



The influence of carbonation on the formation of calcium oxychloride



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ABSTRACT

Some jointed plain concrete pavements in the midwestern region of the United States of America have exhibited damage at the joints. This damage manifests itself in cracking and spalling in a small section (approximately 100 mm wide) along joints. These cracks may be due to either freeze-thaw cycling of concrete with a high degree of saturation or chemical reactions that occur between the deicing salt and the cementitious matrix. For example, deicing salts (e.g., CaCl_2 MgCl_2) may react with the cementitious matrix leading to the formation of calcium oxychloride. The formation of calcium oxychloride leads to matrix damage that results in the cracking and spalling of the concrete.

The objective of this paper is to document the effect of carbonation on the potential for calcium oxychloride formation in a cementitious matrix. This paper examines ground hydrated cement paste powder made of different ordinary portland cements and portland cement containing fly ash, slag or silica fume. Each of these materials are tested for their potential to react with CaCl_2 after exposure to different levels of carbonation. The results indicate that the potential of calcium oxychloride formation decreases with the increase in the degree of carbonation. For long carbonation durations or higher degree of carbonations, there is no calcium oxychloride formation even if the calcium hydroxide is not totally carbonated. It appears that this is due to the fact that carbonation reaction creates a calcite barrier around the remaining calcium hydroxide. The calcite barrier reduces the potential for reaction between calcium hydroxide with the deicing salt. This work indicates that in addition to previous work that has shown that calcium oxychloride formation can be reduced with the use of supplementary cementitious materials and topical treatments (sealers), carbonation is a factor that should be considered in determining the amount of calcium oxychloride that can form in a cementitious matrix.

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1. Introduction

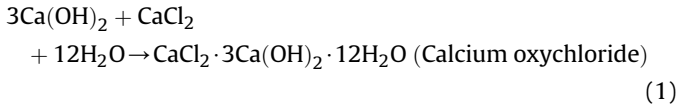
Historically, concrete pavements have been designed to provide an initial service life of 30 years. However, damage and degradation in concrete pavements have recently been observed to occur well before the expected service life is reached [1]. This is increasingly problematic as transportation agencies are requesting pavements with a longer initial service life (40–50 years or more) [2].

In the Midwestern region of the US jointed plain concrete pavements (JPCP) have shown premature damage at the joints [3]. It has been proposed that this damage can occur due to either 1)

increased saturation levels at the joints or 2) a chemical reaction that occurs between the matrix and the deicing salts that result in an expansive product [1,4,5]. It should be noted that several potential sources of damage have historically described damage due to the presence of deicing salts including: 1) scaling of the concrete surface [6–9] or 2) crystallization of the salt in the pores [10–12]. Recently however it has been observed that a phase transformation/reaction can occur between the calcium hydroxide ($\text{Ca}(\text{OH})_2$) in the matrix of the concrete pavement and the calcium chloride (CaCl_2) in the deicing salt [4,13–16]. The product of this phase transformation/reaction is calcium oxychloride and is described by equation (1).

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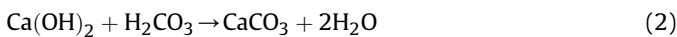
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Recent studies have used the low-temperature differential scanning calorimetry (LT-DSC) to describe the relationship between temperature, salt concentration and calcium oxychloride formation [4,17–19]. In addition, longitudinal guarded comparative calorimetry (LGCC) has been used to relate the formation of oxychloride in paste to damage development in concrete [4,17,20].

Recent research has been focused on reducing the potential for calcium oxychloride formation. Villani et al. [21] demonstrated that the use of a carbonated calcium silicate cement that reacted without forming calcium hydroxide resulted in systems with no calcium oxychloride or associated damage. Monical et al. [22] evaluated the use of supplementary cementitious materials (SCM) and portland limestone cement (PLC) to dilute the cement thereby reducing the calcium hydroxide formation. Some SCMs like fly ash and silica fume are known to react with the calcium hydroxide further reducing the potential for damage. Other SCMs, like slag, are chemically activated by the alkali content which can alter the pH of the solution thereby decreasing the formation of calcium hydroxide [23,24]. Monical et al. [22] indicated that for every one percent volume of fly ash that was used to replace cement (up to 60% replacement), a 0.0056 [(J/g-paste)/(J/g-oxy)] reduction in oxychloride occurred. When slag is used to replace cement, the rate of reduction in oxychloride is 0.0052 [(J/g-paste)/(J/g-oxy)] for every volume percent of slag. Monical et al. [22] examined also the efficiency of different topical treatments to provide a physical barrier between salt and calcium hydroxide, which resulted in mitigating calcium oxychloride formation.

This paper examines whether carbonation in cementitious materials can reduce the potential for calcium oxychloride formation. It is known that carbon dioxide (CO_2) from the atmosphere can diffuse into concrete and react with cementitious matrix. During this reaction, the CO_2 transitions from a gaseous phase to a solid phase while passing through an aqueous phase [25]. The carbonation reaction is described in equation (2) [26]:



Specifically, it is proposed in this study that the reaction between carbon dioxide and calcium hydroxide may reduce the calcium oxychloride development.

Previous studies [27,28] have shown that carbon dioxide concentrations greater than 3% result in accelerated carbonation that is not representative of natural carbonation where the CO_2 concentration is closer to 0.03% [28]. This is due to the fact that at higher concentration the carbon dioxide induces a strong decalcification and polymerization in the silicate chain, which can cause the calcium silicate hydrate gel to disappear. At lower CO_2 concentrations, the loss of the calcium silicate hydrate gel is not detected. It should also be noted that carbonation does not occur readily in completely dried cementitious materials since the reaction requires a liquid phase. Similarly the carbonation reaction is greatly slowed in saturated concrete due to the slower carbon dioxide diffusion rate in fluid. It was shown that the carbonation rate is greatest for relative humidities between 50% and 70% [27,29]. It has also been found that temperatures between 20 °C and 40 °C accelerate carbonation [30] due to favorable transport and thermal-activation [31] while not inhibiting the solubility of hydrates [32]. Several models have been developed that consider the effects of carbon dioxide concentration, relative humidity, and temperature, and they can be used to predict the amount of carbonation in

cementitious systems during their service life [33–36].

This paper addresses the need to better understand the role of carbonation to reduce the calcium oxychloride formation for two critical reasons. First, natural carbonation can occur which should be considered in predictive models for calcium oxychloride formation. Second, it may be possible to preferentially carbonate the concrete in the joints of concrete pavements thereby enhancing their resistance to joint damage. CO_2 curing of concrete were previously used in some research projects [37,38] to enhance the properties of concrete; concrete near the joints can be exposed to CO_2 after construction in the field to carbonate the concrete near joints.

2. The experimental approach

This paper performed a series of tests where cementitious systems were carbonated and the potential for calcium oxychloride formation was then assessed. The extent of carbonation was quantified using two methods 1) mass change and 2) thermogravimetric analysis (TGA). The quantity of calcium oxychloride that developed was quantified using low temperature calorimetry using a ground hydrated cementitious paste in the presence of a calcium chloride deicing salt solution [19].

Eight different paste mixture compositions were evaluated in this study. The water to cementitious ratio of each mixture was 0.42. The mixture proportions for these mixtures are shown in Table 1. The mixtures contained Type I portland cement with different concentrations of SCM (i.e., fly ash, slag and silica fume). Table 2 provides a summary of the chemical composition of the materials used.

Mixing was performed following to ASTM C305-14; however a vacuum mixer was used. After mixing, the paste was cast in cylindrical plastic molds with a 37.5 mm diameter and a 50 mm height. Two different conditioning approaches were used to cure the specimens. The first series of samples included OPC 1, OPC 1 + 7% SF, OPC 1 + 20% SF, OPC 1 + 45% Slag and OPC 1 + 20% FA F. The samples in the first series were sealed, placed at 23 °C and cured for over 2 months. This resulted in a degree of hydration for OPC 1 of 83.0%. The second series of specimens consisted of mixtures made with a different portland cement (OPC 2, OPC 2 + 10% FA C and OPC 2 + 25% FA C). These mixtures were sealed at the time of casting, stored in a sealed container for 3 days at 23 °C and then placed at 50 °C for 25 days to accelerate hydration. The degree of hydration for OPC 2 was measured to be 88.5%.

After the hydrated cementitious samples were obtained, the samples were 1) ground, 2) carbonated, and 3) tested in the low temperature differential scanning calorimeter (LT-DSC) with a calcium chloride solution to determine the extent of calcium oxychloride that formed in the system.

First the hydrated pastes were ground using a milling machine. The obtained powder was passed through a 75 μm sieve. The powder was dried in a vacuum oven at 50 °C. After drying, powder samples were placed in CO_2 chambers (1.5% CO_2 , 55% RH, 25 °C) for varying durations. To monitor the mass gain due only to moisture uptake at 55% relative humidity (RH), 2 g of OPC 1 and 1 g of OPC 2 cement powder samples were kept in regulated desiccators at 55% RH and 25 °C temperature. The mass of the samples in the carbonation chamber were monitored and mass gain was due to both moisture uptake at 55% RH and carbonation. The difference between these two mass gain measurements indicates the mass gain due only to the carbonation. These mass gain measurements were performed for eleven days. The interval between two successive mass measurements varied between the first day and the last day as shown in Fig. 1(b).

As mentioned, the powder samples were exposed to the

Table 1
Testing Matrix and Mixture proportions.

	Mixture ID	W/C	Ordinary Portland cement (kg/m ³)	Water (kg/m ³)	Fly ash (kg/m ³)	Slag (kg/m ³)	Silica fume (kg/m ³)
Mixture 1	OPC 1 plain	0.42	1360	571	0	0	0
Mixture 2	OPC 1 + 7% SF	0.42	1260	566	0	0	88
Mixture 3	OPC 1 + 20% SF	0.42	1110	559	0	0	222
Mixture 4	OPC 1 + 45% Slag	0.42	930	566	0	419	0
Mixture 5	OPC 1 + 20% FA F	0.42	1120	564	224	0	0
Mixture 6	OPC 2 plain	0.42	1360	571	0	0	0
Mixture 7	OPC 2 + 10% FA C	0.42	1230	568	123	0	0
Mixture 8	OPC 2 + 25% FA C	0.42	1070	539	268	0	0

Table 2
Chemical composition of materials used in this study (value in mass percentage).

Materials	Binder type	Binder class	C ₃ S (%)	C ₂ S (%)	C ₃ A (%)	SiO ₂ (%)	Al ₂ O ₃ (%)	CaO (%)	Fe ₂ O ₃ (%)
OPC 1	Ordinary Portland Cement	Type I	60	10	9	19.4	5.4	63.5	3.2
OPC 2			55	14	7	19.5	4.4	62.6	3.0
FA F	Fly ash	Class F	– ^a	–	–	48.6	22.2	3.7	19.4
FA C		Class C	–	–	–	44.1	21.5	21.0	5.6
SL	Slag ^b	–	–	–	–	–	–	–	–
SF	Silica Fume	–	–	–	–	94.7	–	–	–

^a Not Available.

^b Slag cement used in this study meets the requirements of ASTM C989.

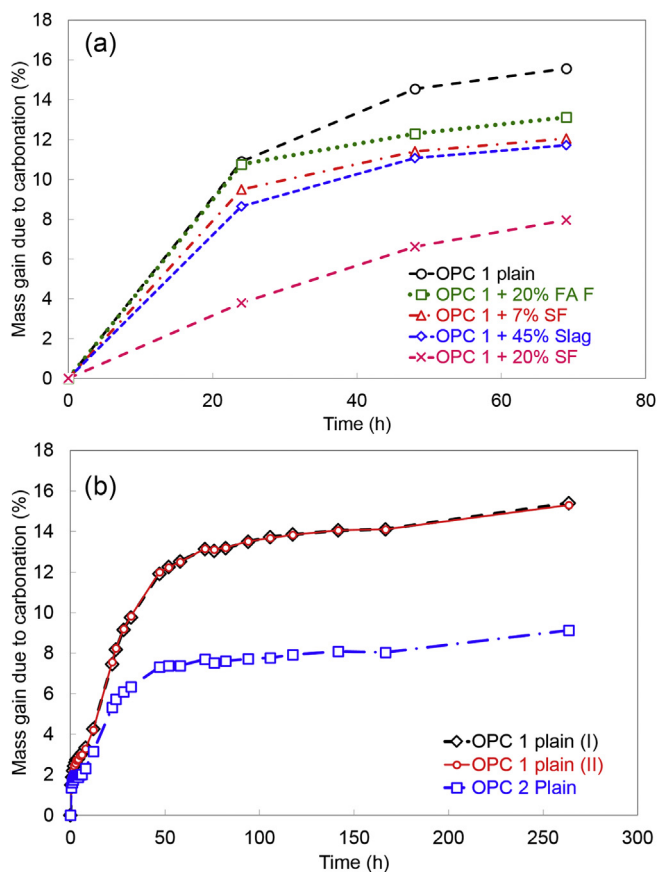


Fig. 1. Mass gain due to carbonation with respect to time: (a) carbonation at 3% CO₂, 55% RH, 25 °C; (b) carbonation at 1.5% CO₂, 55% RH, 25 °C (note that the scale of x-axis is not identical in these two graphs).

carbonation environment for different durations to reach different levels of carbonation. All of the mixtures were tested in the LT-DSC after carbonation durations of 0, 0.5 and 127 h. Additionally OPC 1 was tested at 3.5, 8, 12, 22, and 33 h. Thermogravimetric analysis

was performed on all samples (in triplicate) to determine the amount of calcium hydroxide after 0 h while additional testing was performed on OPC 1 at 0.5, 3.5, 8, 22 and 127 h).

In a preliminary study, the initial carbon dioxide concentration was selected to be 3%. However, as shown in Fig. 1(a) the mass gain due to carbonation was observed to be very fast and the mass stabilized within 24 h (at 3% CO₂ concentration, 55% RH and 25 °C). This may due to the fact that the materials carbonated in this study were in a powder form. Previous research has shown that 3% carbon dioxide concentration is maximum concentration that should be used for accelerated carbonation since higher dosages may alter the structure of the CSH [27,28]. Therefore, to avoid the rapid reaction and a possible aggressive carbonation in powder samples, the carbon dioxide concentration used in this study was reduced to 1.5%, see Fig. 1(b) (1.5% CO₂, 55% RH and 25 °C). The curves labeled OPC 1 plain (I) and OPC 1 plain (II) are tests performed on the same powder and can be used as an indication of the reproducibility in the mass gain due to carbonation. The chamber was maintained at 55% RH using the sodium bromide salt [39].

To determine the amount of calcium hydroxide consumed by carbonation, thermogravimetric analysis (TGA) was performed. The extent of carbonation was estimated based on the amount of Ca(OH)₂ at various times after exposure to carbon dioxide. The TGA analysis was used in addition to mass gain, since mass gain cannot provide a precise measure of the Ca(OH)₂ consumption as carbonation of the calcium silicate and calcium hydroxide can occur simultaneously in cementitious matrix [28]. Previous researchers [40] indicated that the calcium silicate hydrate is more susceptible than Ca(OH)₂ to reactions with CO₂ and the calcite (CaCO₃) formation does not stop when all Ca(OH)₂ is consumed due to calcium silicate hydrate reaction with CO₂ [41,42]. TGA is used to determine the dehydration of Ca(OH)₂ that can be observed to occur as a mass loss between 400 °C and 600 °C [43,44].

To determine the Ca(OH)₂ content, a traditional method found in Ref. [45] is used in this study. This method enables determining the start and end points of Ca(OH)₂ decomposition based on the second derivative curve of the sample's weight loss with respect to temperature. Once these two points are determined, the amount of Ca(OH)₂ can be computed using equation (3).

$$\text{Ca(OH)}_2 = \frac{74.1}{18} \times \frac{M_{\text{Start}}^S - M_{\text{end}}^S}{M_c} \quad (3)$$

where M_{Start}^S and M_{end}^S are the sample masses (g) recorded during the TGA at the start point and the end point of decomposition of Ca(OH)_2 , respectively; M_c is the initial mass of the cement (g) in the TGA sample; and the ratio of 74.1/18.0 is the ratio of the molar mass of Ca(OH)_2 and the molar mass of water [45].

The TGA test was performed using a 2050 thermogravimetric analyzer manufactured by TA Instruments. The samples consisted of a small powder sample (35–50 mg) taken from the sieved material, placed in a platinum crucible, and loaded into the TGA instrument. The sample is first kept at an isothermal condition (i.e., 23 °C) for 3 min and then heated up to 990 °C at 10 °C/min under a nitrogen purge. The thermal analysis was performed in a nitrogen gas atmosphere, with a temperature range of 23 °C–990 °C and a heating rate of 10 °C/min.

An experimental protocol was developed to use low temperature differential scanning calorimetry (LT-DSC) to quantify the amount of calcium oxychloride which can form from reactions between Ca(OH)_2 in cementitious paste and CaCl_2 in a saline solution added to the powder [4,19,22]. The LT-DSC test uses a hydrated ground cementitious paste in the presence of a CaCl_2 solution (20% CaCl_2 by mass) to evaluate the heat released in the temperature range associated with calcium oxychloride formation (30 °C–40 °C) [4]. The heat released with respect to temperature is captured and measured to quantify the energy associated with the calcium oxychloride phase transition. The LT-DSC used in this study was TA instruments Q2000 with temperature accuracy of 0.1 °C. In this test 10 ± 1 mg of sieved hydrated cementitious powder was combined with 10 ± 1 mg of 20% CaCl_2 solution by mass in a stainless steel pan. The sample was cooled to –90 °C and heated at a rate of 0.25 °C/min while the heat flow analysis was determined. The amount of calcium oxychloride that formed was computed as the latent heat absorbed that occurred at 30 °C to 40 °C temperature.

3. Results and discussion

Fig. 2 shows the variation in the amount of calcium oxychloride formation that occurs in samples as a function of the carbonation time as determined from the LT-DSC test. After half an hour of carbonation (~9% degree of carbonation, i.e., 9% of available CH by

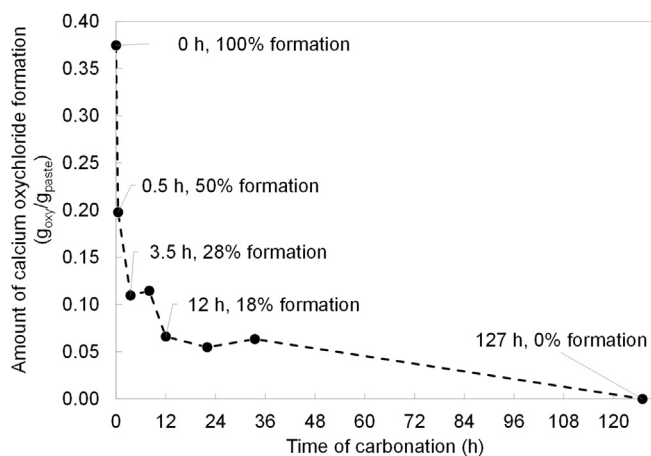


Fig. 2. Effect of carbonation on the calcium oxychloride formation obtained from LT-DSC experiment.

mass is carbonated), the amount of formed calcium oxychloride for carbonated system is 50% lower than the amount of formed calcium oxychloride for initial noncarbonated system. It can also be noted that 72% and 82% reductions in calcium oxychloride are observed after 3.5 and 12 h of carbonation respectively. After 127 h of carbonation, the amount of calcium oxychloride that forms is negligible. It should be remembered that this is a high concentration of carbon dioxide (1.5%), i.e., in comparison to natural concentration (0.03%) [28], that is exposed to a ground powder with a large surface area. As a result, the reaction between Ca(OH)_2 and CO_2 is rapid and significant.

Fig. 3 represents the TGA cumulative mass loss and Table 3 reports the residual Ca(OH)_2 that remains in an ordinary cementitious system prepared using OPC 1 after different carbonation exposure times as determined using TGA. In Fig. 3, mass loss “CH” corresponds to the dehydration of the Ca(OH)_2 and mass loss “calcite” corresponds to the decarbonation of calcite. The mass loss due to the dehydration of the Ca(OH)_2 decreases with an increase in the carbonation duration since the Ca(OH)_2 is consumed by the carbon dioxide to form the calcite. Additional evidence for this reaction can be seen in increased mass loss due to decarbonation of calcite as the length of exposure to carbon dioxide increases. Therefore, we can deduce that the carbonation reaction reduces the formation of the calcium oxychloride due to the consumption of Ca(OH)_2 as suspected.

Fig. 4 shows the reduction in the calcium oxychloride formation as a function of the calcium hydroxide measured in the paste. It can be noticed that for samples with little carbonation, small changes in the calcium hydroxide result in sharp reductions in calcium oxychloride formation. Further, after 127 h of carbonation, no calcium oxychloride formation is observed despite the fact that calcium hydroxide (nearly 50% of its initial noncarbonated value) remains in the sample Fig. 4(b). It can be reasoned and hypothesized based on these two observations that the calcite obtained from the carbonation reaction creates a barrier around the calcium hydroxide which reduces the potential for a reaction between the salt solution (CaCl_2) and the remaining Ca(OH)_2 . In Fig. 4(b), the cementitious material prepared using OPC 1 and not carbonated is considered to be the reference material. Therefore, all the values are normalized using the value obtained for the reference materials.

The barrier effect is schematically described in Fig. 5. When

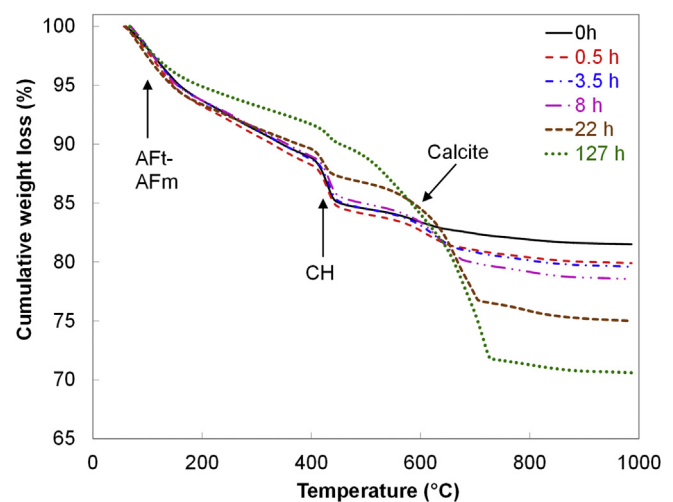


Fig. 3. TGA cumulative mass loss for ordinary cementitious materials prepared using OPC 1 at different levels of carbonations (note that “AFt–AFm” corresponds to dehydration of ettringite and monosulfate, “CH” corresponds to the dehydration of the Ca(OH)_2 , and “calcite” corresponds to the decarbonation of calcite).

Table 3
Amount of Ca(OH)₂ obtained using TGA in cement pastes prepared using OPC 1 and exposed to carbon dioxide.

Carbonation duration (hours)	Amount of the Ca(OH) ₂ in cement paste (% by mass)
0	16.92
0.5	15.68
3.5	15.52
8	14.82
22	10.62
127	7.82

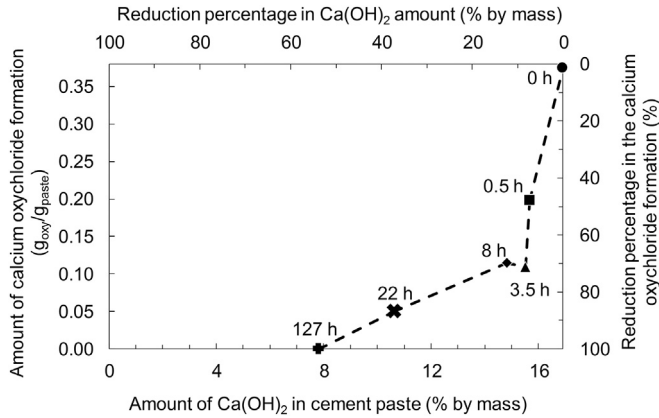


Fig. 4. The amount of calcium oxychloride per mass of hydrated cement and the percentage of reduction of the potential of the calcium oxychloride formation as a function of remaining Ca(OH)₂ in OPC 1 cement paste for different carbonation exposure time.

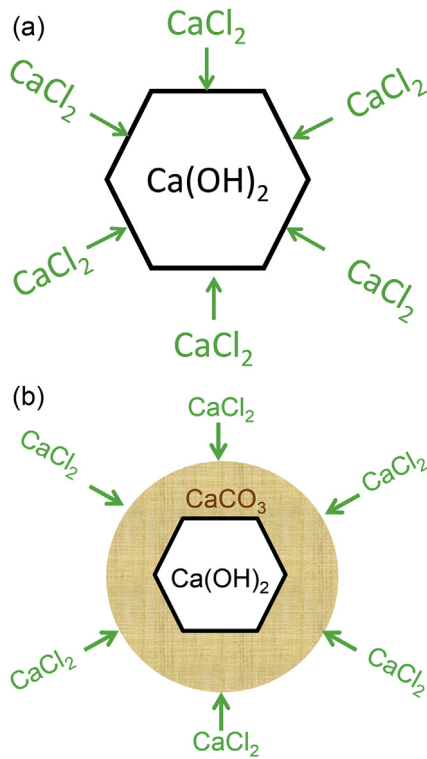


Fig. 5. Schematic representation of the barrier formation: (a) non-carbonated Ca(OH)₂ crystal exposed to CaCl₂ solution, and (b) carbonated Ca(OH)₂ crystal with CaCO₃ barrier exposed to CaCl₂ solution.

there is no carbonation of Ca(OH)₂, salt solution can easily react

with Ca(OH)₂ and since calcium oxychloride has a porous structure, this reaction occurs continuously until one of the reactants (Ca(OH)₂, CaCl₂, or H₂O) is totally consumed (Fig. 5(a)). In case of a carbonated system containing of Ca(OH)₂ (Fig. 5(b)), calcium carbonate creates a barrier around the remainder of Ca(OH)₂, and as a result the reaction between Ca(OH)₂ and salt solution (or CO₂ and H₂O) can substantially decrease. As shown in Fig. 2, it should be noted that ~9% reduction in Ca(OH)₂ due to carbonation resulted in 50% reduction (approximately 5 times more reduction than expected) in the formation of calcium oxychloride, and this is mainly because of barrier effect. This may be very beneficial to decelerate calcium oxychloride formation in non-reinforced concrete exposed to deicing salts as calcium oxychloride formation is expansive and destructive.

Fig. 6 shows the calcium oxychloride formation in the range of mixtures investigated in this paper. It can be noticed that the use of SCM greatly reduces calcium oxychloride formation. This can be explained by reduction in the amount of Ca(OH)₂ content in SCM systems due to (1) dilution (there is less calcium silicate present to react and form calcium hydroxide) and (2) the pozzolanic reaction (where SCM reacts with the calcium hydroxide to form calcium silicate hydrate) [22]. The reduction in calcium hydroxide content in mixtures containing SCM can be seen in the TGA response as shown in Fig. 7. Table 4 also shows the amount of Ca(OH)₂ in cementitious pastes prepared using OPC 1 and various SCMs. The cement paste prepared using OPC 2 also shows lower amount of calcium oxychloride formation than the cement paste prepared using OPC 1. This may be due to the lower C₃S content in OPC 2 than OPC 1 (Table 2) and to the difference in the degree of hydration.

Fig. 8 shows the reduction in calcium oxychloride formation as a function of the reduction in the Ca(OH)₂ content due to the use of SCM. The reduction in calcium oxychloride formation is proportional to the reduction in the Ca(OH)₂. In Fig. 8(a), the cementitious

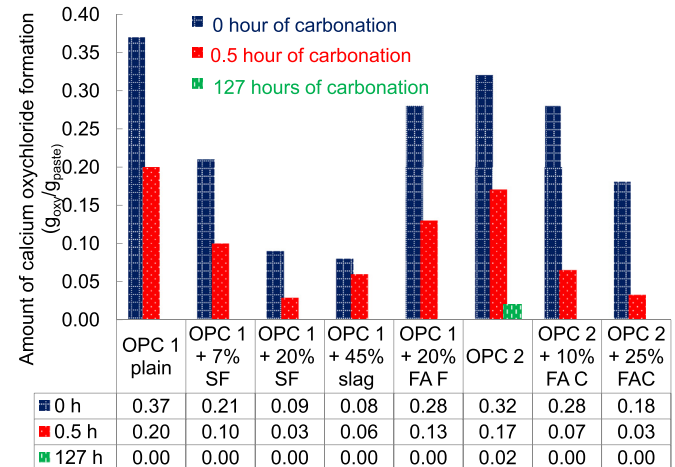


Fig. 6. Effect of SCM and carbonation on the calcium oxychloride formation obtained from LT-DSC experiment.

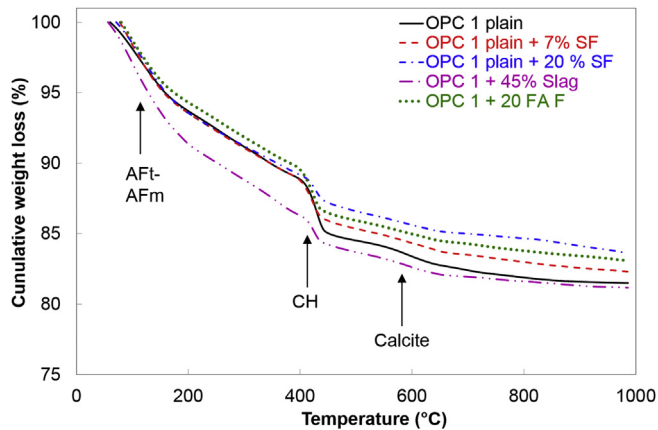


Fig. 7. TGA analysis on ordinary cementitious materials prepared using OPC 1 as well as on the cementitious materials prepared using OPC 1 mixed with different SCM note that "AF_t-AF_m" corresponds to dehydration of ettringite and monosulfate, "CH" corresponds to the dehydration of the Ca(OH)₂, and "calcite" corresponds to the decarbonation of calcite).

Table 4

Amount of Ca(OH)₂ obtained using TGA in cement pastes prepared using OPC 1 and various SCMs.

Materials type	Amount of the Ca(OH) ₂ in cement paste (% by mass)
OPC 1 plain	16.92
OPC 1 + 7% SF	13.59
OPC 1 + 20% SF	8.19
OPC 1 + 45% slag	9.06
OPC 1 + 20% FA F	14.04

material prepared using OPC 1 is considered to be the reference material. In Fig. 8(b), the cementitious material prepared using OPC 2 is considered to be the reference material. Therefore, all the values are normalized using the value obtained for the reference materials.

Fig. 6 shows the amount of calcium oxychloride for variety of cementitious binders after they were carbonated for different durations (0, 0.5, and 127 h). The cementitious binders that contained SCM and are carbonated for a long duration showed a substantial reduction in the amount of calcium oxychloride formation. In fact, the carbonation reaction induces a reduction in the Ca(OH)₂ amount and creates a calcite barrier around the Ca(OH)₂. In addition, the SCMs lead to a reduction in the calcium oxychloride formation due to the reduction of Ca(OH)₂. Therefore, the potential of the calcium oxychloride formation can be substantially decreased in the carbonated specimens prepared using SCM. It is evident that the specimens containing SCM and are carbonated will show a lower amount in the calcium oxychloride because of two phenomena including (1) the carbonation reaction and (2) the use of SCM.

4. Conclusion

Recent research has shown that a chemical reaction can occur between the calcium hydroxide in a cementitious matrix and certain deicing salts (e.g., CaCl₂, MgCl₂) resulting in the formation of calcium oxychloride. The formation of calcium oxychloride is problematic since it is expansive and can result in cracking and spalling of concrete. This work began by hypothesizing that carbonation could reduce the calcium hydroxide available to form calcium oxychloride resulting in the formation of less calcium oxychloride. It appears carbonation forms a barrier of calcite

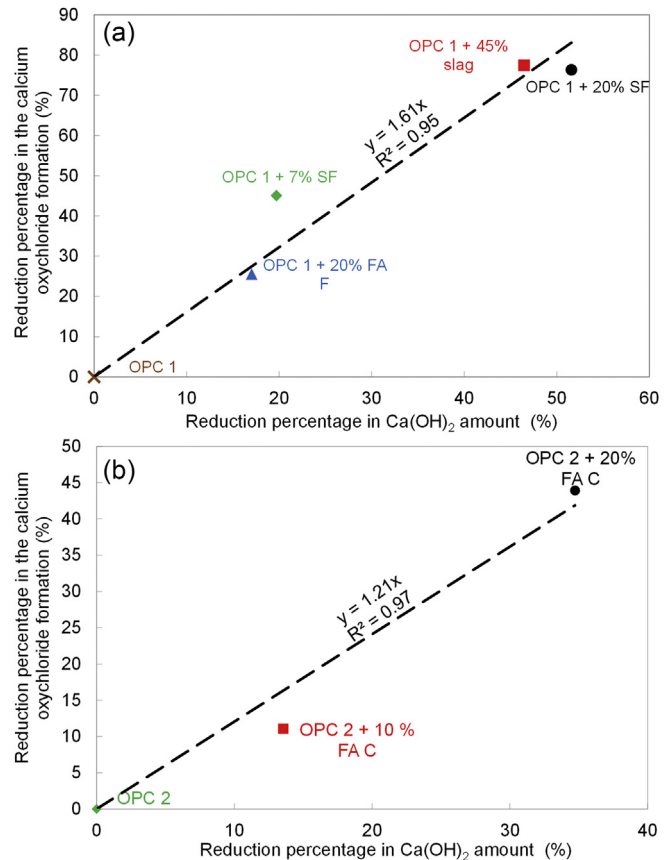


Fig. 8. Reduction of the potential of the calcium oxychloride formation with respect to the reduction in the Ca(OH)₂ due to SCM: (a) in cementitious materials prepared using OPC 1, and (b) in cementitious materials prepared using OPC 2.

around calcium hydroxide which preferentially reduces the potential for oxychloride formation. This work indicates that in addition to previous work that has shown that calcium oxychloride formation can be reduced with use of supplementary cementitious materials and topical treatments (sealers), carbonation is a factor that should be considered in determining the amount of calcium oxychloride that can form in a cementitious matrix. The results of this paper suggest that it may be beneficial to preferentially carbonate the concrete in the joints of concrete pavements thereby enhancing their resistance to joint damage due to calcium oxychloride formation.

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