

The effect of calcium nitrate on the hydration of calcium aluminate cement at different curing temperatures

H. Wang, G. Diao and G. Liu
China Building Materials Academy, Beijing, China

H. Wang
State Key Laboratory of Green Building Materials, China

L. GAO
Shijiazhuang Tiedao University, China

G. Liu
Kaifeng Qiming Refractory Materials Co. Ltd., China

ABSTRACT

Phase conversion in calcium aluminate cements (CAC) induces significant volumetric instability; it would result in an increase in porosity and decrease in strength in CAC. In this study, calcium nitrate (CN) as a phase conversion inhibitor, the effect of CN on the hydration of CAC at different curing temperatures was studied. X-ray diffraction, thermal analysis, SEM, isothermal calorimetry and the compressive strength were conducted on the CAC dosages of 0%, 5%, 10% and 15% CN cured at 20°C, 30°C, 40°C and 50°C. The results show CN can retard CAC hydration, alter the characters of the hydrates of CAC systems and avoid the conversion process. With increasing dosage of CN and curing temperature, the hydration products formed is different. In CAC systems with CN, $\text{NO}_3\text{-AFm}$ and $\text{NO}_3\text{-AFt}$ are more preferred than CAH_{10} and C_2AH_8 and are more thermostable than those typically hydrates. In the presence of CN, The phase conversion to a large extent can be avoided and the compressive strength is significantly improved. The CN dosage has a very important effect on CAC systems with CN. In this study, the optimum dosage for CN is 10 percent. This study may provide a new insight into avoiding the unstable phase conversion in calcium aluminate cements.

Keywords: calcium aluminate cement; phase conversion; calcium nitrate; Compressive strength

1.0 INTRODUCTION

Calcium aluminate cement (CAC) is a special type of cement, usually used in refractory, building materials, petroleum and electric power industries due to its high temperature resistance performance, high early strength and good resistance to a wide range of chemically aggressive conditions. More recently there has been significant interest concerning the use of CAC as a structural repair material and sewage network corrosion protection based on its rapid strength development even at low temperatures and good resistance to biological corrosion. Despite these advantages, however, the phase conversion in CAC accompanies an increase in the porosity and a loss in the compressive strength. Especially, this phenomenon is accelerated by an increase in the surrounding temperature and humidity (Scrivener & Cabiron, 1999). Therefore, based on the above and some failure reports of CAC concrete over the long-term service life, the utilization of CAC as a structural material has been limited in many countries.

The phase conversion of CAC is dependent on temperature, humidity, hydration degree and phase balance. At ambient temperatures (i.e. 30), metastable hydrates (CAH_{10} and C_2AH_8) may persisted for several years, but because thermodynamic force exists, conversion from metastable hydrates to the stable ones (C_3AH_6) is inevitable (Hewlett, 1988; Valentin and Jadvyga, 2013).

Various efforts to prevent phase conversion of CAC have been made. Most of these studies have focused on addition reactive siliceous materials (e.g. granulated blast-furnace slag, silica fume and pozzolanic materials) in CAC system. when CAC system cured at temperature below 40°C, these reactive siliceous materials lead to form strätlingite (C_2ASH_8), which is more stable, C_3AH_6 is very much reduced (Onder Kircaa, *et al.*, 2013; Collepardi *et al.*, 1995). However, when curing temperature higher than 40°C, the XRD analysis indicates that the formation of C_3AH_6 still occurs readily and the strength significantly decreases (Li *et al.*, 2014). It

suggests the phase conversion of CAC system isn't really prevented by reactive siliceous materials. Based on that the phase conversion of CAC hydrates is controlled by thermodynamic preferences of phases and reactions, Gabriel Falzone *et al*/provoked chemical admixtures (calcium nitrate (CN)) to bypass the phase conversion. The studies showed that across a range of w/c and curing temperatures at 25 and 45 °C, the NO₃-AFm phase is formed, and able to bypass the formation of the metastable phases. Furthermore, the efficiency of the approach is related to the CN dosage, higher CN dosages increase successful in bypassing phase conversion (Falzone and Balonis, 2015).

The above research proposed an innovative means, but it is not clear whether the means is universal for all kinds of CAC from different countries. For example, in this research the content of CA in CAC is up to 73.3 percent, but in China the content of CA in CAC is about 50 percent. So except for the NO₃-AFm phase, there may be other hydration product formed.

Furthermore, the temperature to which CAC concretes are exposed during their lifetime has a very important effect on the rate of conversion. So based on this, the paper further studies the influence of various dosage of CN on the phase conversion and the hydrates of CAC at four different curing temperatures: 20, 30, 40 and 50°C.

2.0 EXPERIMENT

2.1 Materials

Analytical pure Ca(NO₃)₂·4H₂O (content 99%) was used. Mix water was tap water. A commercially available yellow CAC CA50-J7 manufactured by Zhengzhou Dengfeng Smelting Materials Co., Ltd. was used. The quantification of mineralogical composition of the CAC was characterized by XRD Rietveld analysis in Table 1. The oxide composition of the CAC as determined by X-ray fluorescence (XRF) was shown in Table 2.

Table 1. The mineralogical composition of CAC w/%

CA	CA ₂	C ₂ AS	C ₄ A ₃ S	CT	C ₁₂ A ₇	MA
46.7	15.6	27.5	1.9	5.2	0.6	2.5

Table 2 The oxide composition of CAC w/%

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	TiO ₂	K ₂ O	Na ₂ O
6.3	53.8	2.16	33.75	1.14	2.63	0.23	0.08

2.2 Sample preparation

Calcium nitrate (CN) was dissolved in mix water and CAC mortars were prepared by adding CN with the amount of 0, 5, 10 and 15% by mass of CAC respectively. The water/cement ratio is determined by the fluidity of mortar reach 160±5mm (according to GB/T 2419-2005) (Table 3). The mortars were poured into modes with the dimensions of 40mm×40mm×160mm. The CAC samples were cured at 20±1 °C and 95% relative humidity for the first 24h, and the samples were removed from the molds, and immediate placed into 20±1 °C, 30±1 °C, 40±1 °C and 50±1 °C water bath respectively. The micro-pastes were cast into 20mm×20mm×20mm steel molds. The curing means were Similar to the mortars specimens.

2.3 Test methods

Compressive strength measurements

According to GB/T201-2015, Compressive strength measurements were carried out at 1, 3, 7 and 28 days.

Table 3. The W/C ratio and fluidity of CAC system

	W/C ratio	Fluidity, mm
CAC	0.44	160
CAC-5%CN	0.42	164
CAC-10%CN	0.40	162
CAC-15%CN	0.38	165

X-ray diffraction analysis

X-ray diffraction analysis was carried out on powdered CAC mixtures at each desired age using a Bruker-D8 diffractometer. The samples were scanned on a rotating stage between 5-and-70° (2θ) in continuous mode with an integrated step scan of 0.02°.

Scanning electron microscopy analysis

The microstructure of paste specimens was studied using an FEI Quanta 250 FEG. An accelerating voltage of 15 kV was employed.

Thermogravimetric and differential analysis

Netzsch thermogravimetric analysis and differential scanning calorimeter (TG-DSC, STA 449C) is utilized to identify solid phases with temperature increasing. The experiment was heated from 30°C up to 1000 °C at the heating rate of 20°C/min⁻¹. The samples were placed in the pure aluminum oxide crucibles and the tests were carried out in flowing nitrogen.

Heat of hydration analysis

The measurement of hydration characterization was carried out at 20°C using a TAM Air calorimeter, during the experiments, the w/c was fixed at 0.5. The heat flow curves were recorded for 7 days.

3.0 RESULTS AND DISCUSSION

3.1 Compressive strength evolutions of CAC with CN systems

Figure 1 shows the development of compressive strength in plain CAC systems and CAC systems with CN. It is noted that the compressive strength of plain CAC systems (0%CN) is mostly higher than that of CAC systems with CN at 20 and 30°C (Fig. 1 (a) and (b)). This can be believed that CN retards the hydration degree of CAC, and alters hydration products at lower temperatures. This will be further elucidated in the following. In Fig. 1 (c), plain CAC and CAC with CN samples cured at 7 days show higher strength. With increasing hydration time, there exists a decrease in strength. It is found that CAC with 10%CN systems have the highest strength at 28 days, while the CN-free system has the lowest strength, only 24.7MPa. When cured at 50°C, the strength of CN-free system decreases rapidly with ages. But for CAC with CN systems, the drop in strength is relatively small. Contrast with CN-free systems, CAC with CN systems has an increase in strength. This phenomenon can be explained that the strength is relative to the type and the quantity of hydration production formed in the system. For CAC systems with CN, the $\text{NO}_3\text{-AFm}$ and $\text{NO}_3\text{-AFt}$ are formed in increasing quantities at the expense of the C_3AH_6 phase. This will be further elucidated in the following.

3.2 Phase Composition of CAC Systems XRD Analysis

Figure 2 shows XRD spectra of plain CAC systems at different curing temperatures with ages. From Fig. 2 (a), it can be seen that CAH_{10} and C_2AH_8 are main hydrates when the specimens cured at 20°C for all the ages (1d, 3d, 7d and 28d). At the same time, there exists a large amount of unhydrated CA and CA_2 even at 28d. Figure 2 (b) shows that CAH_{10} and C_2AH_8 are still the main hydrates when the specimens cured at 50°C for 3 days which supported by the peaks in the XRD pattern. But these phases are no longer present in CAC systems cured at 50°C for longer than 7 days. The amount of C_3AH_6 increases with the age supported by the large increase in the intensity of C_3AH_6 peaks in the XRD pattern. In Figure 2(c), the specimens cured for 28 days, CAH_{10} and C_2AH_8 are the main hydrates when cured at 20°C and 30°C, however, CAH_{10} and C_2AH_8 are not observed in CAC systems cured at 40°C and 50°C, in adverse, C_3AH_6 and AH_3 are the dominated phase. In conclusion, phase conversions dependent on time and temperature are identified. This explains why at 40°C and 50°C low strength occurs in the CAC systems after 28 days of reaction (Fig. 2(c) and Fig. 1(d)).

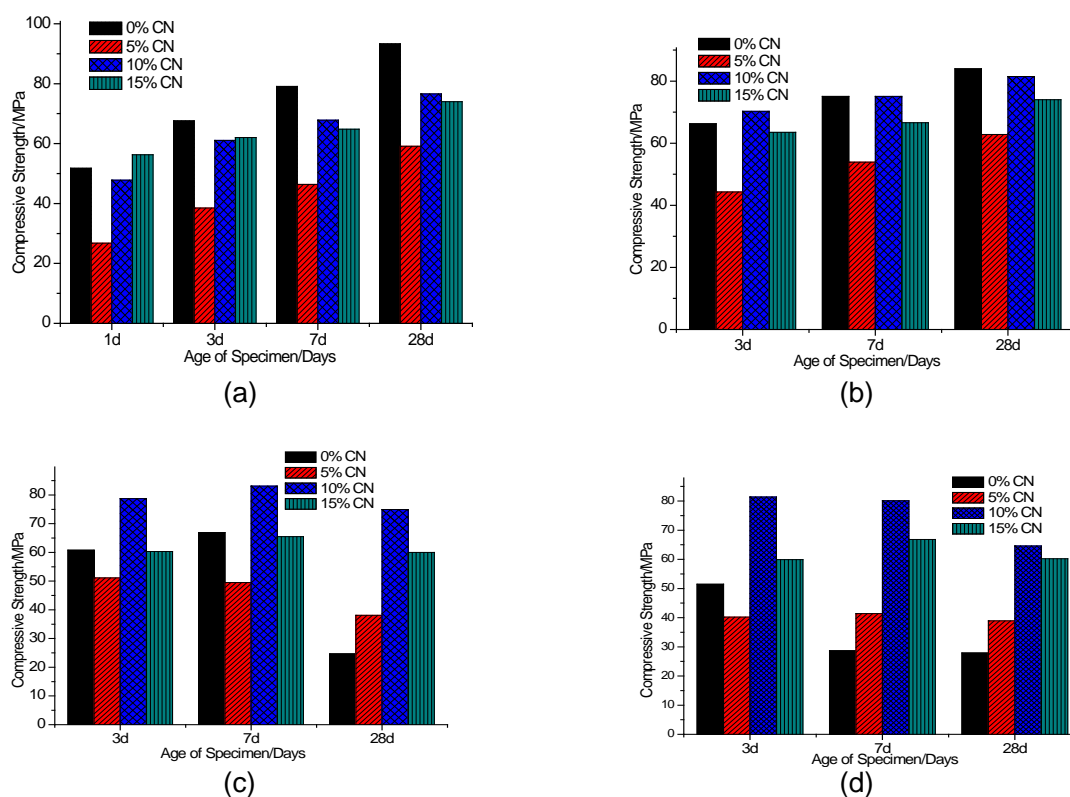


Fig. 1. The evolution of the compressive strength for CAC systems cured at: (a) 20 °C (b) 30 °C (c) 40 °C and (d) 50 °C

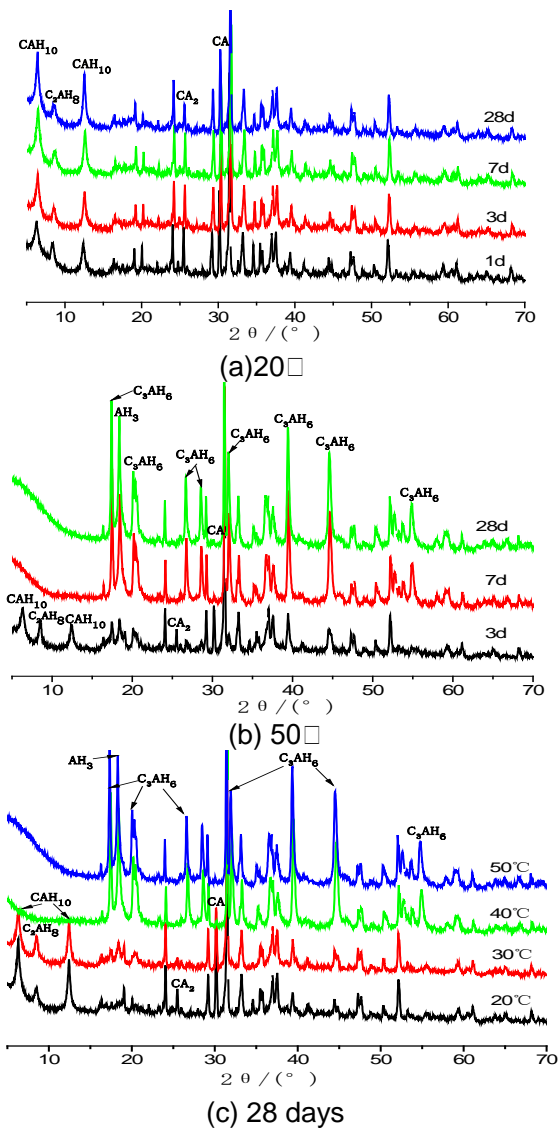


Fig. 2. XRD spectra of plain CAC systems cured at different temperatures and ages

Figure 3(a) and (b) show the XRD spectra of hydrated CAC systems with 10% CN cured at 20°C, 50°C with ages. In Figure 3 (a), NO₃-AFm and NO₃-AFt are the main hydration products, with a large amount of unhydrated CA and CA₂. NO₃-AFm and NO₃-AFt are formed by the hydration CN and calcium aluminate (Balonis, 2010). The intensity of NO₃-AFm peaks increase and intensity of NO₃-AFt peaks decrease with ages. It means that with the expense of CN, NO₃-AFt phase that was formed converts to NO₃-AFm. In Figure 3 (b), NO₃-AFt is not observed in CAC with 10%CN system cured at 50 °C at any time, NO₃-AFm and AH₃ are the major stable phases that exist. With the formation of all other hydrates (e.g., the CAH₁₀, C₂AH₈ and C₃AH₆) being suppressed, the intensity of NO₃-AFm peaks and C₃AH₆ peaks increase with the age. This can be explained that the strength of CAC at 7 days is higher than that of 28 days. The density of NO₃-AFm is 2071kg/m³, which is lower than that of C₃AH₆(2520kg/m³), so due to the amount of C₃AH₆ increases, there is a loss in strength of CAC system with 10%CN for 28 days.

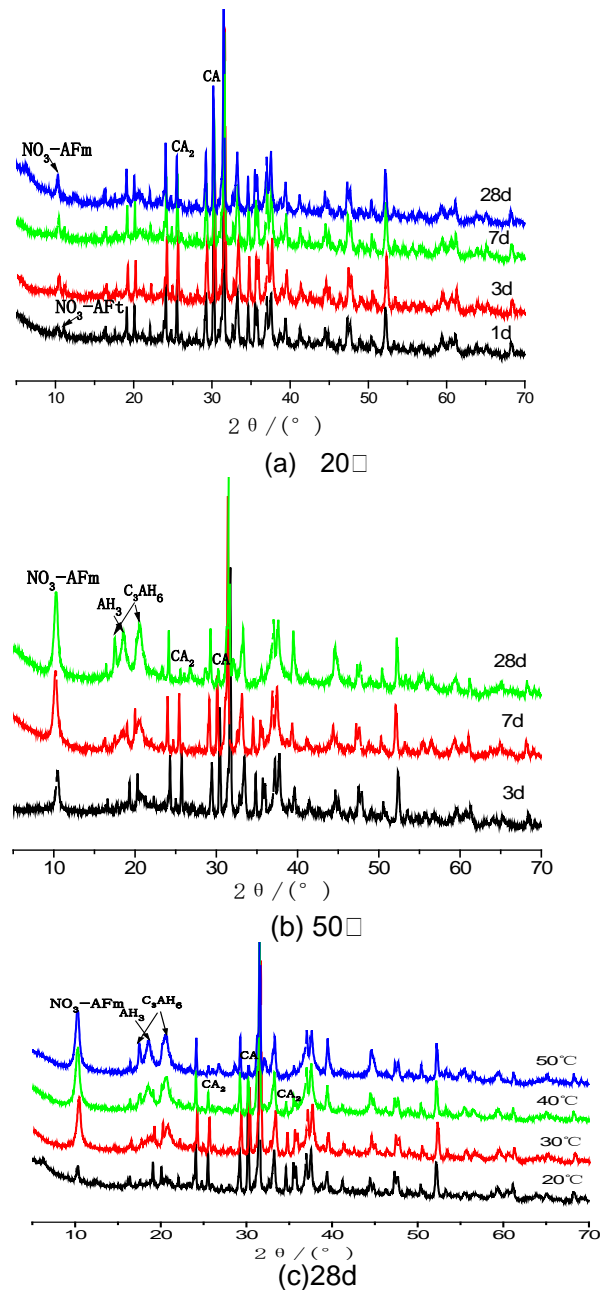


Fig. 3. XRD spectra of CAC systems with 10% CN cured at different temperatures and ages

In Fig. 3 (c), the intensity of NO₃-AFm peaks cured for 28 days increase with temperature rises. It means that higher temperature contributes to NO₃-AFm formation.

Figure 4(a) shows the XRD spectra of CAC systems with CN cured at 20°C for 28 days. It indicated that there is great variability in the type of hydrates relative to dosage of CN. The plain CAC systems only has the typical hydrates ((e.g., the CAH₁₀, C₂AH₈, C₃AH₆ and AH₃), NO₃-AFm is the main hydrates in addition to a small amount CAH₁₀ in CAC systems with 5%CN, NO₃-AFm is dominated and no CAH₁₀ observed in CAC systems with 10%CN, NO₃-AFt is the main hydrates and no NO₃-AFm observed in CAC systems with 15%CN.

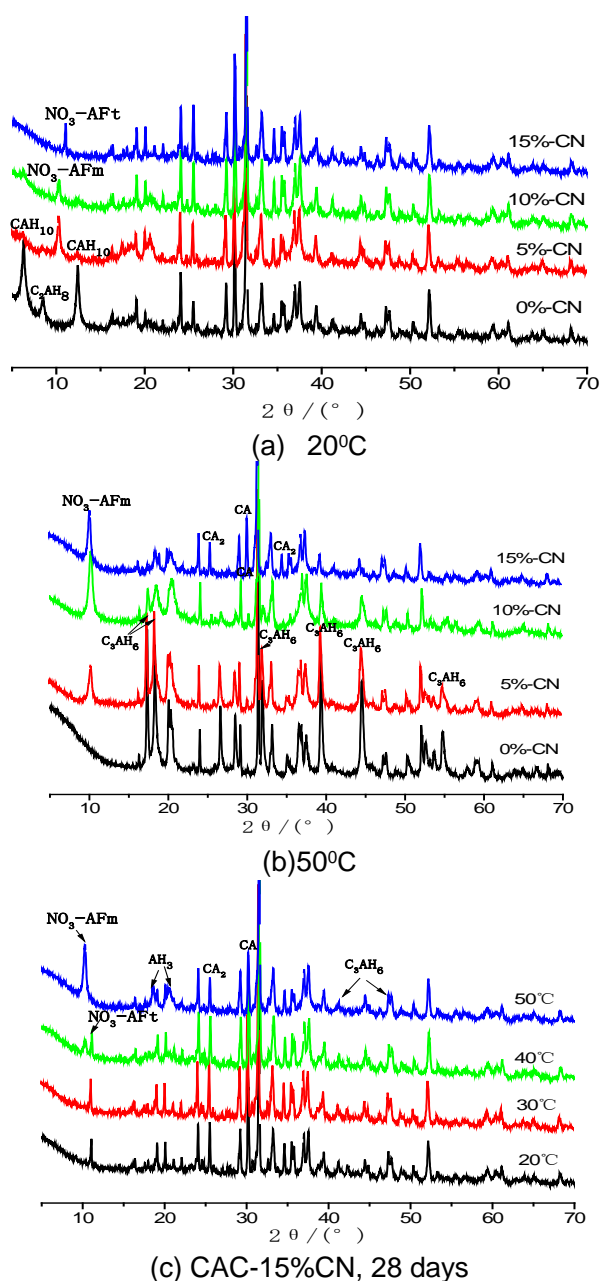


Fig. 4. XRD spectra of CAC-CN systems cured at different temperatures for 28days.

Figure 4(b) shows the XRD spectra of CAC systems with CN cured at 50°C for 28days. There is a large amount of C_3AH_6 and AH_3 in the CN-free system; NO_3-AFm and C_3AH_6 coexist in CAC systems with 5%CN. NO_3-AFm is dominated both in CAC systems with 10%CN and 15%CN. There is more unhydrated minerals (e.g., the CA and CA_2) in CAC systems with 15%CN compared to CAC-10%CN.

Figure 4(c) shows the XRD spectra of CAC-15%CN paste cured at four temperatures (20, 30, 40 and 50°C) for 28days. It indicated that NO_3-AFt is the main hydrates when the specimens cured at 20 and 30°C. Both NO_3-AFm and NO_3-AFt are observed when the specimens cured at 40°C. NO_3-AFm is dominated

and no CAH_{10} observed in CAC systems with 10%CN, NO_3-AFm and AH_3 is the main hydrates in CAC systems with 15%CN.

3.3 DSC Analysis

Figure 5 (a) shows DSC curves for plain CAC systems. In materials cured 20 and 30°C, CAH_{10} and C_2AH_8 are identified as the dominant phase with DSC peaks for these phase identified approximately at 114° and 265°, respectively. AH_3 and C_3AH_6 are the dominant phases in plain CAC system cured at 40 and 50°C, which are identified approximately at about 286° and 310°, respectively. It is in agreement with the above XRD results. Researchers (Balonis *et al.* 2011; Renaudin *et al.* 2000) show that the DSC curves of NO_3-AFm phase follow three major steps: (1) a dehydration occurring approximately at 110 °C, (2) a decomposition of nitrate in the AFm phase to nitrite at 250 °C, and (3) decomposition of nitrite at 520 °C. In Figure 5(b), in the 10% CN sample, DSC curves for four curing temperature are basically in agreement with the DSC of NO_3-AFm phase. The AH_3 and C_3AH_6 are not identified due to its small content, or overlap with NO_3-AFm . From Figure 5(c) and 5(d), it can be seen that with increasing the dosage of CN, the amount of NO_3-AFm increase. The trend is easily identified by noting nitrite decomposition at 520 °C.

3.4 SEM Analysis

A large amount of C_3AH_6 is characterized by cubic crystals in Figure 6 (b). Contrast with Figure 6 (a), the morphology of hydration products from the CAC systems with 10%CN is different form the Plain CAC systems. At the same curing temperature and hydration time, thin needles shape crystals occur in Figure 6 (c), combine with XRD analysis, it is considered as NO_3-AFt phase. With increasing hydration time, a plate-like NO_3-AFm is observed in Figure 6(d). NO_3-AFm phase still occurs at curing temperature 50° in Figure 6 (e). Figure 6 (f) shows hydration products from CAC systems with 15%CN cured at 50° for 28d. The morphology of hydration products exhibits plate-like accumulation in figure 6(f). Combination with XRD and DSC analysis, it can be considered as NO_3-AFm phase.

3.5 Isothermal Calorimetry

The heat flow rate and cumulative heat curves for plain CAC system and CAC system with CN are shown in Fig. 7. From Fig. 7(a), it is observed that CAC hydration is retarded in the presence of CN as compared to the plain CAC system. With the additions of CN from 0% to 10%, the induction periods become longer, values of the main heat-flow peak gradually decrease and the main heat flow peak shift right. But compared with 5% and 10% additions of CN, CAC system with 15%CN shows shorter the induction period.

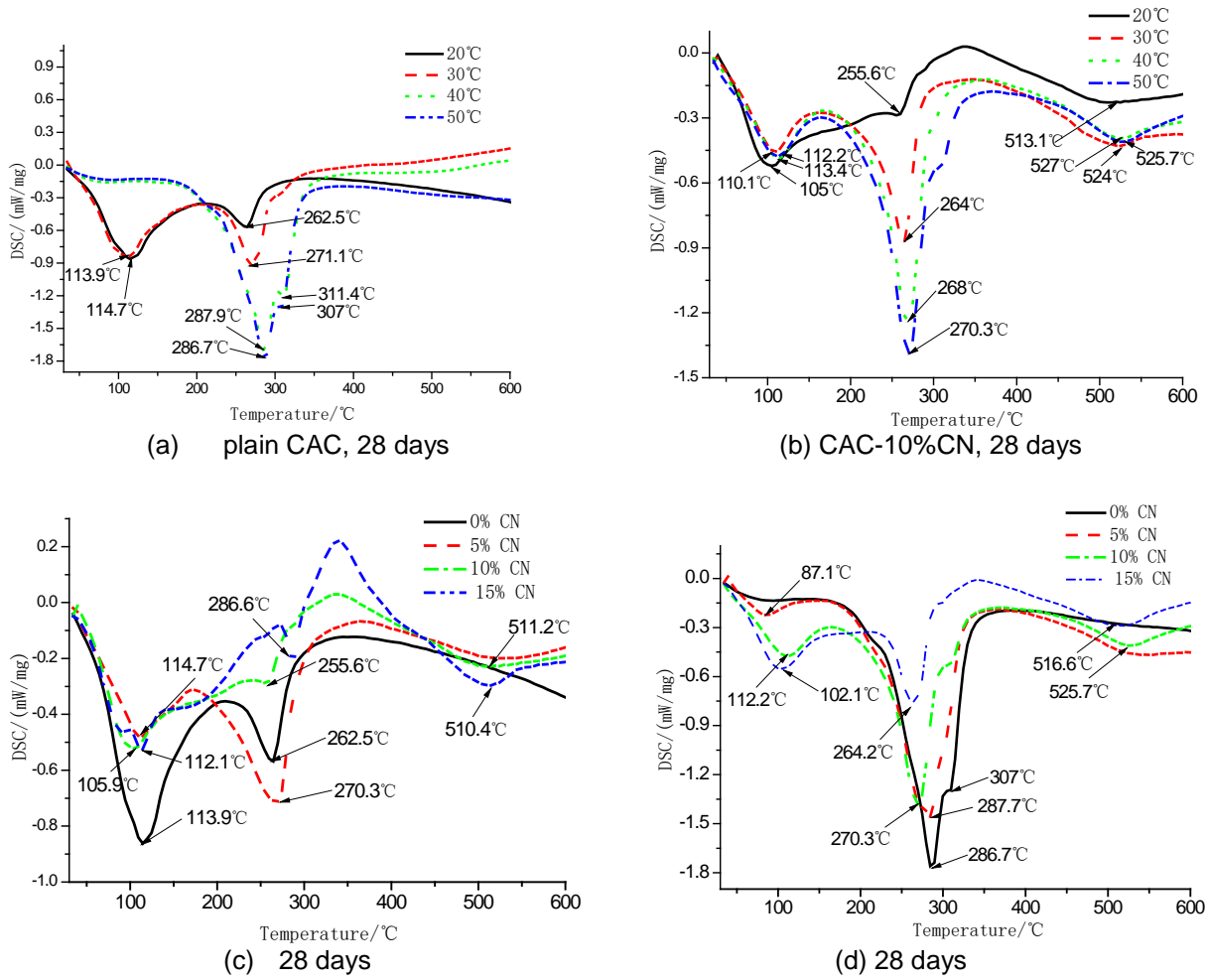


Fig. 5. DSC curves of cured at different temperatures for 28days obtained for: (a) plain CAC system (b) 10% CN dosed CAC, cured at 20 °C 30 °C 40 °C and 50 °C for 28 days for w/c=0.45

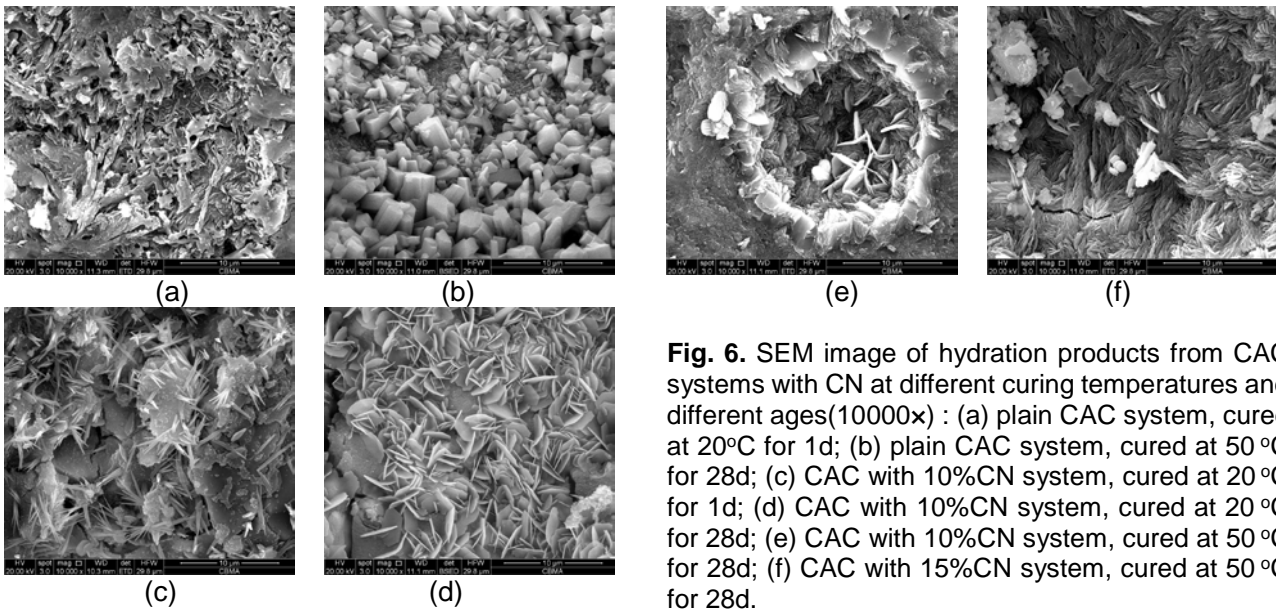


Fig. 6. SEM image of hydration products from CAC systems with CN at different curing temperatures and different ages(10000×) : (a) plain CAC system, cured at 20°C for 1d; (b) plain CAC system, cured at 50 °C for 28d; (c) CAC with 10%CN system, cured at 20 °C for 1d; (d) CAC with 10%CN system, cured at 20 °C for 28d; (e) CAC with 10%CN system, cured at 50 °C for 28d; (f) CAC with 15%CN system, cured at 50 °C for 28d.

Combined with XRD, it can be explained that in the presence of CN, the $\text{NO}_3\text{-AFm}$ is more preferred than CAH_{10} and C_2AH_8 . Furthermore with the amount of CN increasing, $\text{NO}_3\text{-AFt}$ is formed. It is indeed that the heat rate of $\text{NO}_3\text{-AFm}$ and $\text{NO}_3\text{-AFt}$ is lower than that of CAC, but more evidence is needed to confirm this point.

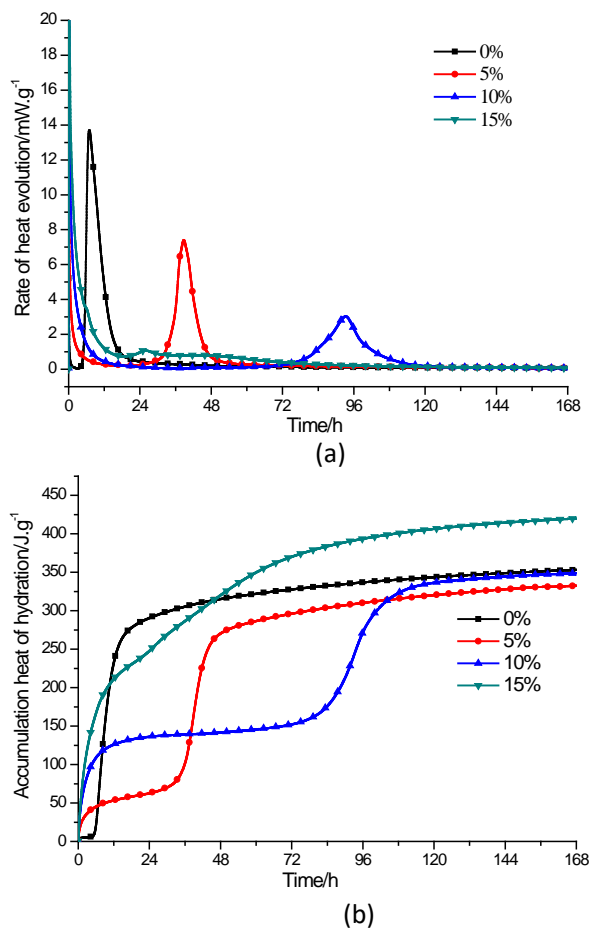


Fig. 7. Heat flow rate curves and cumulative heat curves and for plain CAC system and CAC system with CN at 20 °C (a) heat flow rate curves;(b) cumulative heat curves.

From the cumulative heat curves (Fig.7(b)), it is shown that in the presence of CN, the total heat released by the 7d, 20 °C samples was as follows: 15% additions of CN>0% additions of CN>10% additions of CN>5% additions of CN.

4.0 SUMMARY AND CONCLUSIONS

It can be deduced from the above analysis that CN can retard CAC hydration, alter the characters of the hydrates of CAC systems and eliminate the conversion process. With increasing dosage of CN and curing temperature, the hydration products formed is different.

In the CAC systems with CN cured at 20 °C and 30 °C, there is a general increase in compressive strength

with age. In the CAC system with 5% CN, because less CN may be available for a reaction with CA and CA_2 , A small amount of $\text{NO}_3\text{-AFm}$ phase is formed. It shows much lower compressive strength than plain CAC system. This indicates that $\text{NO}_3\text{-AFm}$ is more preferred than CAH_{10} and C_2AH_8 and CN can suppress the formation of these typical hydrates (Figure1 (a), (b) and Figure 4(a)). In CAC with 10% CN systems, $\text{NO}_3\text{-AFm}$ and $\text{NO}_3\text{-AFt}$ are formed in 1-day. With the increasing of age, the NO_3^- concentration in the liquid phase declines to a concentration at which $\text{NO}_3\text{-AFt}$ is no longer stable and $\text{NO}_3\text{-AFm}$ is formed exclusively. At the same time the $\text{NO}_3\text{-AFt}$ phase that was formed converts to $\text{NO}_3\text{-AFm}$. In the CAC systems with 15% CN, at curing temperatures 20 °C, the amount of NO_3^- available for reaction increase, $\text{NO}_3\text{-AFt}$ phase is formed in three-days. After seven days, the $\text{NO}_3\text{-AFt}$ phase that was formed gradually converts to $\text{NO}_3\text{-AFm}$. Compared with 10% CN, It shows higher strength at early ages (3 days) and relatively lower strength at later ages (7days and 28 days). $\text{NO}_3\text{-AFm}$ phase is formed in 3-days when the materials cured at 30 °C. This is on account of different density of $\text{NO}_3\text{-AFt}$ and $\text{NO}_3\text{-AFm}$. The density of $\text{NO}_3\text{-AFt}$ is 2033kg/m³, which is less than that of $\text{NO}_3\text{-AFm}$ (2071 kg/m³).

CAC with CN systems cured at 40 °C and 50 °C, there is a little decline in compressive strength with age. The CAC systems with CN show higher strengths than their CN-free system. The CAC systems with 10% CN exhibits highest strength in 28-day. With regard to the products of hydration, when the dosage of CN is 5%, C_3AH_6 is formed as the main product of reaction. When the dosage of CN is up to 15%, $\text{NO}_3\text{-AFm}$ and $\text{NO}_3\text{-AFt}$ are formed at 40 °C. At about 50 °C, $\text{NO}_3\text{-AFt}$ phase converts to $\text{NO}_3\text{-AFm}$. This conversion is associated with expansion and crack formation in the cement paste. When the dosage of CN is 10% and the curing temperatures reach about 30 °C, $\text{NO}_3\text{-AFm}$ is formed as the main product. There is no expansion and crack formation in the cement paste.

In generally, in CAC with CN systems, $\text{NO}_3\text{-AFm}$ and $\text{NO}_3\text{-AFt}$ are more preferred than CAH_{10} and C_2AH_8 and are more thermostable than those typically hydrates. The phase conversion to a large extent can be avoided and the compressive strength is significantly improved. The CN dosage has a very important effect on CAC systems with CN. In this study, the optimum dosage for CN is 10 percent. While arguably, it is necessary to study on the durability properties over longer age and the effect of $\text{NO}_3\text{-AFm}$ and $\text{NO}_3\text{-AFt}$ phase on the durability of CAC systems with CN.

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