chloride ($CaCl_2 \cdot 2H_2O$) was used in this work to adjust the hydration rate of calcium aluminate cement containing spinel at 20°C. The hydration behavior of the cement containing spinel with different additions of calcium chloride was determined by the hydration heat evolution, and the dissolution-precipitation rate of cement particles was evaluated by the electrical conductivity of cement aqueous suspensions measurements. Furthermore, the vacuum freeze drying method was used to stop the cement hydration at the designated times. The hydrates were examined by XRD analysis and SEM.

2. Materials and methods

Calcium magnesium aluminate cement (CMA 72, Kerneos, France) was used in this work and calcium aluminate cement (Secar 71, Kerneos, China) as the reference. The mineralogical compositions of these cements are shown in Table 1.

Considering the fact that the initial setting time determined by the standard Vicat needle measurements is significantly affected by the water/cement ratio attributable to the consistency of the tested paste, calorimetry or temperature rise measurements can be used as alternative

Table 1

Mineralogical composition of Secar 71 and CMA 72 cements.

Binder type	CA (%)	CA ₂ (%)	C ₁₂ A ₇ (%)	C ₄ A\$ (%)	C ₂ AS (%)	α-Al ₂ O ₃ (%)	Spinel MA (%)
Secar 71	59.06	35.95	0.30	0.46	0.69	1.79	0
CMA 72	18.5	10	1.21	0.04	0	0	70

Cement chemistry abbreviations: C=CaO, S=SiO₂, A=Al₂O₃, \$=SO₃, M=MgO

Table 2

Compositions of cement pastes

Binder type	Relative mass ratios of calcium chloride to cement wt. %	Composition		
		Cement g	Water g	Calcium chloride g
CMA 72	0	150	45	0
	0.055	150	45	0.083
	0.55	150	45	0.83
	1.113	150	45	1.67
	2.78	150	45	4.17
	5.553	150	45	8.33
	11.113	150	45	16.67
Secar 71	0	150	45	0

techniques to obtain the accurate values of the setting time parameters, such as the induction time and the time of the maximum temperature hydration peak [10, 13]. Therefore, the hydration and setting behaviors of CMA 72 were investigated by means of semi-adiabatic method according the standard of EN196 in the present paper.

In order to modify the hydration behavior of CMA 72, different amounts of calcium chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, analytical pure, Sinopharm chemical reagent Co., Ltd, China) were used as accelerators based on the mass fraction (relative to weight of cement) ranging from 0.055 % to 11.113 %, as shown in Table 2.

All the neat cement pastes were prepared with a water/cement mass ratio of 0.30. To prepare these cement pastes, the cements, calcium chloride and water were all kept at 20°C for 24h before mixing. Then, the adequate amount of water was placed into a plastic cup and calcium chloride was added into the water. After that, the cement powder was gradually added with continuously mixing by hand. After mixing, the fresh cement pastes were vibrated for 1 min to remove air voids and immediately put into an insulating box at 20°C . And the temperature resulted by the heat release as a function of time was recorded by a T-type thermocouple immersed into the paste, which was linked to a data capture system and the temperature was recorded.

Furthermore, the cement pastes with the compositions shown in Table 2 were cured at 20°C for 14h and 24h, respectively. After that, the pastes with different contents of calcium chloride were frozen for 1.5 h at -40°C to stop the cement hydration, and the frozen pastes were immediately dried in a vacuum box under a pressure of 60 Pa at 20°C . The phases and morphology of these dried cement pastes were characterized by X ray diffraction (XRD D8 Focus, Bruker, Germany) and scanning electron microscopy (SEM KYKY-2800B, China), respectively. Additionally, the electrical conductivity measurements were carried out by inserting a conductivity electrode (Inlab731, Mettler Toledo, Switzerland) into the cement aqueous suspensions (with $W/C=5$) containing the same amounts of calcium chloride (as shown in Table 2) at 20°C and 80% RH.

3. Results and discussions

During the hydration of the most reactive phases of calcium aluminate cement, a certain amount of heat is generated, increasing the temperature of cement paste and promoting the cement hydration process. Generally, during the hydration of calcium aluminate cement, two exothermic peaks can be observed. The first minor temperature peak during the first few minutes on the exothermic curve can be attributed to the wetting of cement particles in the solution [14], and

the second large temperature peak should stand for the hydrates precipitation which means the beginning of the cement setting [10]. Consequently, the time between two exothermic peaks is correlated to the dormant period of cement hydration [15]. In this way, the temperature evolution of hydraulic binder pastes can be monitored with the help of a thermocouple and used as a measure of the cements hydration.

It is seen in Figure 1 that CMA 72 paste without calcium chloride has a dormant period about 12h and a setting time about 15h. In comparison, the Secar 71 paste without calcium chloride has a dormant period about 7h and a setting time about 13h. This difference in the hydration behavior between CMA 72 and Secar 71 is especially due to the smaller amount of CA (18.5%) in the CMA 72, compared with the amount of CA (59.06%) in Secar 71 (see Table 1).

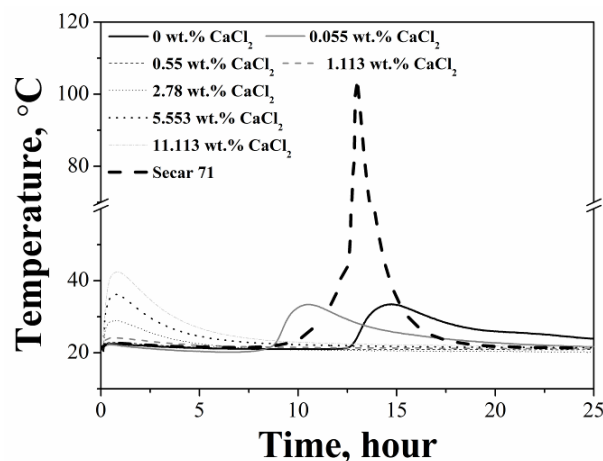


Fig. 1- Exothermic temperature curves for Secar 71, CMA 72 and CMA 72 with CaCl_2 at 20°C .

However, the dormant period and setting time of CMA 72 were reduced by the presence of calcium chloride in pastes. For example, the addition of 0.055wt. % calcium chloride resulted in the setting time of CMA 72 decrease to 10h, which was closer to the one of Secar 71 (13h). Moreover, a further increase of additive contents brought about the dramatic acceleration of the setting behavior. For example, the time corresponding to setting time decreased significantly to 45 min with addition of 1.113wt. % calcium chloride in CMA 72, which indicated the fact that much more calcium chloride addition led to a poorer workability than the one of Secar 71. Therefore, the optimum calcium chloride content for suitable setting time of CMA 72 is seen to be 0.055wt. %, whereas, other contents of calcium chloride made the cement set fast and could not provide sufficient work time for placing and installation. Therefore, 0.055wt. % calcium chloride addition was selected and its effect on the hydration of CMA 72 was explored in details by electrical conductivity, XRD and SEM, respectively.

In order to understand the effect of calcium chloride addition on the dissolution-precipitation rate of calcium magnesium aluminat cement, the electrical conductivity of solution containing the dissolved ions is carried out to monitor the cement hydration process. Because Ca^{2+} and $Al(OH)_4^-$ ions starts to leach from calcium aluminat cement into solution at the beginning of water contact with grains of cement, the electrical conductivity of aqueous cement suspensions increases in the early stages (Fig.2). After that, the plateau with a relatively stable conductivity can be observed. This feature is attributed to the induction period when crystallization nuclei are formed and the saturation stage is attained. Then, a rapid decrease in electrical conductivity is detected, which corresponds to the massive precipitation of hydrates in the solution [16].

In Figure 2 it can be observe that the conductivity of CMA 72 without additive increased slower than the one of Secar 71, which means that saturation or super saturation was attained later for CMA 72 paste without calcium chloride. And the time standing for dissolution-precipitation rate was about 6h for CMA 72 without additive, which was also longer than the one (about 4h) of Secar 71. This feature indicated a slower dissolution-precipitation rate of CMA 72, compared with the one of Secar 71. And these results can be attributed to the fact that CMA 72 has smaller content of hydraulic active phases than Secar 71 (as shown in Table 1), which also coincides with the slow hydration of CMA 72 without additives (as shown in Figure 1).

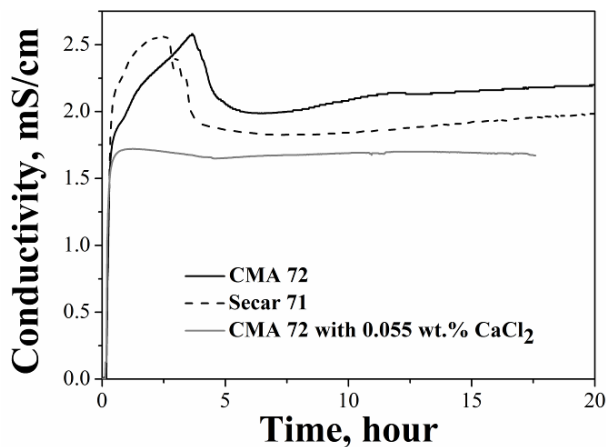


Fig. 2 - Electrical conductivity of cement aqueous suspensions.

However, the conductivity reached the maximum value at 1h for CMA 72 with 0.055 wt. % calcium chloride addition. This change indicated the development of saturation stage was the fastest for the suspension of CMA 72 with calcium chloride, compared with the ones of Secar 71 and CMA 72 without additive. And the dissolution-precipitation time (about 4h) of CMA 72 with calcium chloride was also shorter than the one

(about 5h) of CMA 72 without additive. Therefore, calcium chloride addition determines an accelerating effect on the dissolution-precipitation process of CMA 72, which is in agreement with faster setting behavior of CMA 72 with calcium chloride (as shown in Figure 1).

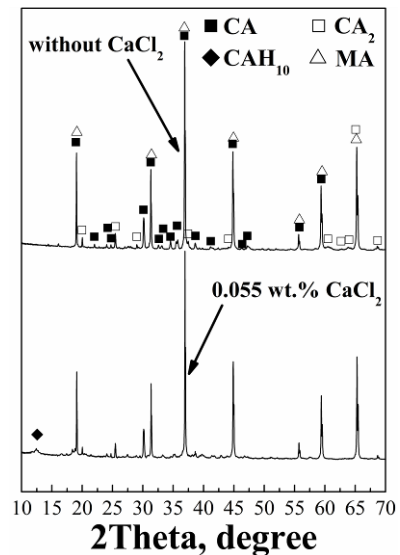


Fig. 3 - XRD patterns of CMA 72 pastes with and without calcium chloride after hydration for 14 hours.

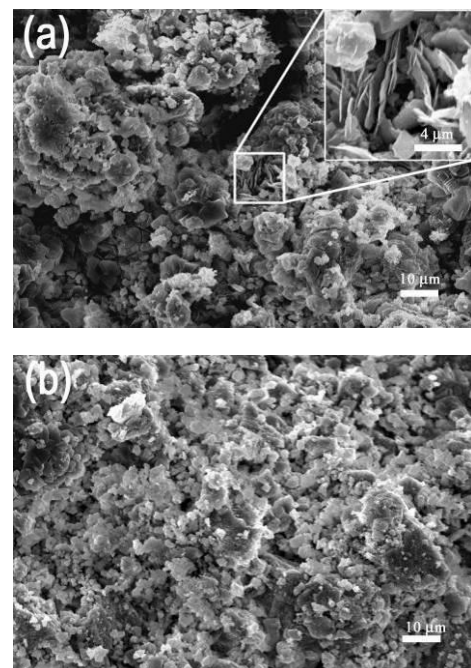


Fig. 4 - SEM images of CMA 72 pastes with (a) and without calcium chloride (b) after hydration for 24 hours.

Figure 3 shows the phase development in CMA 72 pastes with and without calcium chloride after curing at 20°C for 14 hours. The main crystalline phases in the CMA 72 paste without

calcium chloride are anhydrous CA, CA₂ and magnesium aluminate spinel only. In contrast, CAH₁₀ was found in the CMA 72 paste with 0.055wt. % calcium chloride after curing for the same time. These results indicate that the hydration rate of CMA 72 without calcium chloride is slower than that of the one with calcium chloride, suggesting that calcium chloride addition intensifies the hydration of CMA 72. These results are in agreement with the heat evolution (seen in Figure 1) and dissolution-precipitation rate (seen in Figure 2) of the samples.

Figure 4 shows the microstructure development of CMA 72 pastes with and without calcium chloride after hydration for 24h. Some elongated plates-like crystals of the hydrate (CAH₁₀) were found among the cement particles in CMA 72 paste with 0.055wt. % calcium chloride (Fig. 4a). In contrast, none of the similar grains could be observed in CMA 72 paste without calcium chloride after hydration for 24h (Fig. 4b). This difference in microstructure between CMA 72 with and without calcium chloride confirms the above observations that calcium chloride addition had an accelerating effect on the hydration of CMA 72.

4. Conclusions

With calcium chloride addition, the dormant period of CMA 72 was shortened and the dissolution-precipitation process of cement particles was accelerated, demonstrating that calcium chloride addition results in a faster hydration and a shorter setting time of CMA 72. At the same time, mass fraction as small as 0.055wt. % is enough to impart the suitable accelerating effect on the hydration process of CMA 72, compared with the setting time of Secar 71.

Furthermore, the results of XRD and SEM indicated that the hydrates emerged earlier in the CMA 72 with calcium chloride, compared with the CMA 72 without additive, confirming that calcium chloride addition accelerates hydration of CMA 72.

ACKNOWLEDGEMENTS

The authors acknowledge to the Foundation of High level talent research project of Luoyang Institute of Science and Technology (2015BZ05) and the State Key Laboratory of Advanced Refractories of China (201502) for the financial support.

REFERENCES

1. W. E. Lee, W. Vieira, S. Zhang, K. G. Ahari, H. Sarpoolaky, C. Parr, Castable refractory concretes. *International Materials Reviews*, 2001;46:145.

2. I. Ganesh, R. G. Jaganatha, G. Sundararajan, S. M. Olhero, P. M. C. Torres, J. M. F. Ferreira, Influence of processing route on microstructure and mechanical properties of MgAl₂O₄ spinel. *Ceramics International*, 2010, **36**(2), 473.
3. E. Y. Sako, M. A. L. Braulio, V. C. Pandolfelli, The corrosion and microstructure relationship for cement-bonded spinel refractory castables. *Ceramics International*, 2012, **38**(3), 2177.
4. C. Wohrmeyer, C. Parr, H. Fryda, J. M. Auvray, B. Touzo, S. Guichard, New spinel containing calcium aluminate cement for corrosion resistant castables. in *Proceedings of 12th Biennial Worldwide Conference on Refractories 2011*, Kyoto, October 2011, edited by N. Tsukamoto (Technical Association of Refractories, Japan, 2011) p. 476
5. E. Y. Sako, M. A. L. Braulio, P. O. Brant, V. C. Pandolfelli, The impact of pre-formed and in situ spinel formation on the physical properties of cement-bonded high alumina refractory castables. *Ceramics International*, 2010, **36**(7), 2079.
6. S. Mukhopadhyay, P. K. Das Poddar, Effect of preformed and in situ spinels on microstructure and properties of a low cement refractory castable. *Ceramics International*, 2004, **30**(3), 369.
7. N. M. A. Khalil, S. A. S. El-Hemaly, L. G. Girgis, Aluminous cements containing magnesium aluminate spinel from Egyptian dolomite. *Ceramics International*, 2001, **27**(8), 865.
8. J. H. Li, B. Y. Cai, W. W. Feng, Y. Q. Liu, H. W. Ma. Investigations on phase constitution, mechanical properties and hydration kinetics of aluminous cements containing magnesium aluminate spinel. *Ceramics International*, 2013, **39**(7), 8393.
9. J. M. Auvray, H. Fryda, C. Wohrmeyer, C. Parr, O. Pawlig, M. M. Martinez, New insights into corrosion mechanisms of dense refractory castables containing a novel calcium-magnesia-alumina binder. in *Proceedings of the 55th International Colloquium on Refractories 2012*, Aachen, September 2012, edited by P. Quirnbach (ECREF gGmbH, Germany, 1996) p. 166.
10. I. R. Oliveira, V. C. Pandolfelli, Castable matrix, additives and their role on hydraulic binder hydration. *Ceramics International*, 2009, **35**(4), 1453.
11. M. R. Nilforoushan, J. H. Sharp, The effect of additions of alkaline-earth metal chlorides on the setting behavior of a refractory calcium aluminate cement. *Cement and Concrete Research*, 1995, **25**(7), 1523.
12. Q. F. Wang, G. T. Ye, Y. J. Wang, A. P. Fu, C. Y. Zhang, X. J. Shang, Effect of micro-sized calcium carbonate addition on volumetric stability and strength of corundum-based castables. *International Journal of Applied Ceramic Technology*, 2015, **S2**, E166.
13. N. Ukrainczyk, N. Vrbos, and J. Šipušić, Influence of metal chloride salts on calcium aluminate cement hydration, *Advances in Cement Research*, 2012, **24**(5), 249.
14. S. R. Klaus, J. Neubauer, F. Goetz-Neunhoeffer, How to increase the hydration degree of CA - The influence of CA particle fineness. *Cement and Concrete Research*, 2015, **67**, 11.
15. I. R. Oliveira, F. S. Ortega, V. C. Pandolfelli, Hydration of CAC cement in a castable refractory matrix containing processing additives. *Ceramics International*, 2009, **35**(4), 1545.
16. I. R. Oliveira, A. R. Studart, F. A. O. Valenzuela, V. C. Pandolfelli, Setting behavior of ultra-low cement refractory castables in the presence of citrate and polymethacrylate salts. *Journal of the European Ceramic Society*, 2003, **23**(13), 2225.
