

EFFECT OF THE CARBONATION PROCESS ON THE CONCRETE  
DETERIORATION BY  $\text{CaCl}_2$  AGGRESSION

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SUMMARY

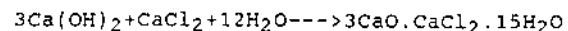
A concentrated aqueous solution of  $\text{CaCl}_2$  (30%) causes a strong deterioration in mortars manufactured with Portland cement. X-ray diffraction analyses indicate the formation of large amounts of hydrated calcium oxychloride accompanied by the consumption of hydrolysis lime.

The cement paste carbonation makes the mortars durable against the  $\text{CaCl}_2$  attack. In this case, x-ray diffraction analyses show the conversion of  $\text{Ca}(\text{OH})_2$  into  $\text{CaCO}_3$ .

INTRODUCTION

The de-icing salts based on calcium chloride are responsible for the severe deterioration of the concrete structures. The deteriorating process causes cracks and swelling of concrete and a rapid decrease in compressive strength (1-4).

This severe attack is accompanied by the formation of small amounts of chloroaluminate hydrate ( $\text{C}_3\text{A} \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$ ). In a previous paper (5) it was assumed that the oxychloride product is formed by the reaction



between lime produced by Portland cement hydration and calcium chloride which diffuses through the concrete.

In order to confirm that hypothesis, mortar specimens partly or completely carbonated have been exposed to the  $\text{CaCl}_2$  attack.

MATERIALS AND PROCEDURES

Prismatic mortar specimens (40\*40\*160) were produced by using high strength Portland cement and two water/cement ratios (0.65 and 0.35).

After 1 day, the specimens of each water/cement ratio, were demoulded and divided into 3 groups: the specimens of the first group were kept under water, the ones of the second group were cured in the air, whereas the specimens of the third group were exposed to the  $\text{CO}_2$ -rich room (30% by volume) and at R.H. of 60%.

After 60 days, the carbonation depth by the phenolphthalein test were measured on all specimens. Then each group was divided into two subgroups the first one concerns the specimens kept under water at 20°C, the second one deals with the specimens immersed under a 30%  $\text{CaCl}_2$  aqueous solution. This solution was maintained for 15 days at 20°C and then at 5°C because the deterioration due to  $\text{CaCl}_2$  attack is mainly exhibited at low temperatures of about 5°C.

On all the specimens compressive strength tests and X-ray diffraction analyses were carried out.

RESULTS AND DISCUSSION

Carbonation

The specimens exposed to the  $\text{CO}_2$ -rich room were completely carbonated after 15 days, while for those exposed to air, the carbonation depth was about 1.5 mm after 60 days.

In the mortar specimens with a water/cement ratio of 0.35, cured in the  $\text{CO}_2$ -rich room, the carbonation depth was about 6 mm, while those exposed to air had a carbonation depth of 1 mm.

Compressive strength

The evolution of the compressive strength of the mortar specimens was determined by the type of preliminary cure.

Figures 1-3 show the compressive strength versus time of the specimens with a water/cement of 0.35.

The comparison of the curves indicates that the compressive strength was increased by exposure in the CO<sub>2</sub> rich room. After the immersion in the CaCl<sub>2</sub> aqueous solution, the specimens cured in the CO<sub>2</sub>-rich room keep the same strength as that of the corresponding specimens cured under water. Substantially, the exposure to the CaCl<sub>2</sub> attack did not cause any mechanical decrease. A progressive decrease in strength after immersion in the aggressive solution, was recorded in the specimens preliminarily cured under water or in the air. In particular, after one month of immersion in the CaCl<sub>2</sub> solution, the specimens cured in the air, which are in the same condition as for the concrete structures before exposure to the de-icing salts, show a strength decrease of about 30% with respect to the value found before immersion.

Similar results can be noted on Figs.4-6 concerning strength evolutions of the specimens with w/c of 0.65. Even in this case, the immersion in the aggressive CaCl<sub>2</sub> solution caused a rapid decrease in strength of the specimens cured under water or in the air. The specimens preliminarily cured in the CO<sub>2</sub>-rich room, even after 6 months of immersion in the CaCl<sub>2</sub> aqueous solution, conserved the same compressive strength as the corresponding specimens cured under water.

Moreover the strength decrease in the specimens with w/c of 0.65, caused by exposure to the aggressive solution, is less rapid than that registered in the specimens with w/c of 0.35. This result appears apparently paradoxal since a faster deterioration in the cement mortar made with a lower water/cement ratio and therefore of better quality is expected.

#### X-Ray diffraction analyses

The deterioration of the mortar specimens preliminarily stored under water or in the air (independently to their w/c ratio) exhibiting a significant compressive strength decrease, were explained by x-ray diffraction analysis.

This analysis showed a progressive formation of the calcium oxychloride and the simultaneous decrease in lime content. Figure 7, for instance, shows the XRD pattern of the cement mortar (w/c=0.35) preliminarily cured under water,

after 6 months of immersion in the CaCl<sub>2</sub> solution. The typical XRD peaks of calcium oxychloride were observed, whereas the Ca(OH)<sub>2</sub> peaks were absent, due to the combination of lime with CaCl<sub>2</sub>.

X-ray diffraction analyses carried out on the carbonated mortar specimens preliminarily cured in the CO<sub>2</sub> rich room have shown the absence of hydrolysis lime (Fig.8). Only in the inner part of the specimens with w/c of 0.35, are the lime reflexes still noticeable (Fig.9). Obviously in these specimens the carbonation has started but has not completed.

In fact, by means of the colorimetric test, a complete carbonation can be shown in the outer part only up to a thickness of about 6 mm, after 60 days; nevertheless, the typical XRD peaks of calcium oxychloride in the carbonated outer portion and in the inner one where the lime is still present, are not observed.

#### CONCLUSIONS

The results of the present work mean that the aggression of the CaCl<sub>2</sub> against cement mortars is due to the calcium oxychloride (3CaO.CaCl<sub>2</sub>.15H<sub>2</sub>O) that is formed by the reaction between CaCl<sub>2</sub> diffused through the material and lime produced by Portland cement hydration.

When the hydrolysis lime is transformed into CaCO<sub>3</sub> because of the carbonation, the CaCl<sub>2</sub> penetration is not able to cause the oxychloride formation growth and therefore material damage does not occur.

These results indicate that the calcium oxychloride hydrate, is responsible for the concrete structures damage when exposed to the de-icing salts based on CaCl<sub>2</sub>.

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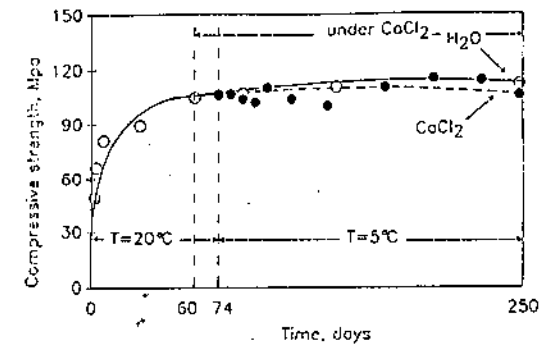


Fig.1 Compressive strength versus time of the specimens ( $w/c=0.35$ ) exposed to the  $\text{CO}_2$ -rich room before the immersion under water or under  $\text{CaCl}_2$  aqueous solution.

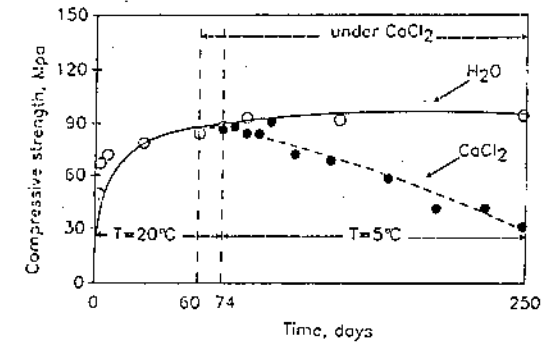


Fig.2 Compressive strength versus time of the specimens ( $w/c=0.35$ ) kept under water before the immersion under water or under a 30%  $\text{CaCl}_2$  aqueous solution.

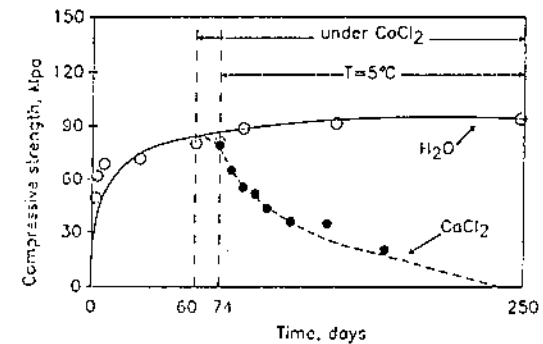


Fig.3 Compressive strength versus time of the specimens ( $w/c=0.35$ ) kept in the air before the immersion under water or under 30%  $\text{CaCl}_2$  aqueous solution.

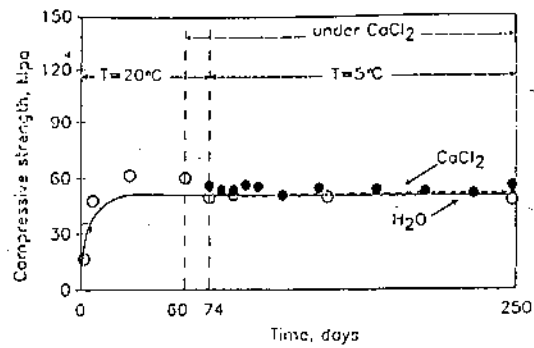


Fig. 4 Compressive strength versus time of the specimens ( $w/c=0.65$ ) exposed to the  $CO_2$ -rich room before the immersion under water or under 30%  $CaCl_2$  aqueous solution.

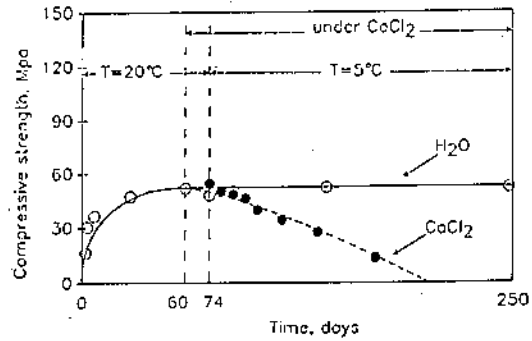


Fig. 5 Compressive strength of the specimens ( $w/c=0.65$ ) kept under water before the immersion under water or under 30%  $CaCl_2$  aqueous solution.

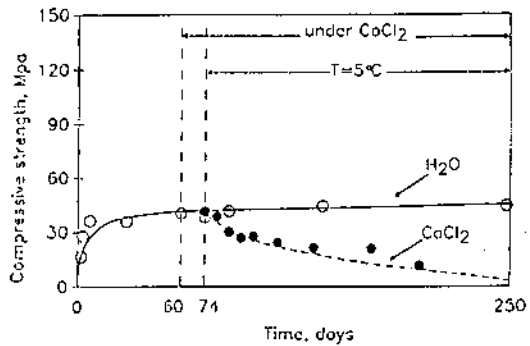


Fig. 6 Compressive strength of the specimens ( $w/c=0.65$ ) kept in the air before the immersion under water or under 30%  $CaCl_2$  aqueous solution.

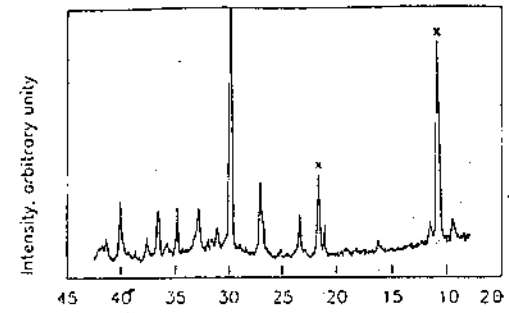


Fig. 7 X-ray pattern of cement mortar ( $w/c=0.35$ ) after 6 months of immersion in  $CaCl_2$  aqueous solution and preliminary curing under water ( $x=C_3A \cdot CaCl_2 \cdot 15H_2O$ ).

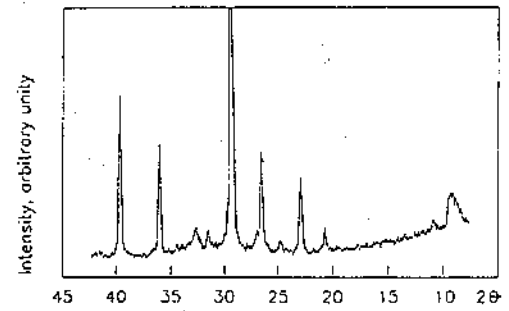


Fig. 8 X-ray pattern of cement mortar ( $w/c=0.35$ ) taken from outer surface of the specimens after 6 months of immersion under  $CaCl_2$  solution and preliminary exposure to the  $CO_2$ -rich room.

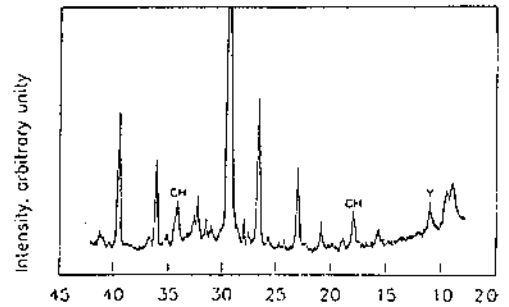


Fig. 9 X-ray pattern of cement mortar ( $w/c=0.35$ ) taken from inner part of the specimens after 6 months of immersion under  $CaCl_2$  solution and preliminary exposure to the  $CO_2$ -rich room ( $CH=Ca(OH)_2$ ;  $Y=C_3A \cdot CaCl_2 \cdot 10H_2O$ ).