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Calcium Oxychloride Formation Potential in Cementitious Pastes Exposed to Blends of Deicing Salt

by Prannoy Suraneni, Jonathan Monical, Erol Unal, Yaghoob Farnam, and Jason Weiss

Chloride-based deicing salt solutions can react with the calcium hydroxide in the cementitious matrix, leading to the formation of calcium oxychloride. Calcium oxychloride formation has been implicated in the premature deterioration of pavement joints and concrete flatwork across cold regions in North America. This study examines the formation of calcium oxychloride in the presence of blends of different chloride-based deicing salts (sodium and calcium chloride). This evaluation was performed using several plain cementitious pastes and pastes with fly ash, slag, and silica fume used as supplementary cementitious materials. Fly ash and slag were used at 20% replacement levels and the silica fume was used at 3 and 6% replacement levels. Thermogravimetric analysis was used to quantify the amount of calcium hydroxide, and low-temperature differential scanning calorimetry was used to quantify the amount of calcium oxychloride formed. When the salt blends consist of less than 20% of calcium chloride by mass, the amount of calcium oxychloride that forms is low and does not depend on the calcium hydroxide content in the pastes. When the salt blends consist of more than 20% of calcium chloride by mass, the amount of calcium oxychloride that forms depends on the calcium hydroxide content in the paste and increases with calcium hydroxide content. This suggests two strategies to mitigate the amount of calcium oxychloride that is formed: reduction in the amount of calcium hydroxide in the pastes through use of supplementary cementitious materials, and the use of deicing salt blends that include lower amounts of calcium chloride. A model is developed to estimate the amount of calcium oxychloride formed in mixtures, given the calcium hydroxide and calcium chloride contents.

Keywords: calcium oxychloride; deicing salts; differential scanning calorimetry; durability; pavements; thermogravimetric analysis.

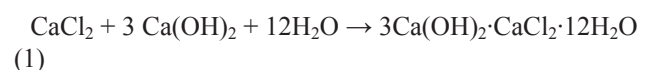
INTRODUCTION

Ice that forms on the surface of pavements in cold regions of North America is typically melted through the use of deicing salts. Numerous materials are used for deicing, including sodium chloride (NaCl), calcium chloride (CaCl₂), magnesium chloride (MgCl₂), potassium acetate, sodium acetate, and potassium formate.¹ Although alternatives to chloride-based deicing salts exist, these are typically more expensive, and most of the deicing salts used for pavement applications are currently chloride-based: NaCl, CaCl₂, and MgCl₂.¹ In practice, it is common to use blends (mixtures) of different chloride-based deicers.¹

The durability of concrete pavements can be severely compromised by freezing-and-thawing damage in locations of high fluid saturation.² In addition, these pavements may be damaged by the presence of deicing salts which may lead to salt scaling,^{3,4} corrosion,^{5,6} or calcium oxychloride forma-

tion.⁷ While freezing-and-thawing, salt scaling, and corrosion have been studied in much detail, this paper examines aspects of the lesser-known distress (calcium oxychloride formation) that is caused by a chemical reaction between the chloride-based deicers and the calcium hydroxide (Ca(OH)₂, denoted CH in this study) in concrete. This reaction leads to the formation of calcium oxychloride, a deleterious reaction product that damages concrete pavements.⁷ The reasons for the damage⁸⁻¹¹ are currently unknown, though crystallization pressure,⁸ “disruptive hydraulic pressure,”⁹ and “expansive pressure”¹⁰ have been suggested as possible reasons.

More than one form of calcium oxychloride (denoted as CAOXY in this study) can exist, depending on temperature and relative humidity conditions.¹² The chemical formula for the form of CAOXY that is most commonly observed is 3Ca(OH)₂·CaCl₂·12H₂O, it is known as the 3:1:12 form.¹² Other forms include Ca(OH)₂·CaCl₂·12H₂O and Ca(OH)₂·CaCl₂.¹² Carbonated forms of CAOXY such as 2.9CaO·0.8CaCl₂·0.2CaCO₃·12.2H₂O have also been reported.¹² The chemical equation showing the formation of the 3:1:12 form upon reaction of CH and CaCl₂ is shown in Eq. (1).¹²



Damage due to CAOXY formation in pavements is usually observed in joints and other zones of high fluid saturation and high concentration of deicing salts. The damage manifests as extensive flaking of the concrete and results in the filling of the joints with flakes of concrete.¹³ This damage is premature and expensive to repair and has been noted in numerous concrete pavements in the United States, often within the first few years of service.¹³ The extent of damage due to CAOXY formation that develops is strongly dependent on the type of deicing salt used. X-ray diffraction,^{10,14} optical microscopy,^{14,15} and scanning electron microscopy^{14,15} results indicate that CAOXY forms with CaCl₂ and MgCl₂ but not with NaCl. Pastes exposed to NaCl did not show any interaction with CH or any chemical deterioration,¹⁰ indicating that NaCl does not form any calcium oxychloride. Compressive strength measurements show

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Table 1—Oxide and phase contents of tested materials (in mass percent)

Name	Binder type	SiO ₂	Al ₂ O ₃	CaO	C ₃ S	C ₂ S	C ₃ A
C1	Ordinary portland cement Type I/II	19.96	5.05	64.45	63.2	9.5	8.4
C2	Ordinary portland cement Type I/II	19.50	5.00	62.90	55.0	14.0	7.7
C3	Ordinary portland cement Type I/II	19.70	4.50	64.20	61.0	7.0	6.0
C4	Ordinary portland cement Type I/II	19.20	4.90	64.20	64.0	—	8.0
C5	Ordinary portland cement Type I/II	20.60	5.20	63.70	57.7	—	9.9
C6	Ordinary portland cement Type III	18.90	5.20	62.90	61.3	7.8	9.0
C7	Ordinary portland cement Type V	21.30	2.60	63.20	64.0	13.1	0.0
FA1	Fly ash Class F	41.19	21.74	4.29	—	—	—
FA2	Fly ash Class C	33.40	18.40	25.65	—	—	—
FA3	Fly ash Class F	45.35	21.98	2.62	—	—	—
FA4	Fly ash Class C	37.16	20.07	22.86	—	—	—
SF	Silica fume	94.73	—	—	—	—	—
SL	Slag	—	—	—	55.3	16.6	7.9

that cementitious materials exposed to CaCl₂ show large decreases in compressive strength,^{9,10} but those exposed to NaCl¹⁰ do not. Measurements of dynamic modulus using a longitudinal guarded comparative calorimeter coupled with acoustic emission show reductions in dynamic modulus with CaCl₂ and MgCl₂ but not with NaCl.¹⁶⁻¹⁸ Recently, low-temperature differential scanning calorimetry has been developed to detect and quantify the amount of CAOXY that forms when cementitious pastes are exposed to various deicing salt solutions.^{7,16-21} Phase isopleths that describe the reaction of CaCl₂ and MgCl₂ with CH^{17,18} have been developed and it has been shown that the amount of CAOXY formed is correlated with the amount of CH²⁰ and to the amount of damage that forms.¹⁶⁻¹⁸

Strategies to mitigate joint damage due to CAOXY formation have only recently been identified.⁷ An important strategy is the use of supplementary cementitious materials (SCMs). The amount of CAOXY that forms is drastically reduced when SCMs are used to replace the cement (due to a reduction in CH contents).^{19,20} Use of fly ash or slag replacements of 20% by volume reduces the CAOXY amount by approximately 40% compared to plain cement pastes; 40% replacements reduce the CAOXY amount by approximately 70%; and almost no CAOXY is detected when 60% replacement levels are used.¹⁹ Silica fume was used up to 10% replacement; however, the CAOXY amount did not decrease by more than 15% when silica fume was used.¹⁹ Carbonated calcium silicate systems, which do not have any CH, do not show CAOXY formation or damage.²¹

This paper examines the reaction that occurs between cement pastes made using various SCMs with blends of NaCl and CaCl₂ salt solutions. This paper has three objectives. First, a relationship between the amount of CH (determined using thermogravimetric analysis) in the cement pastes and the amount of CAOXY formed (determined using low-temperature differential scanning calorimetry) is shown. Second, a relationship between the amount of CAOXY formed and the amount of CaCl₂ (or NaCl) in the salt blends is shown. Third, a simple model to estimate the amount of

CAOXY, given the amount of CaCl₂ and the amount of CH, is developed. Based on the results, strategies to mitigate the amount of CAOXY that is formed (and thus the damage that can occur) are proposed.

RESEARCH SIGNIFICANCE

The formation of CAOXY can lead to damage in concrete pavements, usually in and around joints. Typically, this damage is detected quite late, as much damage occurs inside the joint before it is observed at the surface.² This results in the damage becoming expensive and difficult to repair. Prior research has focused on the formation of CAOXY when cementitious materials are exposed to a single deicing salt (NaCl, MgCl₂, and CaCl₂). In practice, however, blends of different chloride-based deicers are frequently used. To the best of the authors' knowledge, no research has been done on the formation of CAOXY when deicing salt blends are used. As such, this study was performed to fill that research gap. An empirical model is developed to predict the amount of CAOXY that forms based on the CH content and blend composition. This model can aid in understanding mitigation strategies to reduce the amount of CAOXY in field applications.

EXPERIMENTAL PROCEDURES

Constituent cementitious materials

Twenty-eight cementitious paste compositions were tested in this study. These mixtures were made from materials provided by the Indiana Department of Transportation and are typical materials currently used in the state of Indiana for pavement applications. Six different cements, four different fly ashes, one slag (Grade 100-ground granulated blast-furnace slag), and one silica fume were tested. Table 1 summarizes the oxide and phase contents of the materials used (as provided by the manufacturers).

Paste samples were prepared using a water-cementitious materials ratio (*w/cm*) of 0.36 by mass. Fly ash and slag were used at 20% volume replacement level to be consistent with current specifications,^{22,23} whereas silica fume was used at

Table 2—Details of salt blends (all masses expressed as g/100 g [oz/100 oz])

Solution strength = 20%			
Solution	CaCl ₂ mass	NaCl mass	Water mass
100% CaCl ₂ solution and 0% NaCl solution	20	0	80
80% CaCl ₂ solution and 20% NaCl solution	16	4	80
60% CaCl ₂ solution and 40% NaCl solution	12	8	80
40% CaCl ₂ solution and 60% NaCl solution	8	12	80
20% CaCl ₂ solution and 80% NaCl solution	4	16	80
0% CaCl ₂ solution and 100% NaCl solution	0	20	80
Solution strength = 10%			
100% CaCl ₂ solution and 0% NaCl solution	10	0	90
90% CaCl ₂ solution and 10% NaCl solution	9	1	90
80% CaCl ₂ solution and 20% NaCl solution	8	2	80
70% CaCl ₂ solution and 30% NaCl solution	7	3	90
60% CaCl ₂ solution and 40% NaCl solution	6	4	90
50% CaCl ₂ solution and 50% NaCl solution	5	5	90
40% CaCl ₂ solution and 60% NaCl solution	4	6	90
20% CaCl ₂ solution and 80% NaCl solution	2	8	90

3 and 6% volume replacement levels (it was not possible to use higher replacement levels at this *w/cm* as they led to stiff mixtures with poor workability). Specific gravity values for the cement, fly ash, slag, and silica fume were assumed to be 3.15, 2.60, 2.90, and 2.30, respectively. All four fly ashes were tested with cements C1, C5, and C7; both silica fume replacement levels were tested with cements C1, C5, and C7; and the slag was tested with cement C1. No chemical admixtures were used in the preparation of the samples.

Paste sample preparation

Pastes were mixed in a vacuum mixer in accordance with ASTM C305-14.²⁴ After mixing, the paste was placed in plastic cylinders with a diameter of 38.1 mm (1.5 in.) and a height of 50.8 mm (2.0 in.). The containers were sealed and cured for 4 months at a temperature of 23 ± 1°C (73.4 ± 1.8°F). After curing, the cylindrical paste samples were loaded into a milling machine and ground to obtain a powder that subsequently was passed through a No. 200 sieve (75 μm). It is assumed that after 4 months, samples reach a high degree of hydration and any subsequent microstructural change is minimal (according to the Parrot and Killoh model,^{25,26} for the plain cements tested here, the degree of hydration after 4 months is 72% or higher, and does not increase beyond 76% even after 4 years; higher values are not observed due to lack of space²⁷ or low relative humidities limiting further hydration²⁸). Once ground, the powder was stored in a sealed container to minimize the potential for carbonation.

Salt solutions

Two solutions were prepared consisting of only one salt with 20% CaCl₂ and 20% NaCl by mass, respectively. Reagent grade CaCl₂·2H₂O and NaCl were used to prepare these solutions with the extra water in the CaCl₂·2H₂O adjusted for in the preparation of these solutions. Using

the two pure solutions, blends were prepared consisting of: 100% CaCl₂ solution and 0% NaCl solution, 80% CaCl₂ solution and 20% NaCl solution, 60% CaCl₂ solution and 40% NaCl solution, 40% CaCl₂ solution and 60% NaCl solution, 20% CaCl₂ solution and 80% NaCl solution, and 0% CaCl₂ solution and 100% NaCl solution. These are denoted as 100C0N, 80C20N, 60C40N, 40C60N, 20C80N, and 0C100N, respectively.

In addition to the aforementioned solutions, solutions of only one salt with 10% CaCl₂ and 10% NaCl were also prepared. Using these solutions, salt blends were prepared consisting of 100% CaCl₂ solution and 0% NaCl solution, 90% CaCl₂ and 10% NaCl, 80% CaCl₂ solution and 20% NaCl solution, 70% CaCl₂ solution and 30% NaCl solution, 60% CaCl₂ solution and 40% NaCl solution, 50% CaCl₂ solution and 50% NaCl solution, 40% CaCl₂ solution and 60% NaCl solution, and 20% CaCl₂ solution and 80% NaCl solution. These solutions were used to validate the model that was developed to predict CAOXY contents. The details of all solutions are presented in Table 2.

Experimental methods

Thermogravimetric analysis (TGA) was performed on all the powders to determine the amount of CH. Approximately 30 ± 10 mg (1.058 ± 0.353 milli-oz) of ground cement paste was heated to 500°C (932°F) at a heating rate of 10°C/min (18°F/min) under an inert nitrogen atmosphere. The amount of CH in the paste can be estimated based on the mass loss between the temperatures of 380 and 460°C (716 and 860°F).²⁹ Under these conditions, tested samples (of plain cement pastes) had a coefficient of variability (COV) of approximately 1%. CH amounts are presented here as g/100 g paste (oz/100 oz paste), where paste refers to the original mass of the ground paste sample.

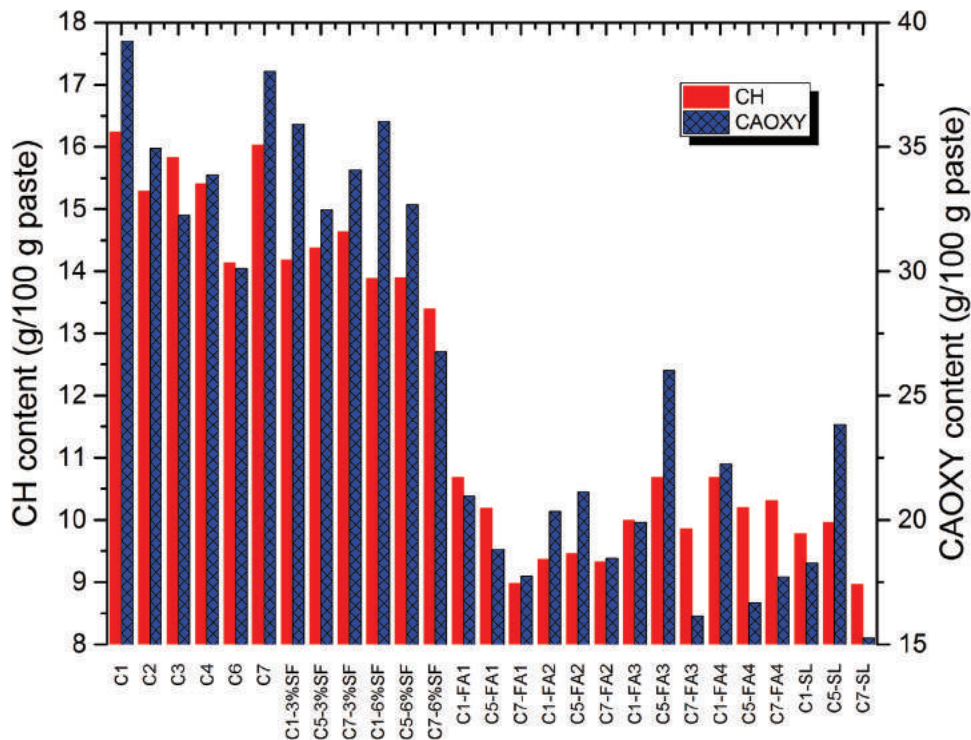


Fig. 1—CH and CAOXY contents (for the 100C0N blend) for tested cement pastes.

A low temperature differential scanning calorimeter (LT-DSC) was used to quantify the amount of CAOXY formed due to the reaction of the cement pastes with blends of CaCl_2 and NaCl solutions. Ground cement paste powder with a mass of 10 ± 0.5 mg (0.353 ± 0.0176 milli-oz) was mixed with an equal mass of salt solution (the composition was varied as described in Table 2) in a high-volume stainless steel DSC pan. The strength of the salt solution is chosen to be 20% and the powder-solution mass ratio resulting from this procedure is 1; this mass ratio is equivalent to a CH-to- CaCl_2 molar ratio lower than 3, ensuring the complete consumption of the CH and the formation of the maximum possible amount of CAOXY.^{17,19} It should be noted that these statements are only strictly true for pure CaCl_2 , because no research on the formation of CAOXY and subsequent damage has been performed for salt blends. The samples were immediately placed in the LT-DSC and initially held at 25°C (77°C) for at least 50 minutes but less than 1 hour to allow any initial heat release associated with hydration of exposed unreacted surfaces of cementitious materials to occur. Then, the temperature is reduced to -90°C (-130°F) at a rate of $3^\circ\text{C}/\text{min}$ ($5.4^\circ\text{F}/\text{min}$). A low-temperature loop is run from -90 to -70 to -90°C (-130 to -94 to -130°F) at a rate of $3^\circ\text{C}/\text{min}$ ($5.4^\circ\text{F}/\text{min}$). Finally, the temperature is increased to 50°C (122°F) at a rate of $0.25^\circ\text{C}/\text{min}$ ($0.45^\circ\text{F}/\text{min}$). The minimum temperature and the low temperature loop are both chosen to ensure freezing of the eutectic solution, which occurs at approximately -54°C (-65.2°F)¹⁷; the maximum temperature is chosen to ensure the phase transition of CAOXY (between 30 and 40°C [86 and 104°F]; the exact temperature depends on the solution composition and the paste CH content). The heating rate is chosen to provide a balance between peak sharpness and testing time, because higher rates reduce testing time

but result in broad peaks.^{17,19} A more detailed description of the effect different temperature regimes have on CAOXY formation is presented elsewhere.³⁰ The latent heat associated with the melting can be measured between the two temperature steps of the transition, and by comparing the latent heat with that measured for pure CAOXY (186 J/g),¹⁹ the amount of CAOXY formed in any chosen mixture can be quantified. CAOXY amounts are presented here as g/100 g paste (oz/100 oz paste), where paste refers to the original weight of the ground paste sample. Under these conditions, cement paste samples had a coefficient of variation (COV) of approximately 5%. Additional details about the LT-DSC experimental procedure are presented elsewhere.¹⁹

RESULTS AND DISCUSSION

Effect of paste composition on CH contents

Figure 1 shows CH and CAOXY contents for the tested cement pastes. For simplicity, only CAOXY values for the 100C0N salt blend are shown. It has been shown in earlier studies that for such salt solutions (pure CaCl_2 salt solutions with a 20% mass strength) that CAOXY values increase as CH values increase.²⁰ From Fig. 1, it can be seen that CH and CAOXY values are highest for plain cements. The replacement of cement by 3% and 6% silica fume only slightly reduces CH and CAOXY contents. Reductions when using 20% of fly ash or slag to replace cement are much more substantial, as has also been pointed out elsewhere.^{19,31} Different cements and different cement-SCM blends do not show large differences in CH or CAOXY contents; therefore, for ease of analysis, data is grouped into the following groups: plain cements, cement-3% silica fume, cement-6% silica fume, cement-fly ash, and cement-slag. Table 1 shows average and standard deviation values for CH and CAOXY contents for each of these different

Table 3—Average CH and CAOXY contents (g/100 g paste [oz/100 oz paste]) for different binder groups

Binder	CH content	CAOXY content
Plain cement	15.49 ± 0.75	34.75 ± 3.45
Cement-3% silica fume	14.40 ± 0.23	34.14 ± 1.71
Cement-6% silica fume	13.73 ± 0.28	31.82 ± 4.68
Cement-fly ash	9.98 ± 0.59	19.68 ± 2.74
Cement-slag	9.57 ± 0.53	19.12 ± 4.35

Table 4—Details of best-fit lines for CAOXY-CH plots for different salt blends

Blend	Best-fit	Slope	X-axis intercept	R ²
100C0N	Y = 2.88 × X - 8.87	2.88	3.08	0.90
80C20N	Y = 3.02 × X - 10.65	3.02	3.53	0.86
60C40N	Y = 2.52 × X - 6.77	2.52	2.68	0.91
40C60N	Y = 1.77 × X - 8.87	1.77	5.01	0.76
20C80N	Y = -0.04 × X + 11.31	-0.04	-282.75	0.00

groups. CH contents show very low standard deviations, but the values for CAOXY are more than five times higher, even though average CAOXY values are approximately twice average CH values. This indicates that the CAOXY content is sensitive to the exact cementitious binder used. A detailed discussion of this observation is not possible here due to the limited number of binders tested, but this is an aspect of interest in this research group and will be explored in further studies.

Correlation between CH contents and CAOXY contents

Figure 2 shows the correlation between CH contents and CAOXY contents for the different salt blends tested. Values of CAOXY for 0C100N are not shown here. Although a very small amount of CAOXY (less than 2 g/100 g paste [2 oz/100 oz paste]) was noted with 0C100N, it was difficult to separate the CAOXY peak from the background noise. Quantification in such cases is not reliable.) If all the CH reacted to form the 3:1:12 form of CAOXY (3Ca(OH)₂-CaCl₂·12H₂O), then 1 mole of CAOXY forms from 3 moles of CH reacting, equivalent to 2.47 g (2.47 oz) CAOXY forming for 1 g (1 oz) CH reacting (2.47 is the ratio of molecular weights of CAOXY, 549.44 and three times the molecular weight of CH, 74.09). The theoretical value of CAOXY that can form is shown in bold in Fig. 2. For the majority of mixtures, the theoretical value from chemistry provides an upper bound of the amount of CAOXY that can form with only a few points appearing above this line (likely due to statistical variability). The CH data in Fig. 2 falls in two clusters, one from approximately 9 to 11 g/100 g paste (9 to 11 oz/100 oz paste) and the other from approximately 14 to 17 g/100 g paste (13 to 17 oz/100 oz paste). Using values from Table 3, it is clear that the first cluster corresponds to pastes with fly ash or slag; the second cluster corresponds to plain pastes or pastes with silica fume. Therefore, it can be concluded that the replacement of cement with fly ash or slag results in lower CH values. It can be seen that pastes with lower CH values also have lower

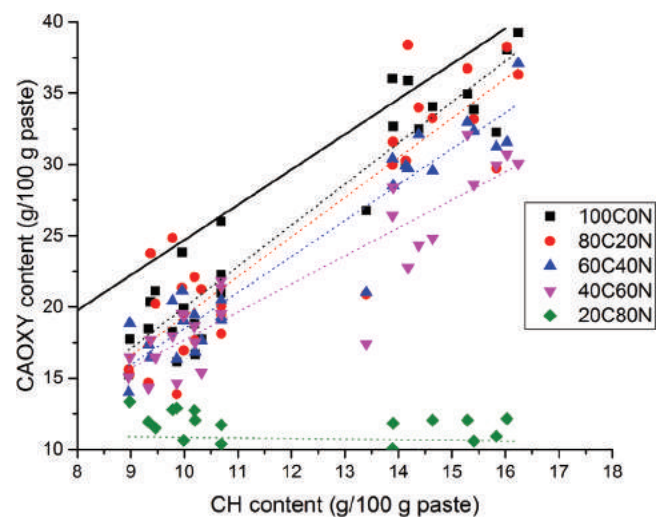


Fig. 2—Correlation between CH and CAOXY contents for different salt blends. Best-fit lines are shown (dotted lines), details of which are provided in Table 4. Theoretically predicted values of CAOXY are shown using a bold line passing through origin, having slope of 2.47.

CAOXY values. However, it should be noted that at these replacement levels, which are comparable to those of the current Indiana Department of Transportation specifications, the reduction in the CAOXY is limited to approximately 40 to 50%. The CAOXY values are fitted to a best-fit line for each salt blend (shown as dotted lines in the figure) and details are provided in Table 4. For a given mixture, the CAOXY values are similar for the 100C0N, 80C20N, and 60C40N blends. They are well-correlated with CH values and CAOXY values approach the theoretical limit based on chemistry. In the case of the 40C60N blend, less CAOXY forms for all mixtures and there is poor correlation between CAOXY and CH contents. The amount of CAOXY formed decreases further in the case of the 20C80N blend and there is no correlation between CAOXY and CH contents. For the 0C100N blend very little CAOXY was measured (less than 2 g/100 g paste [2 oz/100 oz paste]).

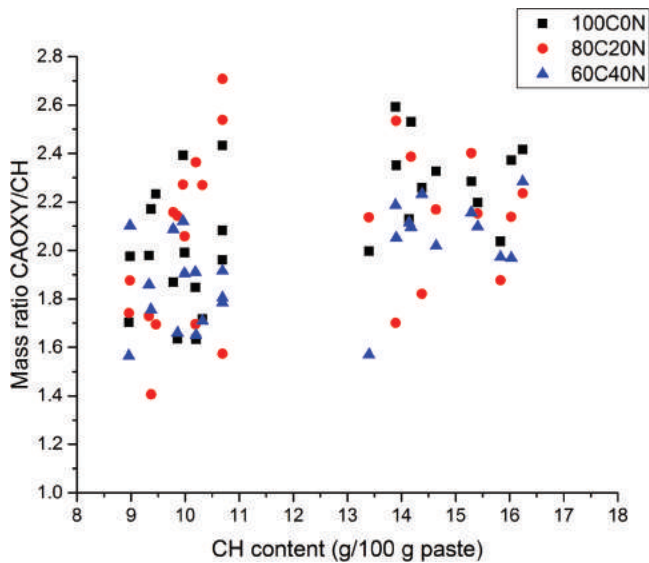


Fig. 3—Mass ratio of CAOXY and CH plotted against CH content.

In the cases where there is a strong correlation between CAOXY amount and CH contents, the best-fit lines do not pass through zero. Rather, the best-fit lines for the 100C0N, 80C20N, and 60C40N intersect the x-axis at a value of 3.09 ± 0.42 (g CH/100 g paste) (oz CH/100 oz paste). This indicates that no CAOXY would be formed for CH amounts below this critical amount. A possible explanation is the hypothesis that the reaction of the CH with the SCM may result in reaction products that encapsulate some of the CH, thereby preventing it from reacting with the deicing salt solution.²⁰ The average slope of the fitted lines is 2.81 ± 0.26 . This fitted value is higher than the theoretically predicted value of 2.47; however, it is quite similar to the value of 2.73 reported elsewhere.²⁰ This difference in slope may be driven by the fact that at low amounts of CH (between 9 and 11 g/100 paste [9 and 11 oz/100 oz paste]), the samples contain some encapsulated CH that does not react with the deicing salt solution, leading to lower CAOXY amounts than expected. For higher amounts of CH (14 to 17 g/100 paste [14 to 17 oz/100 oz paste]), the amount of CAOXY approaches the theoretical value, as these samples do not have SCMs and therefore no encapsulated CH.

Figure 2 clearly suggests two mitigation strategies to reduce the amount of CAOXY that is formed: 1) reduction in CH contents using fly ash, slag, or other supplementary cementitious materials; and 2) using salt blends lower than 20% CaCl_2 by mass.

The use of SCM has also been suggested in other studies^{7,19,20,31} and it has been shown that CAOXY contents (for high CaCl_2 proportions) decrease drastically for higher SCM replacement levels (over 40% by volume). The increased use of SCM is typically accompanied by three main concerns: 1) increased potential for salt scaling; 2) increased potential for corrosion with high SCM replacements; and 3) potential delays in construction scheduling due to slower strength gains. While some literature has shown that salt scaling does increase with SCM,^{32,33} field studies have not confirmed this, and in fact, low-slump mixtures,

typically used in pavements show good resistance to salt scaling.³⁴ In terms of corrosion, SCMs typically improve corrosion resistance,^{35,36} although the use of large amounts of SCMs may theoretically result in the consumption of all the CH, resulting in a loss of pH buffer, which can accelerate the potential for corrosion.³⁷ Scheduling delays can be caused because use of SCMs can result in lower early-age strengths; however, the use of accelerating admixtures can help in increasing strengths. Care must be taken to ensure that the used SCM and accelerators are compatible; otherwise, adequate strength gain may not be achieved.³⁸

Nature of CAOXY formed

Figure 3 shows a plot of the mass ratio of CAOXY and CH versus the CH content for the 100C0N, 80C20N, and 60C40N blends (the cases where there is a strong correlation between the CAOXY and CH amounts). As pointed out earlier, in terms of CH contents, data can be grouped into two distinct groups: higher CH contents with cement or silica fume, and lower CH contents with fly ash or slag. For the cements or silica fume, the mass ratio occupies a narrower range (1.9 to 2.7) and generally is higher than for the cases with fly ash and slag (1.4 to 2.6). Average values using all data are 2.24 ± 0.18 for cement or silica fume and 1.92 ± 0.26 for fly ash or slag. These values are lower than the theoretically predicted values of 2.47 for full consumption of CH, especially for the cases with fly ash and slag. This data may be explained by the CH encapsulation hypothesis. Because some of the CH is encapsulated, it is not consumed in the reaction to form CAOXY, and therefore, the values of the CAOXY to CH mass ratio are lower than expected. CH encapsulation has clearly been shown in the case of carbonation,³⁹ although the samples in this paper do not have sufficient carbonation, it is likely that other hydration products may behave similar to calcium carbonate. It should also be noted that a small amount of carbonation in these samples might be inevitable. It is clear from these results that some of the CH is inaccessible to the salt solution and therefore does not react; however, the exact reason as to why this is so is unknown and needs to be further investigated. It should be pointed out that this analysis assumes that only the 3:1:12 form of CAOXY forms; it may be possible that another type also forms and coexists with the 3:1:12 form. While this scenario seems rather unlikely, it cannot be completely ruled out.

Correlation between CaCl_2 contents and CAOXY contents

Figure 4 shows a plot of the CAOXY formed in the different pastes as a function of the proportion of CaCl_2 solution to NaCl solution in the salt blends. To simplify analysis, data points have been grouped into the following categories based on their CH contents, as earlier: plain cements, cement-3% silica fume, cement-6% silica fume, cement-fly ash, and cement-slag. Average values and standard deviations for all the mixtures in each different category are shown in the figure.

As pointed out earlier, CAOXY contents increase with the proportion of CaCl_2 solution in the blends. At lower propor-

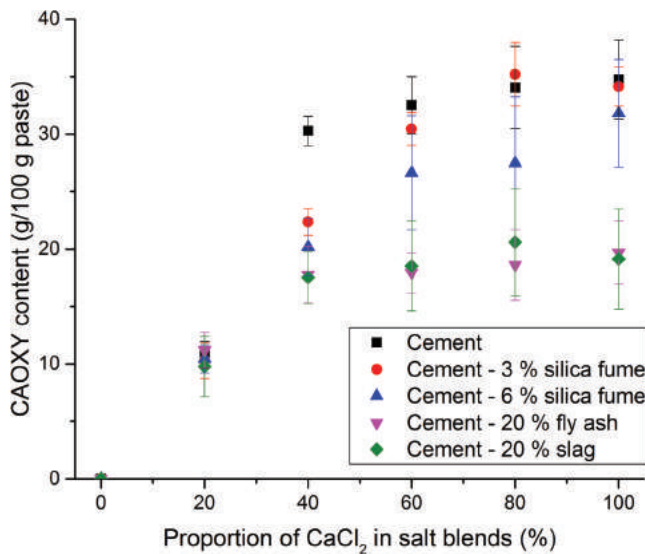


Fig. 4—Relation between CAOXY formed and proportion of CaCl_2 in salt blend.

tions of CaCl_2 solution in the blends, the reaction is controlled by the amount of CaCl_2 . At higher proportions of CaCl_2 solution in the blends, the reaction is controlled by CH. The concentration at which this switch occurs depends on the amount of CH in the paste. For the mixtures containing fly ash and slag, which have lower amounts of CH, the CAOXY that forms increases until a proportion of 40% CaCl_2 solution in the blends. At higher proportions of CaCl_2 , the amount of CAOXY produced plateaus. This plateau is caused by the CaCl_2 consuming all the CH in these pastes. The cement and silica fume pastes have higher amounts of CH than the SCM pastes and the values of CAOXY continue to increase until the proportion of CaCl_2 solution in the blends is 60% or 80%. The values then plateau, as all the CH has been consumed by the CaCl_2 at this point. At very low proportions of CaCl_2 in the blends (0 and 20% CaCl_2), there is no difference in the CAOXY contents for a given mixture; this is because the CH contents are substantially greater than the CaCl_2 contents, and the reaction is limited by CaCl_2 content.

Figure 5 shows the data plotted in a similar manner as in Fig. 4; however, individual mixtures are plotted here with their CH contents (for example, 16.03CH refers to a paste with a CH content 16.03 g/100 g paste [16.03 oz/100 oz paste]). For this figure, two additional mixtures with much lower CH contents that were not in Fig. 4 are plotted. These mixtures, denoted 4.93CH and 2.40CH, have a greater replacement of slag and therefore much lower CH contents (these mixtures were made for another study²⁰; 40 and 60% volume replacement of slag; a different slag and cement from the ones reported here were used, the w/cm was 0.36 and the samples were 49 days old). For the paste with the lowest CH content (2.40CH), a very small amount of CAOXY is formed and does not depend on the CaCl_2 content. For the mixture 4.93CH, higher amounts of CAOXY are formed, but they plateau at a proportion of 20% CaCl_2 in the salt blends. For the mixture 8.96CH, higher amounts of CAOXY are formed, and they plateau at a proportion of 40% CaCl_2 in the salt blends. For the mixture 10.69CH, higher amounts

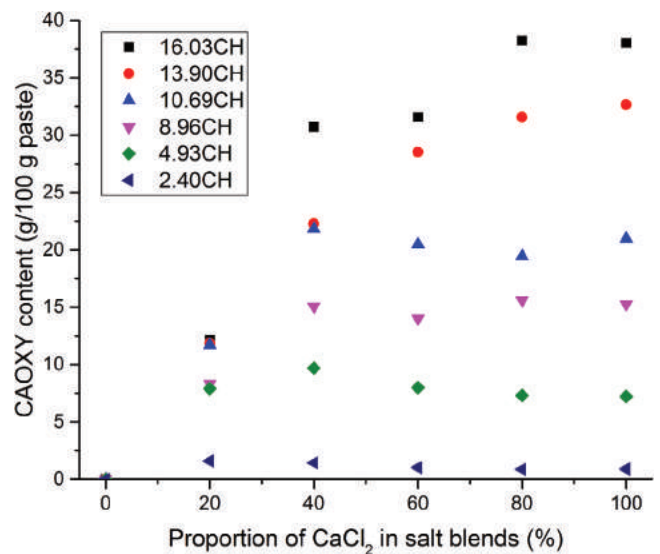


Fig. 5—Relationship between CAOXY formed and amount of CaCl_2 in salt blend for mixtures with different CH contents.

of CAOXY are formed, and they plateau at a proportion of 40% CaCl_2 in the salt blends. The mixtures with the highest amount of CH form the highest amounts of CAOXY, and these values they plateau at a proportion of 80% CaCl_2 in the salt blends. This leads to the same conclusion as from Fig. 4; mixtures with higher amounts of CH form higher amounts of CAOXY and these amounts plateau at higher proportions of CaCl_2 in the blends.

General model to estimate CAOXY contents

Although the relationships established in previous sections are useful, they are somewhat specific. It is much more useful and beneficial to develop a general model to estimate CAOXY contents for cases with any amounts of CH and CaCl_2 and NaCl blends. Consider a case where 100 g (100 oz) of ground cement paste is mixed with 100 g (100 oz) of CaCl_2 and NaCl blends. All blends have an overall concentration of 20% mass and different proportions of CaCl_2 and NaCl. To develop the model, the following assumptions are made:

1. The NaCl has a negligible contribution to the formation of CAOXY. It adds to the weight of the solution but does not participate in the reaction. It can be assumed to be water for all practical purposes.
2. Not all the CH reacts to form CAOXY because some of the CH is encapsulated by other hydrates in the presence of SCMs. This amount is denoted as CH_0 .
3. Some of the CaCl_2 is bound by hydrated aluminate phases and calcium silicate hydrate (C-S-H) in the cement paste. This amount is denoted as CC_0 .

As presented in Eq. (1), 3 moles of CH react with 1 mole of CaCl_2 . Because the molar weights of CH and CaCl_2 are 74.09 and 110.98, respectively, this is equivalent to 2 g (2 oz) of CH reacting with 1 g (1 oz) of CaCl_2 . Whenever there is excess CH, the reaction is controlled by CaCl_2 , and vice versa. Assuming that CH_0 g/100 g paste (CH_0 oz/100 oz paste) of CH and CC_0 g/100 g paste (CC_0 oz/100 oz paste) of

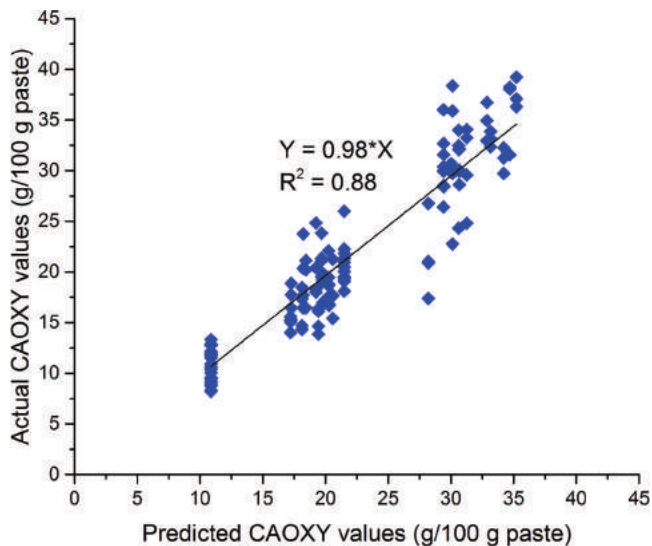


Fig. 6—Predicted and expected CAOXY values.

CaCl₂ does not react, this leads to a simple model to estimate the amount of calcium oxychloride:

If the amounts of CH or CaCl₂ are lower than the encapsulated CH or bound CaCl₂ amount, then no CAOXY is formed. This condition can be expressed as follows:

$$\text{If } CH < CH_0 \text{ or } CaCl_2 < CC_0, \text{ then } CAOXY = 0 \quad (2)$$

If there is excess CH in the system, the amount of CAOXY is controlled by CaCl₂, and 1 mole of CAOXY is formed for 1 mole of CaCl₂ reacting, equivalent to 549.44 g (549.44 oz) CAOXY forming for 110.98 g (110.98 oz) CaCl₂ reacting. This condition can be expressed as follows:

$$\begin{aligned} &\text{If } 2 \times (CaCl_2 - CC_0) < (CH - CH_0), \\ &\text{then } CAOXY = \frac{549.44}{110.98} \times (CaCl_2 - CC_0) \end{aligned} \quad (3)$$

If there is excess CaCl₂ in the system, the amount of CAOXY is controlled by CH, and 1 mole of CAOXY is formed for 3 moles of CH reacting, equivalent to 549.44 g (549.44 oz) CAOXY forming for 222.28 g (222.28 oz) CH reacting. This condition can be expressed as follows:

$$\begin{aligned} &\text{If } 2 \times (CaCl_2 - CC_0) > (CH - CH_0), \\ &\text{then } CAOXY = \frac{549.44}{222.28} \times (CH - CH_0) \end{aligned} \quad (4)$$

All amounts (CaCl₂, CH, CAOXY) are expressed as g/100 g paste (oz/100 oz paste). The CH encapsulated value can be determined as follows. The x-axis intercept in Fig. 2 for the cases where there was a strong correlation between CAOXY amount and CH contents is 3.09, which indicates that no CAOXY should be formed for CH contents below 3.09 g/100 g paste (3.09 oz/100 oz paste). Nevertheless, results from Fig. 4 show some CAOXY formation when the CH content was 2.40 g/100 g paste (2.40 oz/100 oz paste). Another set of data (unpublished) showed no CAOXY formation when the CH content was 1.80 g/100 g paste (1.80 oz/100 oz paste). Therefore, an assumption was made

that the critical value is somewhere between 1.80 and 2.40; for ease of calculations, this value is assumed to be 2 g/100 g paste (2 oz/100 oz paste) of CH that does not react.

The bound CaCl₂ value can be determined as follows. In the 20C80N blend, there is far more CH than can be completely consumed by the CaCl₂. Therefore, the amount of CAOXY formed should be dictated by the amount of CaCl₂ present, which is equal to the overall amount minus the amount bound in the cement pastes. For the pastes tested here, the CAOXY content is 10.76 ± 1.53 g/100 g paste (10.76 ± 1.53 oz/100 oz paste). Because this amount is reasonably constant, one can assume a similar magnitude of chloride binding in all the pastes. If there is no binding, the CAOXY content should be 19.78 g/100 g paste (19.78 oz/100 oz paste); this leads to a chloride binding of approximately 1.8 g/100 g paste (1.8 oz/100 oz paste). This value agrees well with chloride binding between 1.5 and 2 g/100 g paste (1.5 and 2 oz/100 oz paste) from various studies.⁴⁰⁻⁴² Therefore, the value of CH₀ is 2 g/100 g paste (2 oz/100 oz paste) and the value of CC₀ is 1.8 g/100 g paste (1.8 oz/100 oz paste).

The criterion for determining if CaCl₂ or CH controls the reaction is, therefore, or)

$$2 \times (CaCl_2 - 1.8) > (CH - 2) \text{ (or) } 2 \times CaCl_2 - 1.6 > CH \quad (5)$$

Using this criterion, Eq. (2), (3), and (4) simplify to

$$\text{If } CH < 2 \text{ or } CaCl_2 < 1.8, \text{ then } CAOXY = 0 \quad (6)$$

$$\begin{aligned} &\text{If } 2 \times CaCl_2 - 1.6 < CH, \\ &\text{then } CAOXY = \frac{549.44}{110.98} \times (CaCl_2 - 1.8) \end{aligned} \quad (7)$$

$$\begin{aligned} &\text{If } 2 \times CaCl_2 - 1.6 > CH, \\ &\text{then } CAOXY = \frac{549.44}{222.28} \times (CH - 2) \end{aligned} \quad (8)$$

Applying the model to the entire data set results in Fig. 6. As can be seen from the figure, the agreement between predicted and actual CAOXY values is excellent, especially considering the simplicity of the assumptions made.

The usefulness and power of the model can also be illustrated by attempting to predict CAOXY values for various CH and CaCl₂ values. To do this, the model is applied to the data shown earlier in Fig. 5. The results are shown in Fig. 7, with experimental points being shown as symbols and modeled data being shown as straight lines. The agreement with experimental data is excellent, and modeled and experimental CAOXY values do not differ by more than 5 g/100 g paste (5 oz/100 oz paste). As was stated earlier, at low proportions of CaCl₂, the CAOXY value depends on CaCl₂, and at high proportions of CaCl₂, the CAOXY value depends on CH. In other words, the slope of the initial part (a linear increase) is determined by CaCl₂ and the plateau value is determined by the CH. All mixtures have the same initial slope, and the plateau value increases as the CH content in the mixture increases. The model allows for the development of this entire plot for different CaCl₂ and

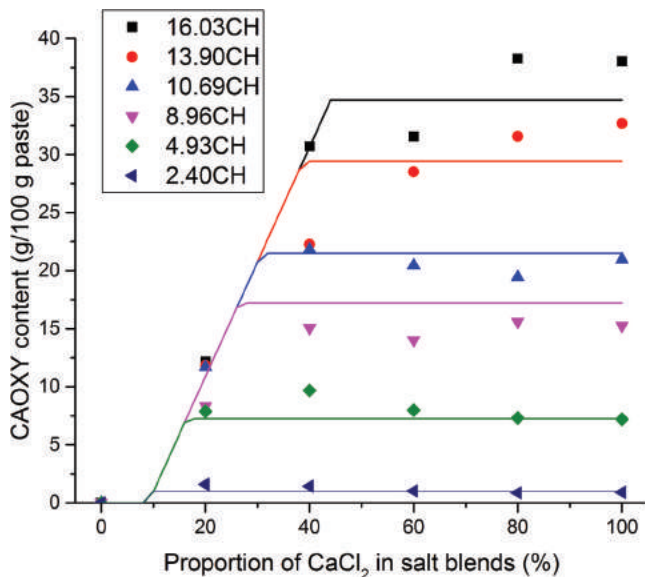


Fig. 7—Application of model to estimate CAOXY values for various CH and CaCl₂ values. Experimental data is same as Fig. 5, and modeled data is shown as solid straight lines.

CH contents, thereby significantly reducing experimental effort. The model suggests that CAOXY formation can be reduced by reducing CH contents and by using salt blends lower than 20% CaCl₂ by mass. As an example, when the CH content is below 8.96 g/100 g paste (8.96 oz/100 oz paste), the CAOXY content never exceeds 15 g/100 g paste (15 oz/100 oz paste); when the salt blends are lower than 20% CaCl₂ by mass, the CAOXY content never exceeds 13 g/100 g paste (15 oz/100 oz paste). The exact amount of CAOXY to mitigate damage is not known, and likely also depends on other factors such as air content and *w/cm*. Other strategies to mitigate joint damage due to CAOXY formation have been discussed elsewhere.⁷

Although the model was developed in this specific case with 1:1 powder-solution ratio with an overall solution strength of 20%, the predictions should be valid for any other mixing ratio and solution concentrations, assuming the 3:1:12 form of CAOXY forms. To validate the model, tests were performed using salt blends at a lower solution concentration of 10% (the compositions are described in Table 2). These solutions were tested with three different cement pastes (a plain cement, a cement with fly ash, and a cement with slag: C1, C7SL, C1FA1). Tests were performed as earlier, and the developed model was applied to predict the results. Figure 8 shows that experimental and predicted values are well correlated. Results are similar to earlier, and the model predicts experimental values well, although predicted values are slightly higher than actual values. It should be noted that at very high concentrations of CaCl₂, other phases may form, if that is the case, this model is not valid and a more comprehensive model that accounts for different forms of CAOXY needs to be developed.¹⁷ Finally, it should be pointed out that a limited amount of data was used to determine CH₀ and CC₀ and more experiments are needed in order to more accurately determine these values. Additionally, CH₀ and CC₀ likely depend on factors including SCM amount and

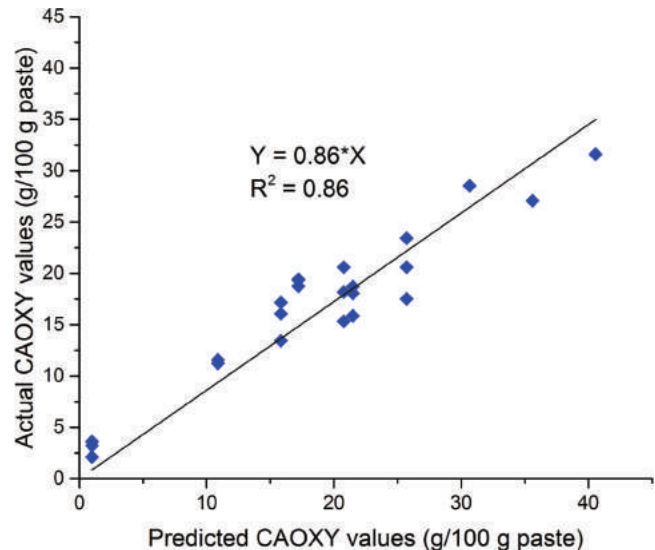


Fig. 8—Predicted and expected CAOXY values for 10% mass solution blends.

sample age. These factors need to be taken into account to develop a more comprehensive model.

FURTHER RESEARCH

A model that can be used to estimate the amount of CAOXY when cement pastes are exposed to various blends of CaCl₂ and NaCl has been proposed, and strategies to reduce the amount of CAOXY are discussed. At this point, the relationship between damage in concrete and the amount of CAOXY is currently being developed. The factors that affect damage observed due to CAOXY formation (such as air content and *w/cm*) need to be quantified and related to field performance.

CONCLUSIONS

In this work, the formation of calcium oxychloride (CAOXY) in cement pastes with blends of NaCl and CaCl₂ is studied. The main conclusions from the study are as follows:

1. CAOXY contents increase with the proportion of CaCl₂ solution in the salt blends. At lower proportions of CaCl₂ solution in the salt blends, the reaction is controlled by the amount of CaCl₂.
2. At higher proportions of CaCl₂ solution (more than 20%) in the salt blends, the reaction is controlled by calcium hydroxide (CH). The concentration at which this switch occurs depends on the amount of CH in the paste. At higher proportions of CaCl₂, CAOXY amounts increase as the CH content in the paste increases.
3. A simple model has been developed to estimate the amount of CAOXY formed in the pastes, depending on the CaCl₂ and CH contents.
4. CAOXY amounts can be reduced by reducing CH amounts through use of supplementary cementitious materials but this needs to be balanced with concerns over scaling, reduction of the pH buffer leading to increased corrosion potential, and slower early strength development.
5. CAOXY amounts can be reduced by the use of deicing salt blends with lower CaCl₂ proportions, but this needs to

be balanced with the possibility of reduced deicing performance at lower temperatures as well as public safety.

AUTHOR BIOS

Prannoy Suraneni is a Post-Doctoral Research Associate in the School of Civil and Construction Engineering at Oregon State University, Corvallis, OR. He received his B.Tech in civil engineering from the Indian Institute of Technology Madras, Chennai, India; his MS in civil engineering from the University of Illinois at Urbana-Champaign, Champaign, IL; and his PhD in civil engineering from ETH Zürich, Zurich, Switzerland. His research interests include the chemistry and durability of cementitious materials.

Jonathan Monical is a Graduate Teaching Assistant in the Lyles School of Civil Engineering at Purdue University, West Lafayette, IN. His research interests include concrete pavements and concrete durability.

Erol Unal is a Graduate Researcher in the School of Civil and Environmental Engineering at Georgia Institute of Technology, Atlanta, GA. His research interests include concrete pavements and concrete durability.

ACI member **Yaghoob Farnam** is an Assistant Professor in the Department of Civil, Architectural, and Environmental Engineering at Drexel University, Philadelphia, PA. He received his BSc in civil engineering from K.N. Toosi University of Technology, Tehran, Iran; his MS in civil engineering from University of Tehran, Tehran, Iran; and his PhD in civil engineering from Purdue University.

Jason Weiss, F.A.C.I., is the Miles Lowell and Margaret Watt Edwards Distinguished Chair in Engineering and Head of the School of Civil and Construction Engineering at Oregon State University. He received his BAE in architectural engineering from Pennsylvania State University, State College, PA, and his MS and PhD in civil engineering from Northwestern University, Evanston, IL.

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