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Formation and stability of $3CaO \cdot CaCl_2 \cdot 12H_2O$

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Abstract

Formation of $3CaO \cdot CaCl_2 \cdot 12H_2O$, which is a very unstable complex salt, in deteriorated concrete attacked by calcium chloride has been regarded as a main cause for the deterioration of cement concrete. In this study, a slurry from $Ca(OH)_2-CaCl_2-H_2O$ system was examined under different conditions. X-ray diffraction (XRD) analysis indicates that $3CaO \cdot CaCl_2 \cdot 12H_2O$ cannot be detected in the original slurry, but is detected after acetone washing of the slurry. $3CaO \cdot CaCl_2 \cdot 12H_2O$ disappears when the acetone-washed sample is air-dried at 20°C and 20% relative humidity. Thus, cautions should be taken during the preparation of samples during the examination of calcium chloride attacked concrete. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Formation; Stability; X-ray diffraction; $3CaO \cdot CaCl_2 \cdot 12H_2O$

1. Introduction

It is well known that chlorides cause the corrosion of steels in concrete, while, high concentration of calcium chloride also deteriorates concrete very quickly. Hydrated monochloroaluminate ($C_3A \cdot CaCl_2 \cdot xH_2O$) is always identified in calcium chloride attacked cement concrete. However, it cannot be regarded as the main cause of deterioration because this salt forms in cement pastes, which do not deteriorate. At the same time, a complex chloride-containing salt was also noted but could not be fully characterized [1,2]. Thus, the mechanism of the $CaCl_2$ attack on portland cement concrete was not clearly stated until the elucidation of $3CaO \cdot CaCl_2 \cdot 12H_2O$ in calcium-chloride-attacked cement concrete [3–5].

Monosi and Collepardi [4] found that $3CaO \cdot CaCl_2 \cdot 12H_2O$ in wet $CaCl_2$-attacked cement pastes disappeared if the paste samples were ground, washed with methyl alcohol and dried at relative humidity less than 1%. Birnin-Yauri and Glasser [6] studied the phase relations in the $Ca(OH)_2-CaCl_2-H_2O$ system at 20°C, and concluded that the $3CaO \cdot CaCl_2 \cdot 12H_2O$ could coexist with an aqueous phase, as well as with $Ca(OH)_2$, but was not stable in contact with aqueous solution and was likely to occur only in cement zones that had undergone severe desiccation such that aqueous phase was absent. Thus, $3CaO \cdot CaCl_2 \cdot 12H_2O$ is very unstable. The effect of pretreatment of samples for characterization testing on the formation and stability of $3CaO \cdot CaCl_2 \cdot 12H_2O$ is still not fully understood. The purpose of this study was to investigate the effect of sample preparation of a slurry from $Ca(OH)_2-CaCl_2-H_2O$ system on the formation and stability of $3CaO \cdot CaCl_2 \cdot 12H_2O$.

2. Experimentation

Chemical reagents $Ca(OH)_2$, $CaCl_2 \cdot 2H_2O$ and distilled water were used in this study. They were mixed in the proportions as shown in Table 1. $CaCl_2$ was dissolved in distilled water first then well mixed with $Ca(OH)_2$ in sealed plastic bottles. Three samples were prepared and cured in water baths with temperatures of 20°C, 35°C and 50°C. The slurries were stirred once a day for 2 days. After 28 days of curing, the settlements at the bottom of each bottle were cooled down to 20°C and divided into two parts for X-ray diffraction (XRD) analysis using a Phillips X-ray diffractometer. The first part of the slurry was coated onto the XRD sample holder and tested immediately after curing. The second part of the slurry was washed with acetone and then analyzed using XRD under different conditions: (i) with-

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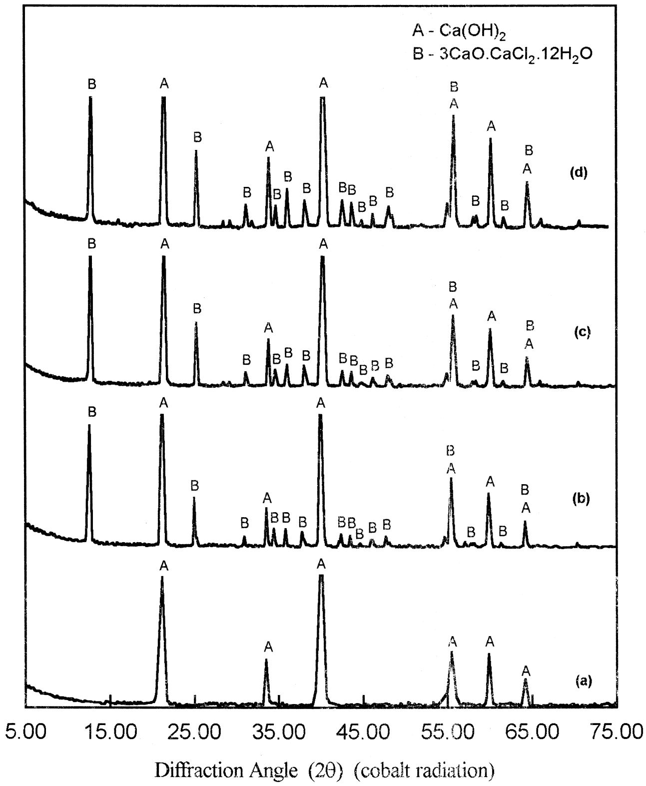

Fig. 1. XRD patterns of $CaCl_2$–$Ca(OH)_2$ slurries. (a) Cured for 28 days at 20°C without acetone washing; (b) cured for 28 days at 20°C and washed by acetone; (c) cured for 28 days at 35°C and washed by acetone; (d) cured for 28 days at 50°C and washed by acetone.

out drying; (ii) 24 h of air-drying at 20°C and 20% relative humidity and (iii) 6 h of oven-drying at 80°C.

Table 1
Mixing proportion of the slurries

Component	Proportion (%)	
	By mass	By mole
$Ca(OH)_2$	27.03	8.64
$CaCl_2$	4.08	0.87
H_2O	68.89	90.49

Precautions were taken to prevent uptake of CO_2 during the preparation of samples.

3. Experimental results and discussions

3.1. *Effect of acetone washing on the formation of $3CaO{\cdot}CaCl_2{\cdot}12H_2O$*

Slurries cured for 28 days at 23°C, 35°C and 50°C were analyzed. Fig. 1 shows the XRD patterns of the slurries before and after acetone washing. $Ca(OH)_2$ was the only detected phase in the slurry before acetone washing regardless of curing temperatures. Only the XRD patterns of the slurry cured at 20°C before acetone washing are shown here (Fig. 1a). However, two compounds — $Ca(OH)_2$ and $3CaO{\cdot}CaCl_2{\cdot}12H_2O$ — were identified in the slurries after acetone washing regardless of curing temperatures (Fig. 1b, c and d).

The $Ca(OH)_2$–$CaCl_2$–H_2O phase diagram is shown in Fig. 2. According to the composition of the mixture as indicated in Table 1, $3CaO{\cdot}CaCl_2{\cdot}12H_2O$ should not form

Item	Compatible Phases
I	Aqueous Solution (Aq)
II	$Ca(OH)_2$ + Aq
III	$Ca(OH)_2$ + 3:1:12 + Aq
IV	3:1:12 + Aq
V	$CaCl_2.6H_2O$ + Aq
VI	Ca(OH) + 1:1:1 + 3:1:12
VII	1:1:1 + 3:1:12 + Aq

Key: 1:1:1 = $Ca(OH)_2.CaCl_2.H_2O$
3:1:12 = $Ca(OH)_2.CaCl_2.12H_2O$

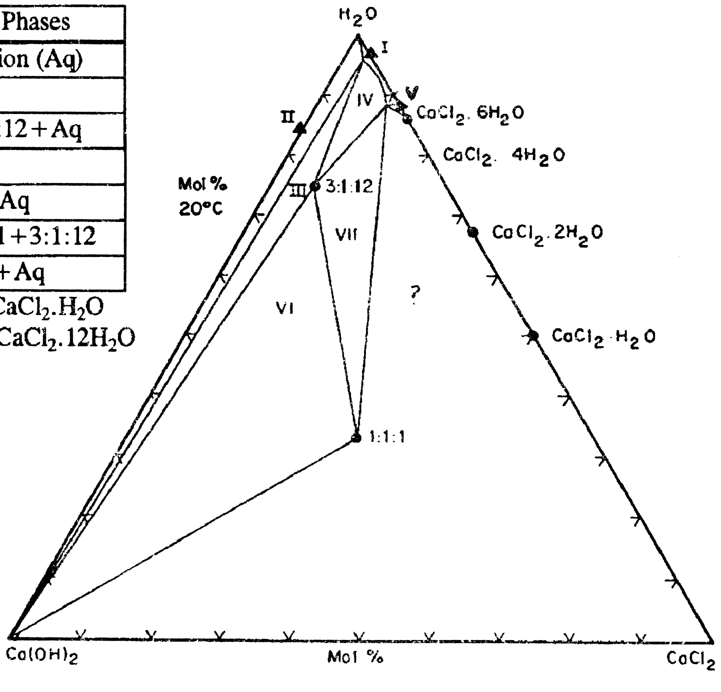

Fig. 2. Phase diagram of $CaCl_2$–$Ca(OH)_2$–H_2O system at 20°C [6].

and $Ca(OH)_2$ is the only detected phase. This is in agreement with the XRD analysis of the slurries before acetone washing.

Acetone washing extracted some free water and changed the chemical composition of the mixture, which resulted in the formation of $3CaO{\cdot}CaCl_2{\cdot}12H_2O$. Thus, curing temperature did not affect the product in the $CaO-CaCl_2-H_2O$ slurry and would not have an effect on the formation of $3CaO{\cdot}CaCl_2{\cdot}12H_2O$ after the acetone washing.

3.2. *Effect of drying on the stability of $3CaO{\cdot}CaCl_2{\cdot}12H_2O$*

Fig. 3 shows the XRD patterns of the acetone-washed slurries without drying, 24 h of air-drying at 20°C and 20% relative humidity, and 6 h of oven-drying at 80°C. Compared with XRD patterns immediately after acetone washing (Fig. 3a), only a small peak of $d = 8.17$, which belonged to $3CaO{\cdot}CaCl_2{\cdot}12H_2O$, was identified in the sample after 24 h of air-drying at 20°C and 20% relative humidity (Fig. 3b). While, $3CaO{\cdot}CaCl_2{\cdot}12H_2O$ completely disappeared after 6 h of drying at 80°C (Fig. 3c). A previous study indicated that $3CaO{\cdot}CaCl_2{\cdot}12H_2O$ transformed to $CaO{\cdot}CaCl_2{\cdot}2H_2O$ during the drying process [4]. However, no other compound rather than $Ca(OH)_2$ was identified after the disappearance of $3CaO{\cdot}CaCl_2{\cdot}12H_2O$ in this study.

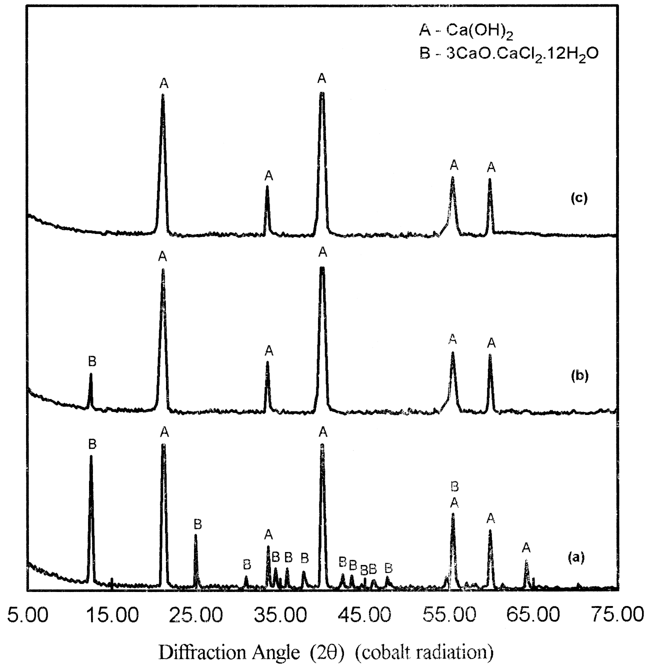

Fig. 3. Effect of drying conditions on XRD patterns of $CaCl_2-Ca(OH)_2$ slurry after acetone washing. (a) Before drying; (b) 24 h of air-drying at 20°C and 20% relative humidity; (c) 6 h of oven-drying at 80°C.

4. Conclusions

$3CaO{\cdot}CaCl_2{\cdot}12H_2O$ can form easily when the composition of a mixture is within the stable range of the compound.

$3CaO{\cdot}CaCl_2{\cdot}12H_2O$ is very unstable and even decomposes at 20°C and 20% relative humidity. Cautions should be taken during the preparation of the sample in order to detect $3CaO{\cdot}CaCl_2{\cdot}12H_2O$.

References

[1] S. Chatterji, Mechanism of $CaCl_2$ attack on portland cement concrete, Cem. Concr. Res. 8 (4) (1978) 461–468.
[2] L. Berntsson, S. Chandra, Damage of concrete sleepers by calcium chloride, Cem. Concr. Res. 12 (1) (1982) 87–92.
[3] S. Monosi, I. Alver, M. Collepardi, Chemical attack of calcium chloride on the portland cement paste, Cemento 86 (2) (1989) 97–104.
[4] S. Monosi, M. Collepardi, Research on identification in concretes damaged by $CaCl_2$ attack, Cemento 87 (1) (1990) 3–8.
[5] K. Torii, T. Sasatani, M. Kawamura, Effects of fly ash, blast furnace slag and silica fume on resistance of mortar to calcium chloride attack, Proceedings of 5th International Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, American Concrete Institute, Detroit, MI, vol. 2, 1995, pp. 931–950.
[6] U.A. Birnin-Yaui, F.P. Glasser, Chlorides in cement: Phase studies of the $Ca(OH)_2-CaCl_2-H_2O$ system, Cemento 88 (3) (1991) 151–157.