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Verifying the Calcium Oxychloride Threshold in Cementitious Pastes

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Verifying the Calcium Oxychloride Threshold in Cementitious Pastes

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science in Civil Engineering

by

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ABSTRACT

Calcium oxychloride (CAOXY) formation is a serious deterioration mechanism known to cause joint damage in concrete pavements. CAOXY is the product of a chemical reaction between calcium chloride (CaCl_2) or magnesium chloride (MgCl) deicing salts and calcium hydroxide in the cementitious matrix. Currently, the accepted CAOXY threshold at which deterioration is mitigated in cementitious paste is 15 g/100 g paste (15 oz/100 oz paste); however, this limit was developed using flexural strength testing. For this investigation, the current threshold was evaluated using compressive strength and mass change over time in paste specimens exposed to CaCl_2 . Fly ash is used to replace cement (up to a 50% mass replacement) in order to limit CAOXY deterioration. While compressive strength reduction was observed in all specimens despite fly ash replacement level, the results generally validate the current CAOXY threshold level in cementitious paste determined from flexural strength testing.

Keywords: Calcium oxychloride; Compressive strength; Mass change; Thermogravimetric analysis; Low-temperature differential scanning calorimetry

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1. INTRODUCTION

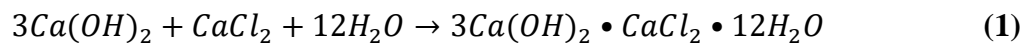
1.1. Calcium oxychloride background

Numerous investigations have been conducted in order to determine the impact of chloride-based deicing salts on portland cement concrete pavements.¹ Typical deterioration mechanisms attributed to their use are corrosion of reinforcing steel² and surface salt scaling;³ however, it should be noted that freeze-thaw deterioration may occur simultaneously.⁴ Another deleterious impact associated with chloride-based deicing salts is their ability to react with hydration products found in the cementitious matrix^{1,5,6} and some of these interactions cause significant damage to cement paste⁷ and concrete.⁸

Chloride ions can interact with the hydrated aluminate phases of portland cement to form Kuzel's salt⁹ or Friedel's salt.¹⁰ Calcium chloride (CaCl_2) or magnesium chloride (MgCl_2) can also react with calcium hydroxide (Ca(OH)_2) from the cementitious matrix to form an expansive phase known as calcium oxychloride (CAOXY).^{7,11-19} Many studies show that the magnitude of the damage caused by this expansion is strongly dependent on the type and concentration of deicing salt used.¹³⁻¹⁷ CAOXY forms when CaCl_2 and MgCl_2 are used but does not appear to form when sodium chloride (NaCl) is used. The formation of CAOXY has been shown to cause rapid damage to concrete pavement joints that are saturated with deicing solution.¹⁹ While the literature agrees that extensive deterioration occurs, the exact damage mechanism is still unknown. It has been postulated that hydraulic pressure,⁷ expansive pressure¹⁷, or crystallization pressure¹⁸ are possible causes. CAOXY formation is affected by numerous factors including temperature, relative humidity, and solution concentration, and the material is stable at room temperature (i.e. 23 °C (73 °F)) at a solution concentration of 11.3%.²⁰ The quantity of CAOXY formed is also strongly influenced by the amount of Ca(OH)_2 available in the cementitious

matrix and increases with an increase in the Ca(OH)_2 amount.⁵ Phase diagrams have been developed for the cement paste- CaCl_2 ²¹ and Ca(OH)_2 - CaCl_2 ^{12,22} systems to predict the temperature/solution concentration at which CAOXY is stable. From these diagrams, it is observed that the temperature at which CAOXY forms is above the freezing point of water.²³ The CAOXY precipitant is stable in low (< 10%) CaCl_2 solution concentrations near 5 °C (41 °F) and increasing solution concentrations are required for continued stability as the temperature increases. Though CAOXY phase stability is theoretically possible at 50 °C (122 °F) for a 30% CaCl_2 solution, no deterioration has been observed in concrete above 40 °C (104 °F).⁵

Various phases of CAOXY can exist based on temperature and relative humidity,^{15,23} but the phase believed to be responsible for damage in cementitious systems is given in **Eq. 1**.^{16,21,22} It is sometimes referred to as the 3:1:12 phase.¹⁶



Damage related to deicing salt deterioration is expensive to repair;^{24,25} therefore, mitigation techniques based on minimizing CAOXY formation are critical and have been the subject of several studies using five different approaches. First, the use of sealants^{24,26,19} can help prevent CaCl_2 and MgCl_2 solutions from penetrating concrete pavements. Second, preferential carbonation has been suggested to remove Ca(OH)_2 from the outer region of the cementitious paste and replace it with non-reactive calcium carbonate (CaCO_3) limiting the reaction extent.²⁵ Third, supplementary cementitious materials (SCM) can be used to reduce the amount of Ca(OH)_2 in the cementitious paste, thereby decreasing the amount of potential CAOXY formation.^{13,16,27-29} Fourth, the presence of entrained air helps relieve pressure related to CAOXY

formation by providing deposition locations for the crystals reducing the resulting damage.¹⁵ Finally, the use of salt blends containing lower percentages of CaCl₂ and MgCl₂ could help lessen CAOXY deterioration.^{30,31}

While many investigations have focused on mechanical property reduction due to damage associated with CAOXY, new tests have also been developed to better understand the mechanism of CAOXY formation and the resulting damage. These tests are summarized as follows:

- Thermogravimetric analysis (TGA) – Used to determine Ca(OH)₂ content in cementitious mixtures.^{27,31}
- Low-temperature differential scanning calorimetry (LT-DSC) – Used to quantify the amount of CAOXY that can form in cementitious mixtures.^{32,33}
- Volume change measurements (VCM) – Used to quantify the volumetric changes due to formation of CAOXY and its associated phase change.^{21,22}
- Longitudinal guarded comparative calorimeter-acoustic emission (LGCC-AE) – Used to detect cracking associated with CAOXY formation in cementitious systems.^{20,30}
- Ball-on-three-ball test (B3B) – A flexural strength test to quantify the damage due to CAOXY formation in paste specimens exposed to chloride solutions.^{34,35}

1.2. Research significance

An effective strategy to prevent CAOXY damage is through a partial replacement of cement with fly ash.^{27,29,36,37} A preliminary threshold value for CAOXY of 15 g/100 g paste (15 oz/100 oz paste) was proposed by Suraneni et al.²⁹ for damage mitigation in cementitious paste due to CAOXY formation based on flexural strength testing. The paste threshold has been tentatively linked with concrete damage.¹⁹ The goal of this study is to verify the paste threshold using

compressive strength and mass change measurements of pastes exposed to a 30% (mass) CaCl₂ solution to clearly outline SCM replacements needed to mitigate CAOXY damage.

2. EXPERIMENTAL PROCEDURES

2.1. Cement paste mixture design development

Cementitious paste samples were cast using a Type I/II portland cement. For the paste samples requiring a partial cement replacement with SCM, three Class C fly ashes (ASTM C618³⁸) and one Class F fly ash (ASTM C618³⁸) were utilized. Suraneni et al.^{27,29} have shown that different types of fly ash types mitigate CAOXY formation at a similar level, therefore, only four fly ashes are studied here. Utilizing ASTM C114,³⁹ bulk chemical oxide compositions of the cement were determined while the bulk chemical compositions of the fly ash were determined using ASTM C311.⁴⁰ The chemical composition and specific gravity of the cement and each fly ash are presented in **Table 1**.

Table 1 – Chemical constituents of the cement and each fly ash. Constituents given as bulk percentage (%)

Chemical constituents	Portland cement (PC)	Fly ash (C) (CFA1)	Fly ash (C) (CFA2)	Fly ash (C) (CFA3)	Fly ash (F) (FFA1)
SiO ₂	20.25	34.57	36.23	35.47	56.25
Al ₂ O ₃	4.45	20.26	19.25	19.41	18.91
Fe ₂ O ₃	4.20	5.69	6.15	6.34	9.59
CaO	63.73	26.47	25.54	26.2	7.61
MgO	0.91	4.85	5.87	5.59	1.88
SO ₃	3.09	1.73	1.58	1.64	1.47
Na ₂ O	0.16	1.60	1.68	1.65	1.27
K ₂ O	0.54	0.50	0.53	0.5	2.61
TiO ₂	0.19	1.66	1.46	1.54	0.90
P ₂ O ₅	0.16	0.88	1.23	1.02	0.53
LOI	2.53	0.58	0.95	0.34	0.50
Specific gravity	3.15	2.58	2.67	2.70	2.40

Cement was replaced in the paste specimens with fly ash at levels of 0, 10, 20, 30, 40, and 50% by mass. This work is part of a larger project investigating the correlation of CAOXY deterioration in cementitious paste and concrete; therefore, a mass replacement was utilized to simulate typical field construction procedures of concrete pavements. Given that some literature uses volumetric cement replacement with fly ash, equivalent volumetric fly ash levels were computed using the average specific gravity (2.59) of the four fly ashes, which correlate to the mass levels at 0, 12, 23, 34, 45, and 55%, respectively. For low (10%) cement replacement levels, deviations between individual volumetric fly ash levels are minor at approximately 1% while at higher mass cement replacement levels (50%) there is nearly a 3% difference in fly ash volume of similar samples. A consistent water-to-cementitious material ratio (w/cm) of 0.45 was maintained for each batch, and no chemical admixtures were added. A minimum of (12.3 kg) (27.1 lb) was required for mixing and mass proportions of each constituent utilized in the cementitious mixture designs provided in **Table 2**.

Table 2 – Mass proportions for the cementitious paste mixture designs.

Fly ash replacement, % mass	Cement, kg (lb)	Fly ash, kg (lb)	Water, kg (lb)
0	8.49 (18.72)	0.00 (0.00)	3.82 (8.42)
10	7.64 (16.85)	0.85 (1.87)	3.82 (8.42)
20	6.79 (14.97)	1.70 (3.74)	3.82 (8.42)
30	5.94 (13.10)	2.55 (5.62)	3.82 (8.42)
40	5.09 (11.23)	3.40 (7.49)	3.82 (8.42)
50	4.25 (9.36)	4.25 (9.36)	3.82 (8.42)

2.2. Mixing process and specimen curing

The paste was mixed in a standard mortar pan mixer in general accordance with ASTM C305.⁴¹ It is noted that in order to avoid unmixed paste (i.e. clumping), the mixing time was doubled. It is believed that due to the large batch size and lack of aggregate in the mixture that

this step was needed to ensure homogeneous pastes. After mixing, 36 cubes, 51 mm x 51 mm x 51 mm (2 in x 2 in x 2 in), were cast with the paste and wrapped in polyethylene sheeting. The samples were then covered with wet towels and sealed in plastic bags to avoid moisture loss. The specimens were stored in an environmental chamber for 24 hours at 23 ± 1.5 °C (73 ± 3 °F) with a relative humidity of $50 \pm 4\%$. After 24 hours, the specimens were demolded and cured until testing. Specimens utilized for strength analysis were cured in a lime water bath in accordance with ASTM C511.⁴² Upon demolding, specimens to be tested using thermogravimetric analysis (TGA) and low-temperature differential scanning calorimetry (LT-DSC) were wrapped in polyethylene sheeting and placed in a sealed container to cure for 91 days. Similar procedures are followed in Monical et al.;³² however, the specimens were not demolded but were left in the molds for the duration of curing in that research. A 91 day curing duration is also in accordance with other literature²⁷ which allows for the pozzolanic reactions between the fly ash and $\text{Ca}(\text{OH})_2$ in the cementitious paste to occur.

3. EXPERIMENTAL METHODS

3.1. Visual observations

Visual examinations of the specimens were made prior to compressive strength testing and mass change measurements. Photographs were taken periodically throughout testing to record damage. In addition, observations were conducted visually with a stereo-microscope (AmScope SM-4) equipped with a MU1000 camera attachment after specimens were exposed to 30% CaCl_2 solution. Visual observations indicated different stages of damage throughout the 91-day testing cycle.

3.2. Thermogravimetric analysis (TGA)

TGA was performed on each cementitious paste sample in order to quantify the amount of Ca(OH)_2 . Following the 91-day curing period, the specimens to be tested for TGA were ground and sieved (using a No. 200 sieve) to obtain a fine powder. Around 30 to 40 mg (0.0011 to 0.0014 oz) of powder was loaded into the TGA apparatus and the sample was heated to 500 °C (932 °F) at a rate of 10 °C/minute (18 °F/minute) under an inert nitrogen atmosphere. Testing was performed in accordance with ASTM C1872,⁴³ however, the Ca(OH)_2 content was determined using a tangential baseline approach in typical mass loss temperature range of 380 to 460 °C (716 to 860 °F).⁴⁴ This approach is consistent with similar work from the literature.^{21,29,34}

3.3. Low-temperature differential scanning calorimetry (LT-DSC)

In order to determine the amount of CAOXY that formed when the pastes were exposed to the CaCl_2 solution, LT-DSC was conducted in accordance with AASHTO T365.³³ This method uses approximately 10 mg (0.0004 oz) of ground paste mixed with 10 mg (0.0004 oz) of a 20% CaCl_2 solution in a stainless-steel pan that is sealed and placed into an LT-DSC chamber. The samples were maintained at 25 °C (77 °F) for about one hour and then cooled to -90 °C (-130 °F) at a rate of 3 °C/minute (5.4 °F/minute). Then a low-temperature loop was run from -90 °C (-130 °F) to -70 °C (-94 °F) and back to -90 °C (-130 °F) at the same rate of 3 °C/minute (5.4 °F/minute). This phase was followed by a heating cycle till 50 °C (122°F) at a rate of 0.25 °C/minute (0.45 °F/minute) under which CAOXY undergoes a phase transition (around 30 to 40 °C [86 to 104 °F] for the pastes studied here). The LT-DSC instrument measures the heat flow in the paste- CaCl_2 solution system, and the amount of CAOXY formed is quantified by comparing the heat release with that associated with the formation of pure CAOXY.^{27,29,34,35}

3.4. Mass change

Mass measurements were collected on each compressive strength specimen prior to submersion in the CaCl_2 solution and prior to strength testing. At 91 days of age, the specimens were removed from the limewater bath and scraped to remove the free lime from all surfaces. Then, they were rinsed with tap water, dried with paper towels to reach a surface dry condition and weighed before submersion into the CaCl_2 solution. Before each compressive strength test, the specimens were removed from solution, rinsed and dried again before the final mass was measured. A similar procedure has been followed for mass measurements of paste specimens exposed to chloride-based deicing salts in Mori et al.⁷ In this experiment, however, the initial curing time was increased to allow for the pozzolanic reaction between the $\text{Ca}(\text{OH})_2$ and the fly ash. The presence of CAOXY crystals and surface scaling of some specimens made it difficult to obtain consistent surface moisture levels for mass measurements (especially at later ages).

3.5. Compressive strength

Compressive strength of the paste was measured at 1, 7, 28, 56, and 91 days age using ASTM C109.⁴⁵ Three specimens per batch were tested at each age and the average of the three is reported. At 91 days, the remaining samples were placed in a 30% mass CaCl_2 solution following the procedures for mass recordings. A commercially available 96% pure CaCl_2 product was dissolved in deionized water to obtain the solution. While a 30% CaCl_2 solution is aggressive, it ensures that $\text{Ca}(\text{OH})_2$ is the limiting reactant in an accelerated test. The specimens were then stored at a temperature of 5 ± 1 °C (41 ± 2 °F) for the remainder of the experiment. For each mixture, compressive strength measurements were performed after 1, 7, 28, 56, and 91 days submersion in CaCl_2 solution. It should be noted that CAOXY levels determined using AASHTO T365³³ were tested using a 20% CaCl_2 solution, which is the standard. CAOXY levels

used for threshold verification are based on those obtained using AASHTO T 365.³³ A 30% storage solution was chosen to accelerate deterioration during the intended testing timeframe. It is likely that increased CAOXY levels would be reported similar to Monical et al.³² if a 30% solution were also used for LT-DSC testing; however, since $\text{Ca}(\text{OH})_2$ is the limiting reactant, the CAOXY values are not expected to be significantly different.

4. RESULTS AND DISCUSSION

4.1. Visual observations

During storage in a CaCl_2 solution, three stages of deterioration were observed as shown in **Fig. 1**. Initial damage (the first stage) was observed approximately 24 hours after the samples were placed into solution. It manifested as micro-cracks visible on all surfaces of the samples as shown in **Fig. 1A**; however, these initial cracks appeared less obvious in specimens cast with increasing levels of fly ash. To the authors' knowledge, similar deterioration at early ages has not been reported elsewhere due to exposure to CaCl_2 solution. Despite attempting to remove surface lime deposits from curing, a potential exists that the CaCl_2 reacted with residual lime on the surface of the specimens initiating this damage. Cracking may also have been initiated due to thermal differences as the specimens were stored at 5 °C (41 °F) following placement in the solution. The second damage mechanism was surface scaling and it was typically observed after 28 days of submersion. This damage mechanism (shown in **Fig. 1B**) was widely visible on samples with 30 and 40% fly ash levels. Scaling has been reported in portland cement based materials exposed to deicing solutions;³ however, in this investigation, the scaling also could be caused by a minor amount of CAOXY formation. Given that it is readily observed in the 30 and 40% fly ash specimens, a similar deterioration to the third damage stage is likely occurring; however, due to lower CAOXY levels, the deterioration rate/level is also reduced. The third type

of damage was also visible after 28 days of exposure. It manifests itself as paste flaking along the edges and spalling of layers from all exposed surfaces toward the center of the deteriorated samples as shown in **Fig. 1C**. The damage increased over time, and was more severe in cement only pastes with clear separation of the layers. This damage mechanism decreased as the fly ash percentage increased in the samples and is likely attributed to the formation of CAOXY.²⁹ As shown in **Fig. 2**, deterioration decreases as cement is replaced with increasing levels of fly ash following 91 days in solution.

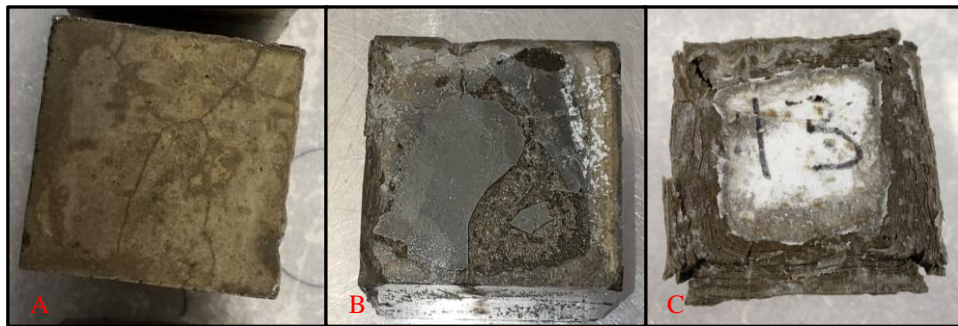


Fig. 1 – Various deterioration mechanisms in cementitious pastes following exposure to a 30% mass CaCl_2 solution at 5 °C: (A) initial cracking; (B) surface scaling; and (C) heavy flaking/disintegration.

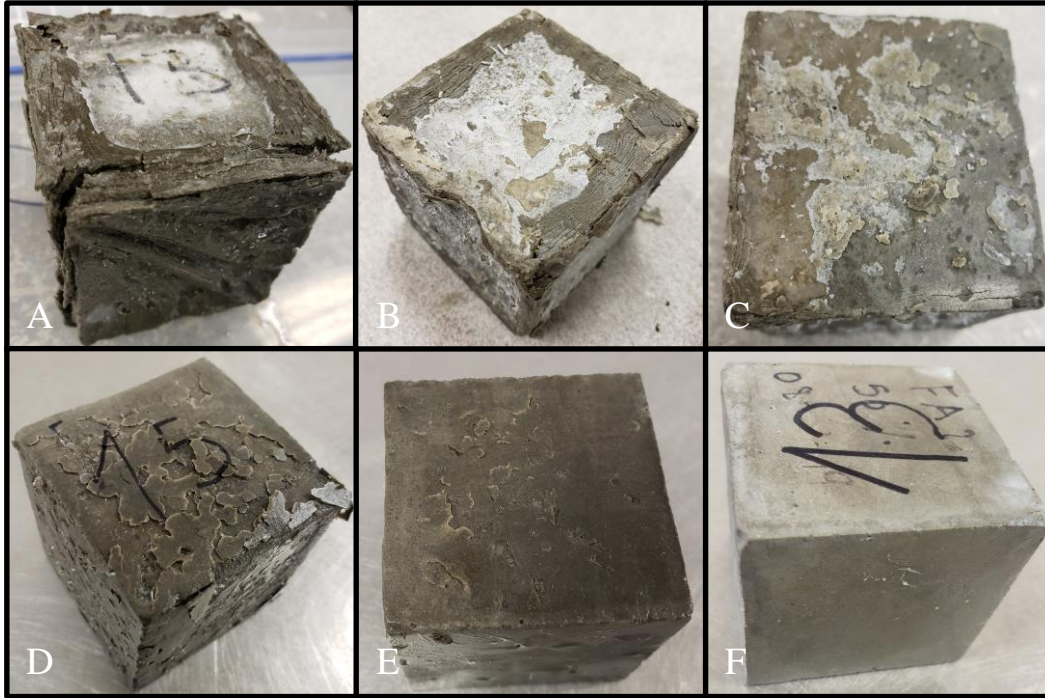


Fig. 2 – Deteriorated states of specimens containing different cement replacement levels with fly ash after 91 days of exposure to a 30% mass CaCl_2 solution: (A) PC; (B) 10% CFA1; (C) 20% CFA1; (D) 30% CFA1; (E) 40% CFA1; (F) 50% CFA2.

4.2. Thermogravimetric analysis

Presented in **Fig. 3** are the amounts of Ca(OH)_2 formed in the paste specimens as a function of each individual fly ash level based on TGA. An average Ca(OH)_2 value is presented in **Fig. 4** with one error bar on each side of the average representing the standard deviation. The results show a linear reduction in the Ca(OH)_2 content as the fly ash replacement level increases which is in good accordance with Suraneni et al.^{27,29} A black dotted line represents pure dilution due to the removal of cement from the system and the results indicate that the reduction in Ca(OH)_2 is greater than that expected from pure dilution, which is clear evidence for the pozzolanic reaction between fly ash and Ca(OH)_2 in the paste.³⁷

As shown in Suraneni et al.,^{27,29} Ca(OH)_2 and CAOXY are linearly correlated. Using this correlation, a red, dotted horizontal line (8 g Ca(OH)_2 /100 g paste [8 oz Ca(OH)_2 /100 g paste]) is

plotted on **Fig. 3 and Fig. 4** to represent the correlated limit of $\text{Ca}(\text{OH})_2$ to the CAOXY threshold value (covered in **section 4.3**). For the present research, the level at which $\text{Ca}(\text{OH})_2$ is mitigated below this limit corresponds to a 37% fly ash replacement by mass (~41% volume). Below this limit, damage related to CAOXY formation is expected to be mitigated.²⁹ It should be noted this fly ash level is higher than typical replacements used in practice and could lead to other potentially negative effects (such as low early-age strength).

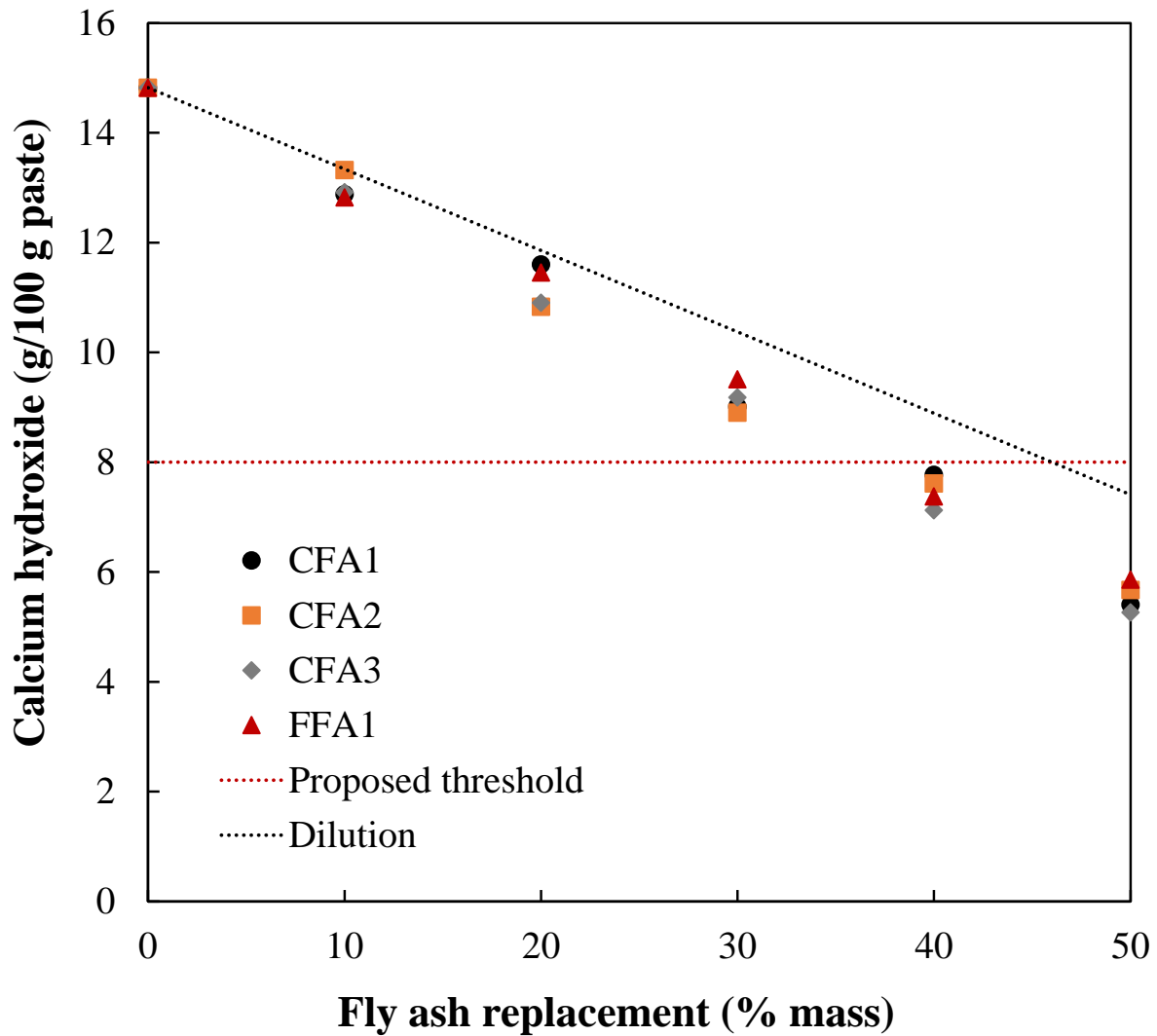


Fig. 3 – Calcium hydroxide reduction due to cement replacement with fly ash for individual fly ashes.

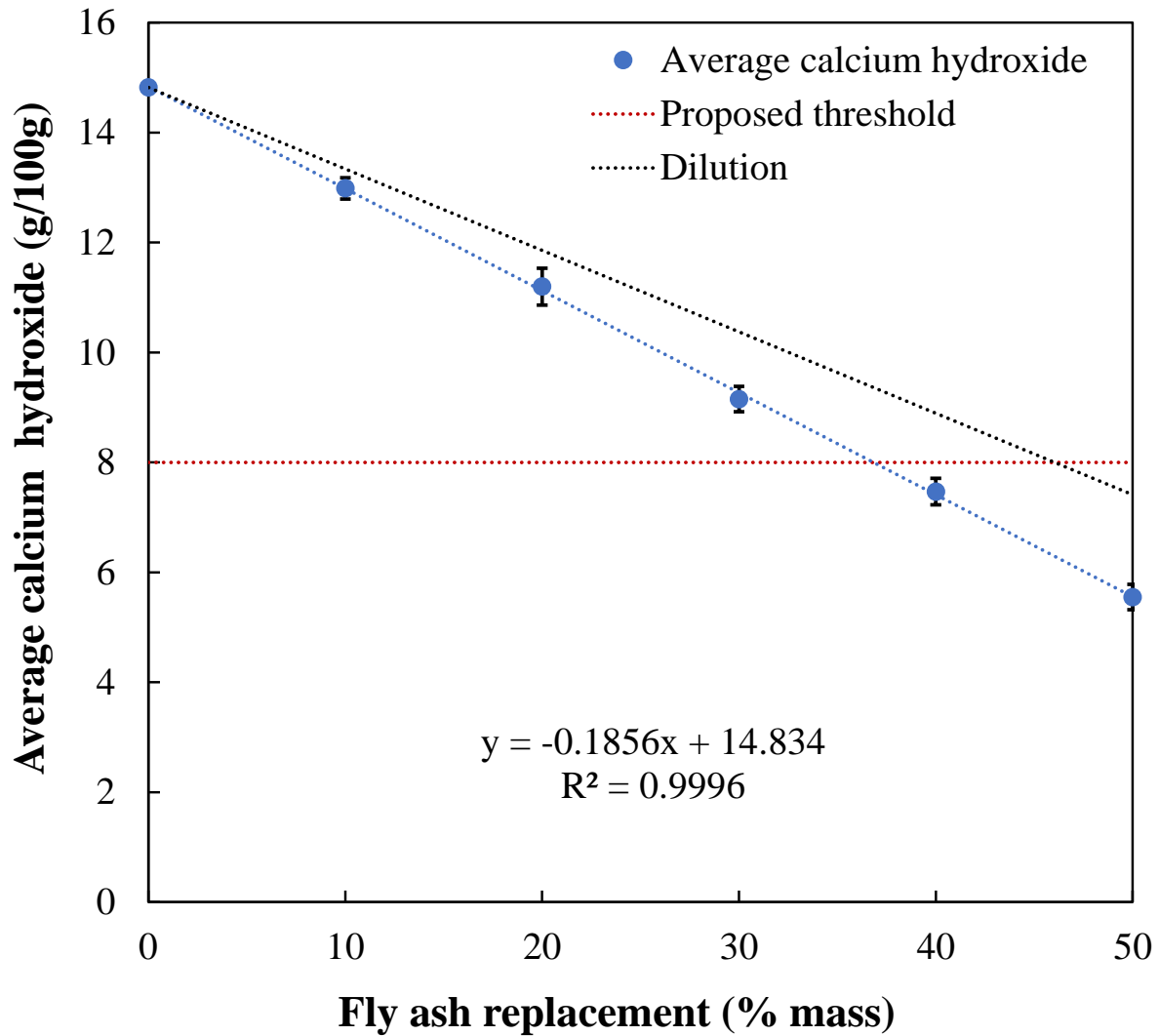


Fig. 4 – Average calcium hydroxide reduction due to cement replacement with fly ash.

4.3. Low-temperature differential scanning calorimetry

CAOXY contents for the individual pastes obtained through LT-DSC testing are shown in **Fig. 5**. It should be noted that LT-DSC testing was unable to be completed on three pastes (CFA2 30%, CFA3 20, and CFA3 30%). The variation in the amount of CAOXY was significantly greater than in the $\text{Ca}(\text{OH})_2$ amounts, as also noted earlier in literature.^{29,34} This variability could be because a portion of the $\text{Ca}(\text{OH})_2$ quantified by TGA is unavailable for reaction (i.e. encapsulated by the hydration products) with the deicing solution as suggested by

Suraneni et al.^{27,29} and/or minor carbonation of specimens prior to testing. **Fig. 6** shows the average CAOXY levels with error bars representing the standard distribution. Results indicate that CAOXY amounts linearly decreased with increasing fly ash replacement levels as presented in the literature.^{29,34} This indicates that a partial replacement of cement with fly ash decreases the amount of CAOXY formed; therefore, reduced damage in the cementitious paste is expected. The red horizontal line (15 g CAOXY/100 g paste [15 oz/100 oz paste]) represents the preliminary threshold value proposed below which CAOXY damage should be limited.²⁹ In the present research, a 27% cement replacement with fly ash by mass (~30% volume) is needed to mitigate CAOXY below the proposed limit. This fly ash level is somewhat lower than results provided in the literature at 35% by volume.³⁰ Again, this may be due to the smaller sample size of fly ashes tested or possibly minor carbonation prior to testing. In addition, the use of different cements, which provide different CAOXY amounts in pastes without fly ash may also influence the threshold level. CAOXY and Ca(OH)_2 amounts both decrease linearly as fly ash levels increase indicating that Ca(OH)_2 is a major factor affecting CAOXY formation; however, the fly ash levels required to mitigate levels below the two thresholds are different (i.e. 37 and 27% mass fly ash). This discrepancy could be caused by the differences in testing. In TGA, the total Ca(OH)_2 is quantified while in LT-DSC only the Ca(OH)_2 available for reaction with the deicing solution is quantified because of Ca(OH)_2 .^{27,29} Therefore, caution should be used when using correlated TGA values to predict CAOXY formation in paste specimens.

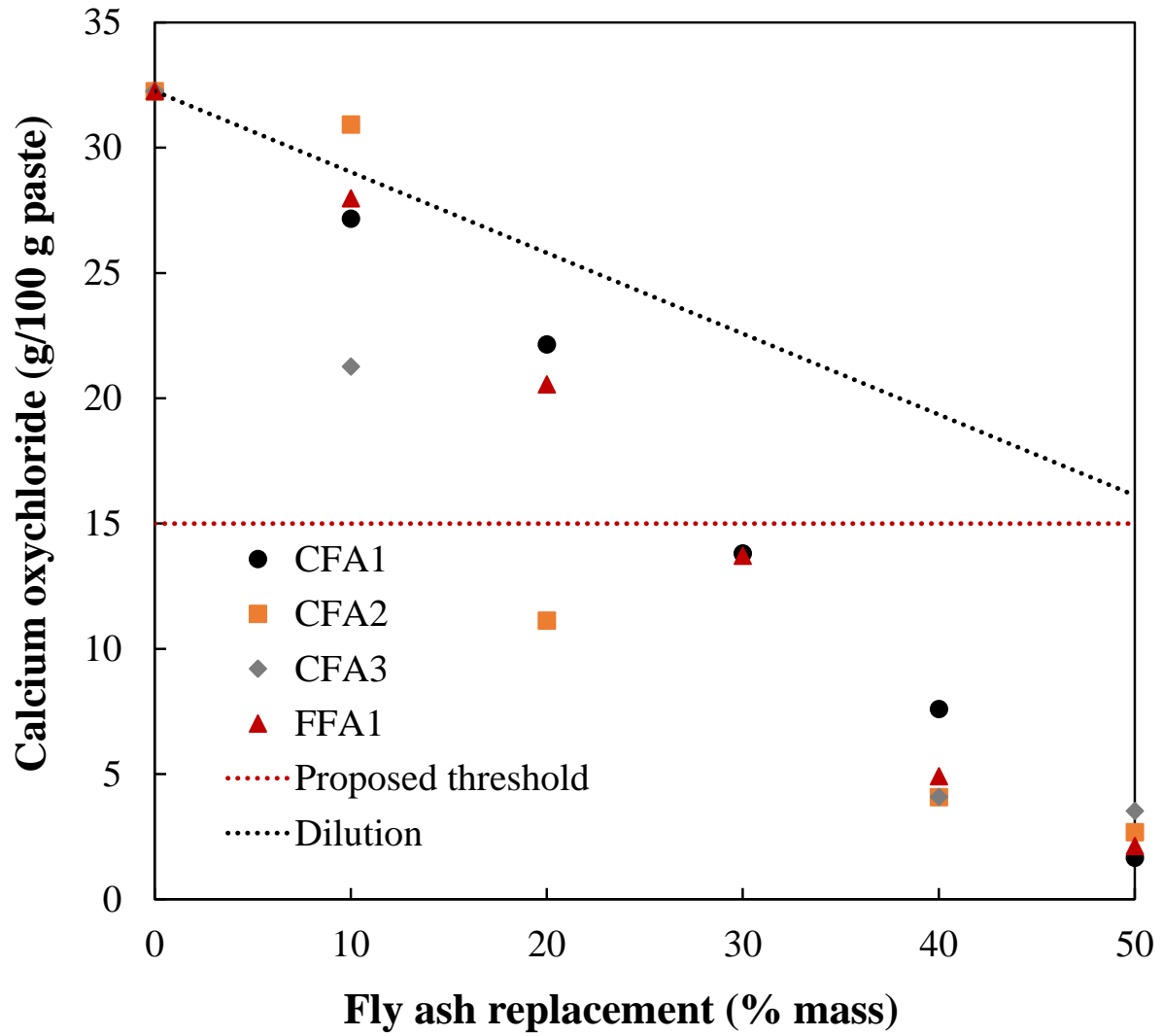


Fig. 5 – Calcium oxychloride reduction due to cement replacement with fly ash for individual fly ashes

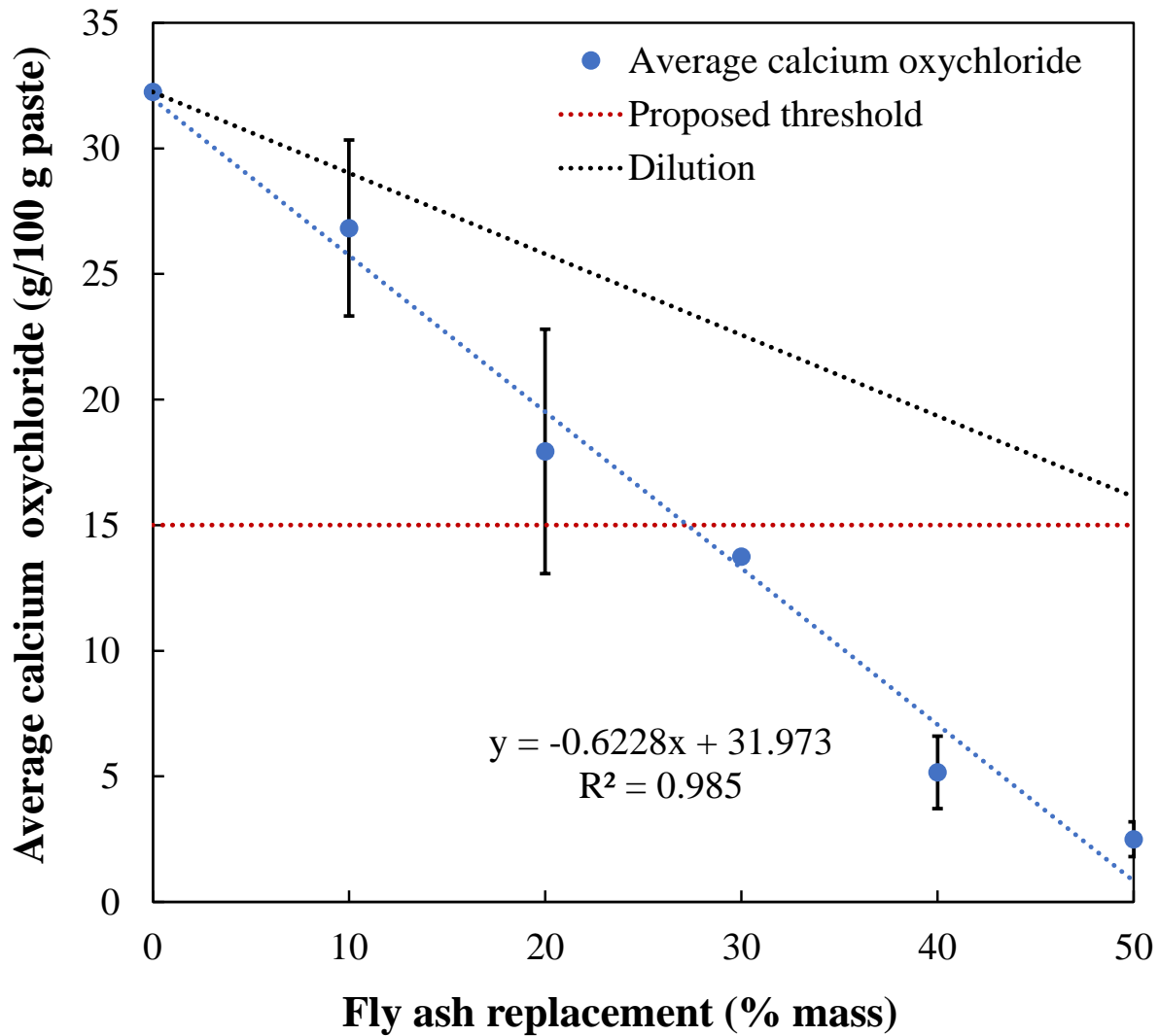


Fig. 6 – Average calcium oxychloride reduction due to cement replacement with fly ash.

4.4. Mass change

Fig. 7 shows the average mass change measurements of the specimens throughout the duration of storage in a 30% mass CaCl₂ solution. Error bars for this data represent the standard deviation of the four samples tested at each fly ash level. Two distinct behaviors were exhibited by the pastes. In specimens containing a cement replacement with fly ash at 20% or greater, minor mass loss (0.02 to 1.68% on average) was observed during testing. Similar observations were reported in paste samples by Mori et al.⁸ While it is likely that solution ingress occurs in

these specimens, mass loss governs which might be due to calcium leaching from the specimens and/or minor spalling of the exterior surface. This is further observed in **Fig. 8**. In specimens cast with cement only and 10% fly ash, considerable mass gain is observed after 7 days of submersion in the CaCl_2 solution. At extended testing durations (91 days), the effect was exacerbated in the cement only specimens recording a 9% mass increase and those with 10% fly ash recording a 6% mass increase. The mass gain is likely due to massive infiltration of the solution into the cracked specimens, followed by a saturation of the layers progressively moving inward engendering the delamination.⁷

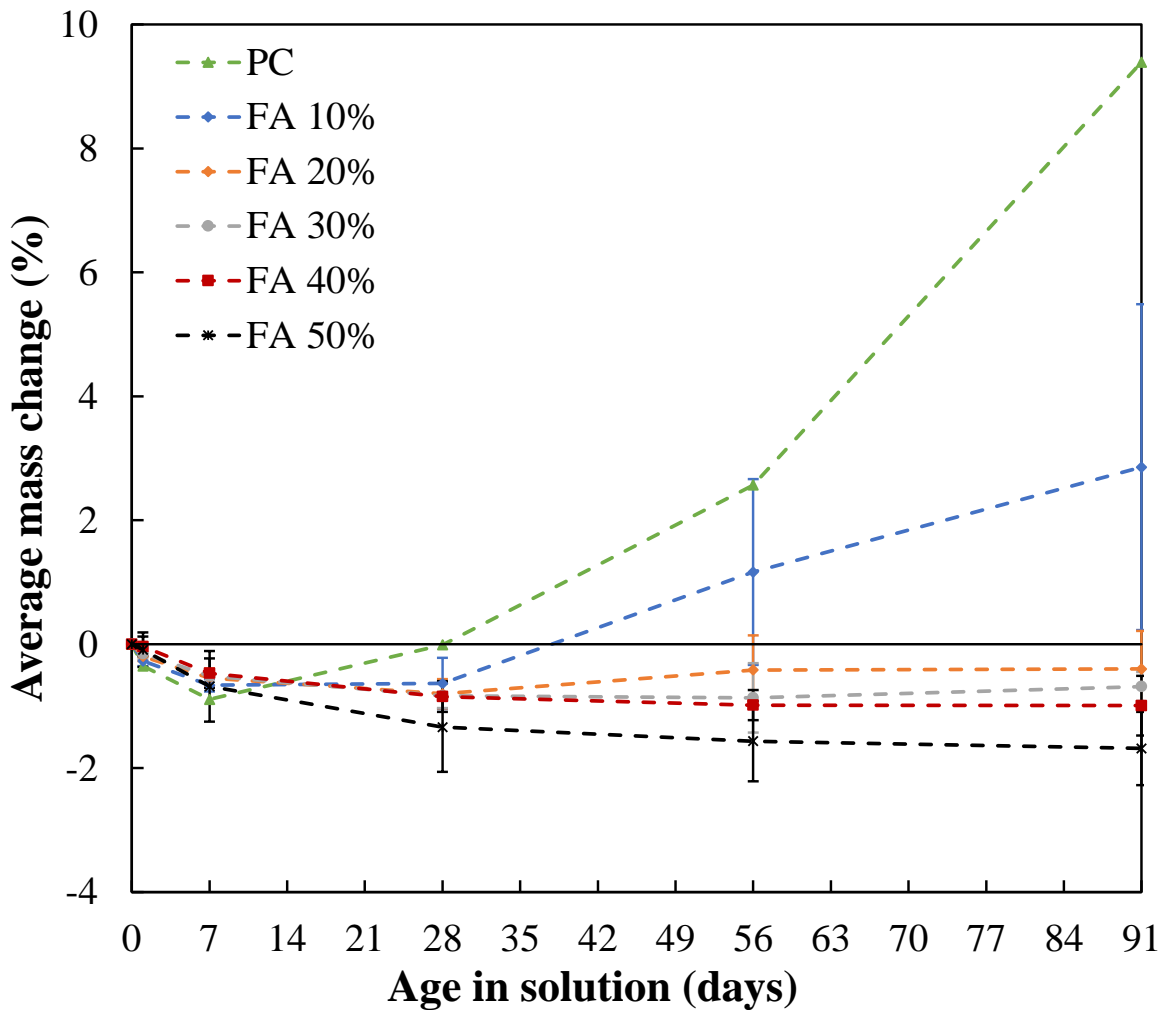


Fig. 7 – Average mass change of specimens submerged in 30% mass CaCl_2 solution.

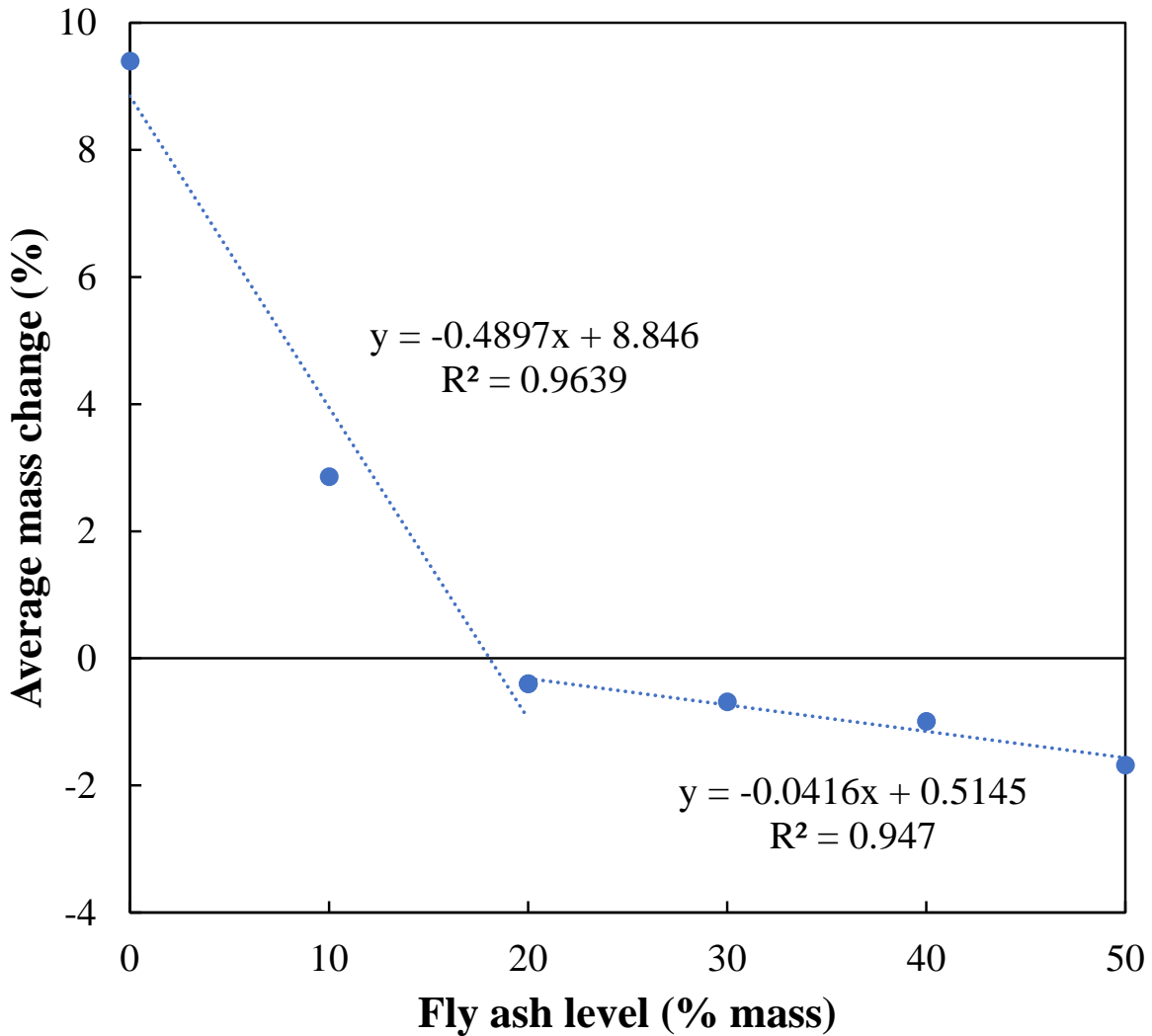


Fig. 8 – Average mass change of submerged specimens as a function of fly ash level.

4.5. Compressive strength

The average compressive strength of the paste samples during the curing period in lime water is provided in **Fig. 9**. At 91 days, the compressive strength of samples made with less than 30% fly ash was equal to or higher than that of the control sample. Compressive strength began decreasing when the cement replacement level was above 30%, possibly due to low reactivity at higher fly ash levels. In **Fig. 10**, a decrease in compressive strength is observed following placement of the specimens in solution. Reductions in strength are observed for all specimens,

but samples with higher fly ash levels (above 20% by mass) have less reduction compared to those with little or no fly ash. This compressive strength reduction is likely the result of the damage observed in the samples as shown in **Fig. 1C** and is consistent with the mass change data in **Fig. 7**. Error bars in **Fig. 9** and **Fig. 10** represent the standard deviation of the averages for each set of breaks. There is an increase in the standard deviation following placement in solution. Considering the averages of the coefficient of variation of the specimens cured in lime water, the maximum (7.5%) does not exceed the maximum permissible (8.7%) allowed in ASTM C109/109M;⁴⁷ however, for specimens placed in solution, this permissible range is exceeded. This is likely the result of reduced planeness in the specimen surface due to flaking/spalling of some specimens from swelling/saturation of the outer layers. Planeness specifications were unable to be achieved following deterioration of the samples; therefore, specimens were tested “as is” for this portion of quantifying strength reduction. Also, in some specimens non-planar failures occurred rather than conical failure, and could be caused by early age cracking (**Fig. 1A**). The average compressive strength reduction of the specimens after 91 days of submersion in CaCl₂ solution is presented in **Fig. 11**. Compressive strength reduction is determined by comparing the specimens stored in solution to the 91-day strength of equivalent specimens cured in lime water. Strength reduction decreases as the fly ash replacement increases, which is in agreement with the literature.³⁴ Fly ash 30, 40 and 50% mass replacements levels decreased the paste compressive strength reduction from 73% in cement only specimens to 42, 31, and 18%, respectively. These fly ash levels correspond (from **Fig. 4**) to CAOXY levels of 13.8, 5.2, and 2.5 g/100 g paste (oz/100 oz paste), respectively. These results are in good accordance with studies using the B3B test methodology to test flexural strength of the paste. In Qiao et al.,³⁴ flexural test specimens had an 11% reduction in strength in 60% volume fly ash paste samples

exposed to a heating-cooling (50 °C – 5 °C – 50 °C) cycle in 30% CaCl₂. Though the test methods differ greatly (i.e. curing and exposure conditions and strength test methodology), samples with similar fly ash levels (57 and 60% volume) showed similar strength loss (18 and 11%) between this current study and Qiao et al.³⁴ The proposed cement replacement level with fly ash of 40% volume in the literature²⁹ corresponds to approximately 33% compressive strength reduction in this investigation.

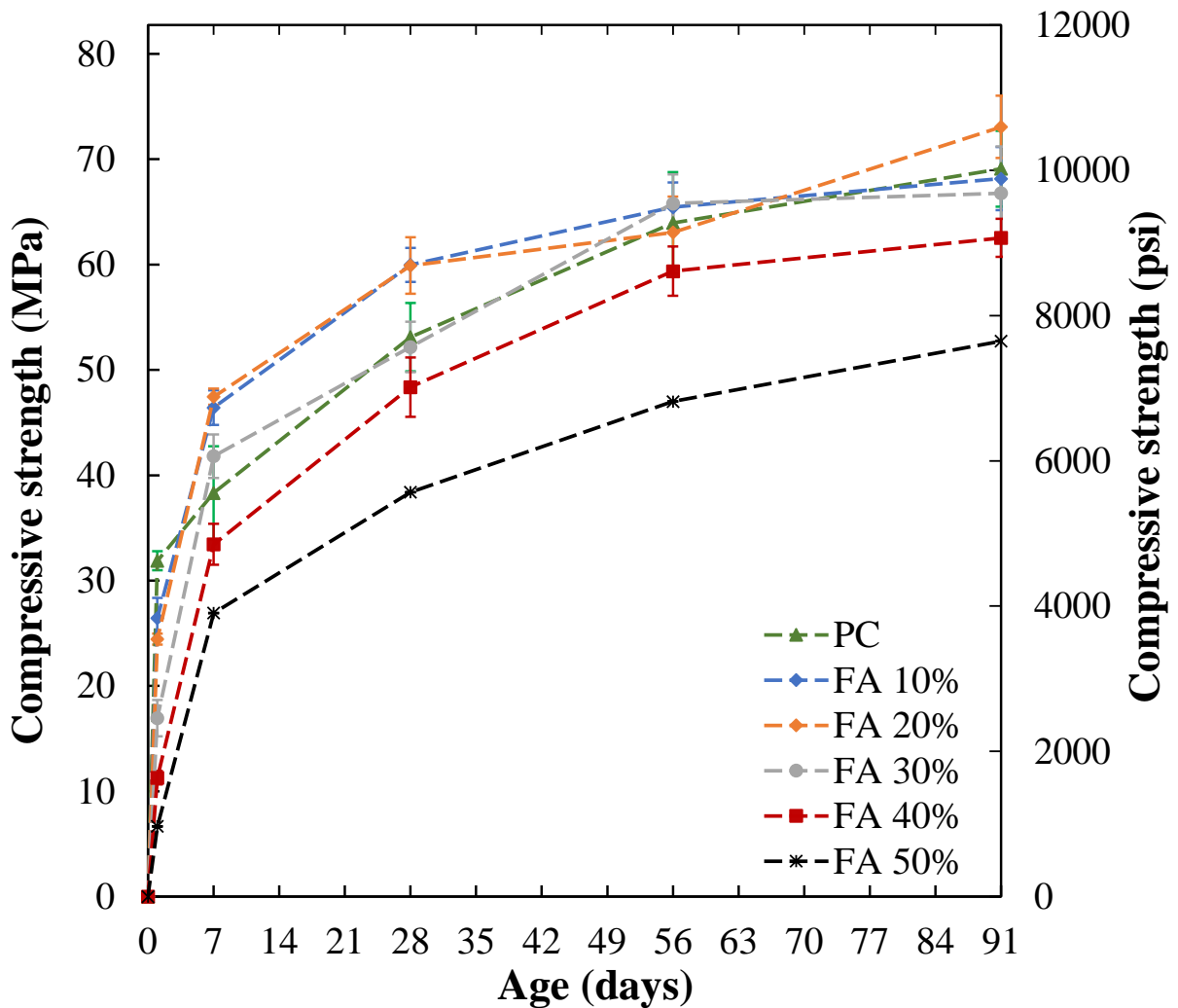


Fig. 9 – Average compressive strength of paste specimens cured in lime water bath.

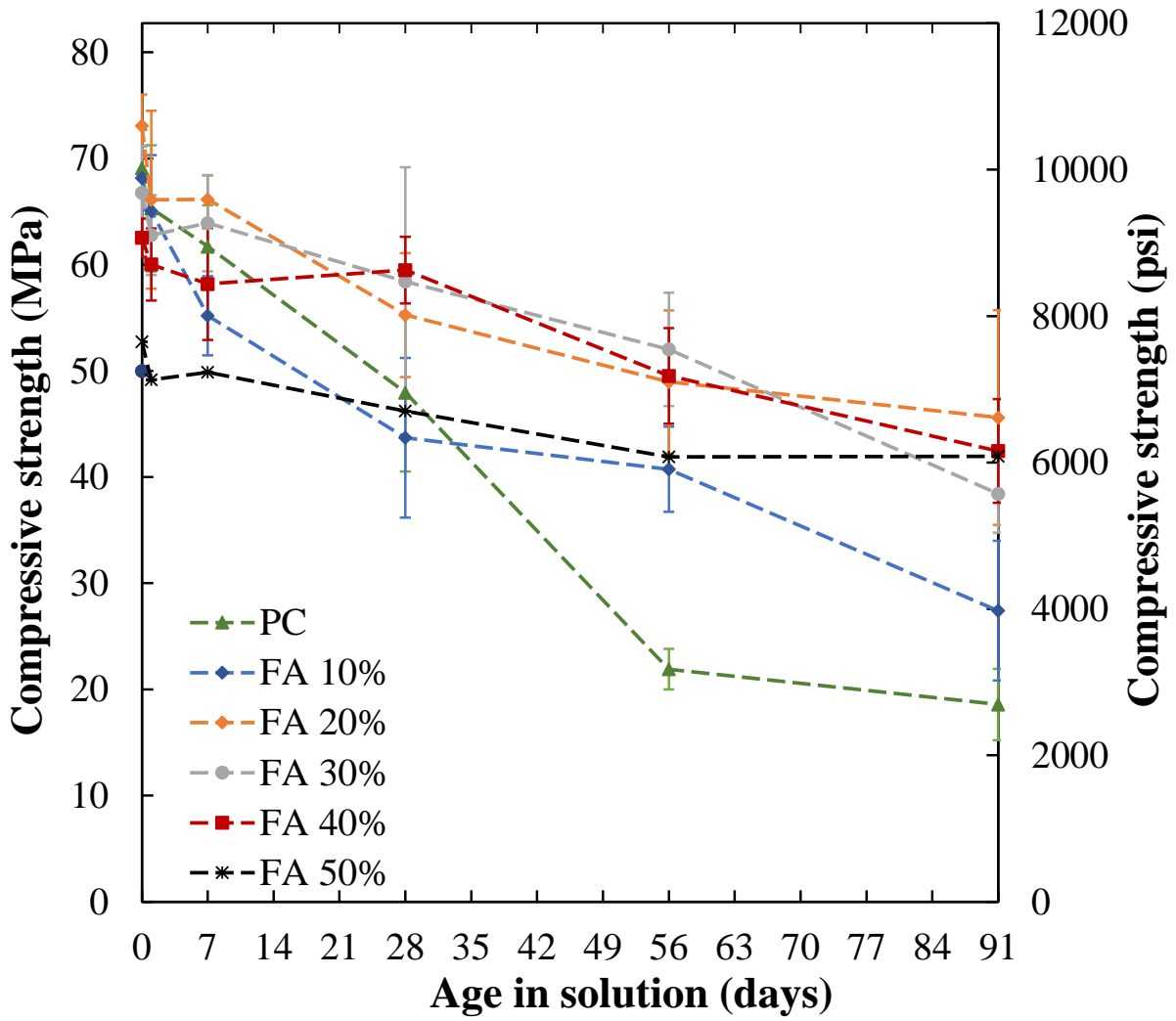


Fig. 10– Average compressive strength of paste specimens stored in 30% mass CaCl₂ solution.

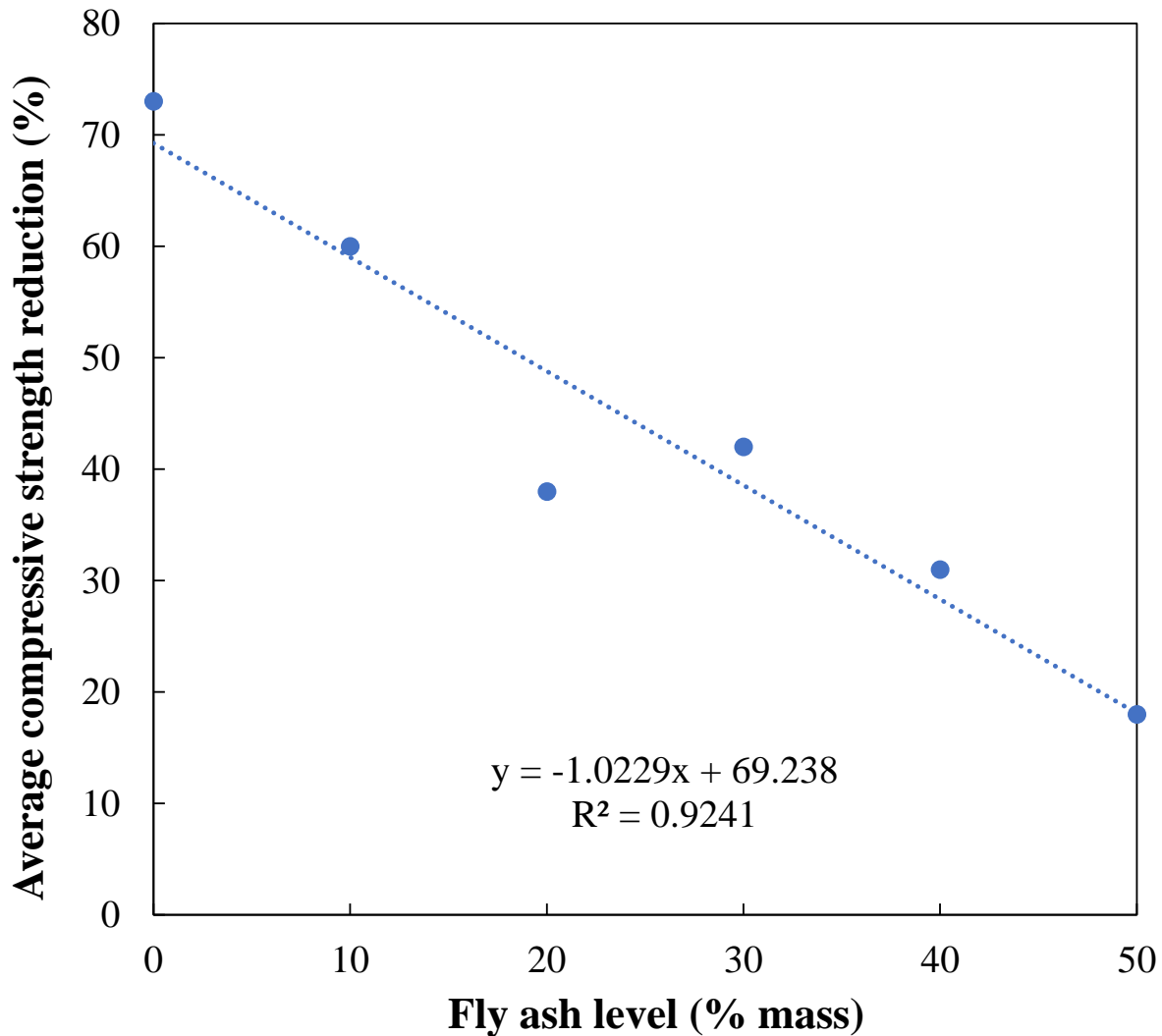


Fig. 11 – Average compressive strength reduction following 91-day submersion in CaCl_2 .

4.6. Correlation of $\text{Ca}(\text{OH})_2$ and CAOXY levels on compressive strength reduction

As shown in **Fig. 3**, the $\text{Ca}(\text{OH})_2$ content decreases as the fly ash level increases. **Fig. 12** shows that the compressive strength reduction is strongly linked to the $\text{Ca}(\text{OH})_2$ content and decreases linearly as this content decreases. This is an important finding and clearly shows the value of the information provided by the TGA as a quality control tool in designing for CAOXY durability. According to the literature^{29,34} and TGA results of **Fig. 3**, specimens made with 40% (7.5 g/100 g paste [7.5 oz/100 oz paste]) and 50% cement replacement with fly ash (5.6 g/100 g

paste [5.6 oz/100 oz paste]) should not experience high deterioration in CaCl_2 solutions. The compressive strength results show that the reduction was greatly reduced in these specimens (31 and 18% strength reduction). These results are in accordance with the proposed theoretical Ca(OH)_2 limit of 8 g Ca(OH)_2 /100 g paste (8 oz Ca(OH)_2 /100 oz paste) below which deterioration is limited. However, the TGA results alone should not be used to determine mixture composition to reduce CaCl_2 damage in concrete specimens because of encapsulation effects discussed previously.

Fig. 13 shows that the compressive strength reduction is also linearly correlated to the CAOXY content and decreases as CAOXY is mitigated. The preliminary threshold value of CAOXY proposed (15 g/100 g paste [15 oz/100 oz paste])²⁹ to limit damage corresponded to a mass cement replacement level with fly ash of 27% (30% volume) in this present research (**Fig. 6**). At a fly ash level of 27% mass, the compressive strength reduction was reduced from 73% in cement only specimens to 42%. Strength reduction was observed in all specimens despite the fly ash level, but these strength reductions are similar to those of the flexural strength loss from Qiao et al.³⁴ Given the similarity in strength reduction between this work and Qiao et al.,³⁴ the CAOXY threshold of 15 g/100 g paste (15 oz/100 oz paste) is verified; however, damage is still observed at this level of CAOXY in paste. To the authors' knowledge, no known paste deterioration level exists to state that the observed paste deterioration corresponds to limited/no damage in concrete. In order to mitigate damage completely, a higher fly ash replacement level (above 50% mass) is required in cementitious paste samples. It should also be noted that in concrete, reduced fly ash levels may be needed to mitigate CAOXY as entrained air significantly reduces degree of saturation and also provides a deposition location for the expanding crystals.

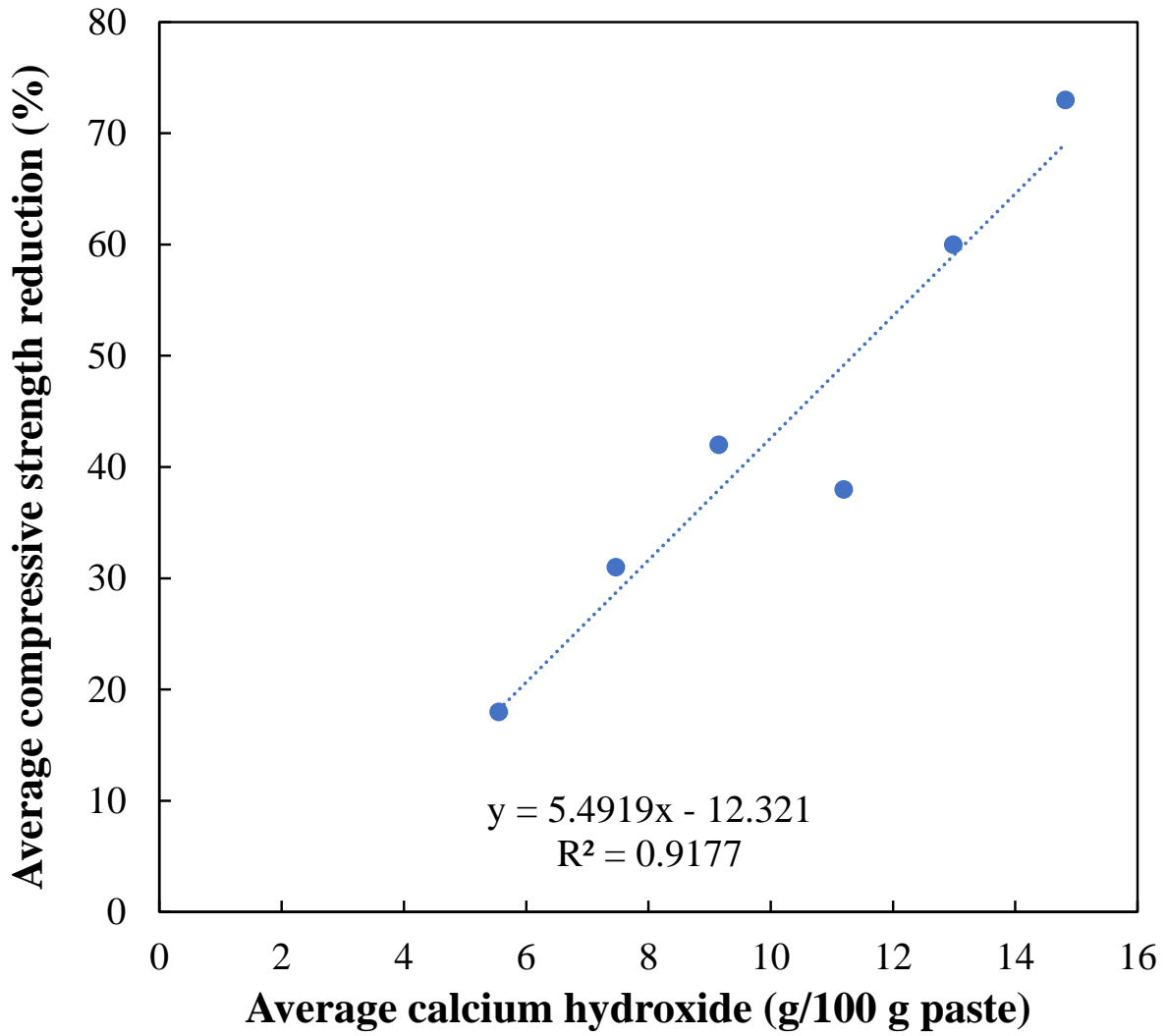


Fig. 12 – Effect of calcium hydroxide on compressive strength reduction following 91-day submersion in CaCl_2

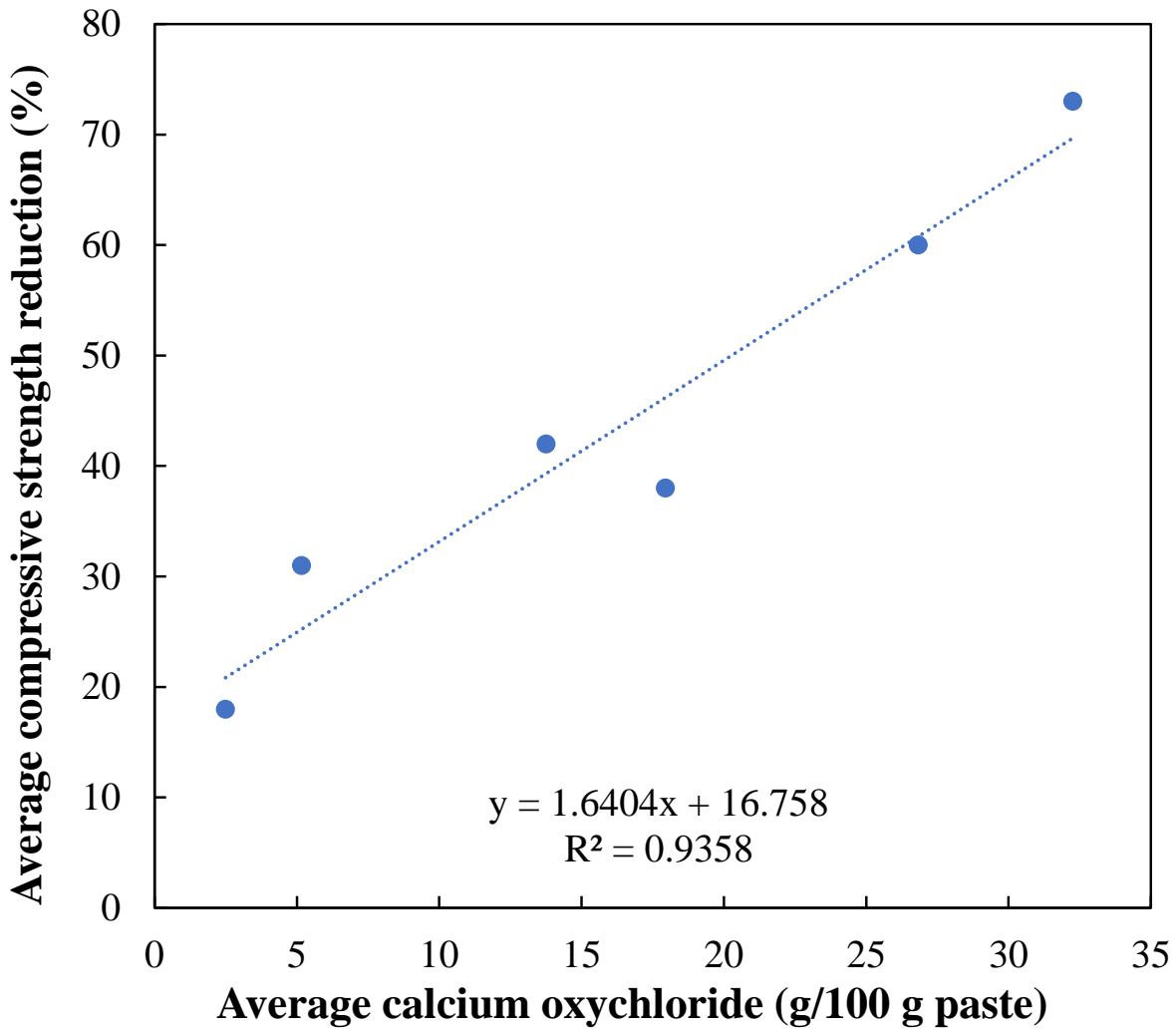


Fig. 13 – Effect of calcium oxychloride on compressive strength reduction following 91-day submersion in CaCl₂.

4.7. Relationship between mass change and CAOXY content

In **Fig. 14**, mass loss is correlated to CAOXY levels in order to investigate the current threshold. Mass change is insignificant until CAOXY levels exceed about 20 g/100 g paste (20 oz/100 oz paste). This is somewhat greater than the current threshold indicating that the 15 g CAOXY/100 g paste (15 oz CAOXY/100 oz paste) is conservative using mass measurements. Regardless, it shows the presence of a threshold, which is significant, given the complex deterioration mechanisms (i.e. leaching and spalling vs. absorption).

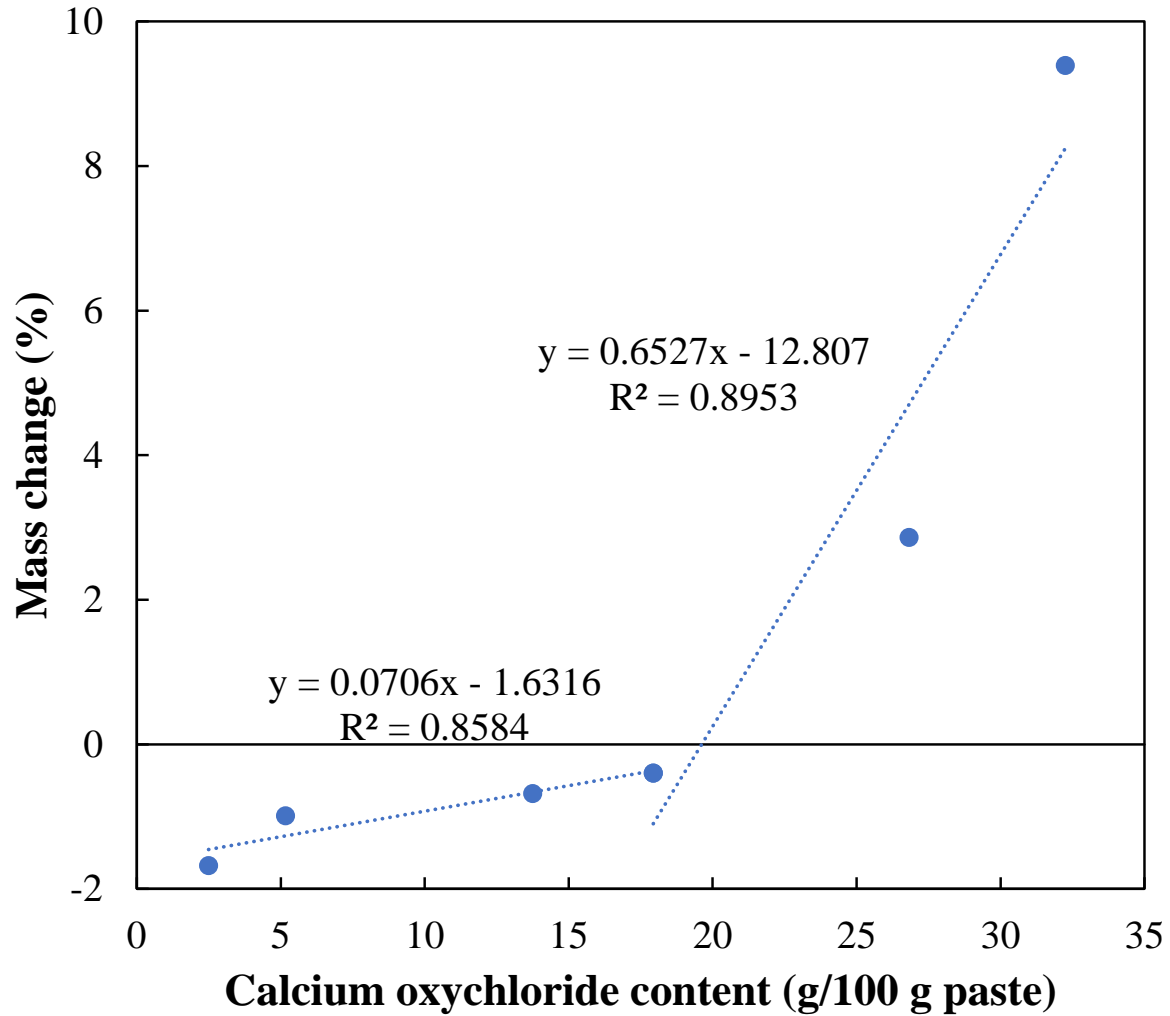


Fig. 14 – Mass change as a function of calcium oxychloride following 91-day submersion in 30% CaCl₂ solution.

4.8. Relationship between mass change and compressive strength reduction

In **Fig. 8**, the specimens made with fly ash levels below 20% experienced significant mass gain after 91 days in a 30% CaCl₂ solution which corresponds to those with higher compressive strength loss as shown in **Fig. 11**. Moreover, **Fig. 15** indicates that the compressive strength reduction of these specimens is correlated to the increase in recorded mass. The specimens with 40% compressive strength reduction or less did not experience any mass gain; contrarily, mass loss was recorded in these specimens due to potential leaching of the hydration products and

minor spalling. However, at strength reductions greater than 40%, a significant increase in mass was recorded. The increase in mass is believed to be primarily the result of CaCl_2 solution infiltration in the specimens.²² Similar findings by Julio-Betancourt²³ have reported a correlation between mass gain and compressive strength reduction. Still, the compressive strength reduction includes several other variables such as specimen porosity, the presence of cracks at the exposed surfaces, CAOXY formation, decomposition, leaching of hydration products and other possible chemical reactions could impact the mass change measurements. It should be noted also that an extended testing duration may impact these results.

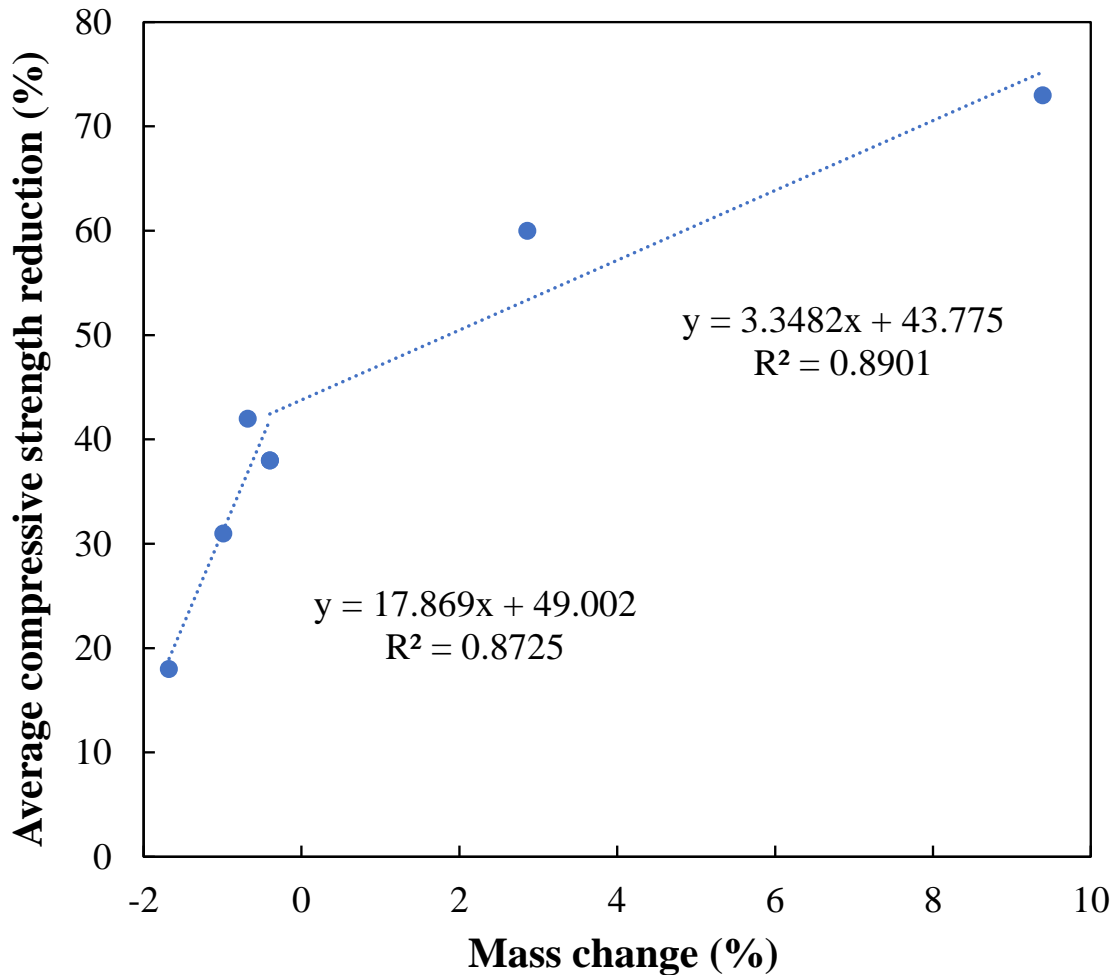


Fig. 15– Compressive strength reduction as a function of mass change following 91-day submersion in a 30% mass CaCl_2 solution.

5. CONCLUSION

In this study fly ash was used as a partial cement replacement in cementitious paste in order to mitigate damage in specimens exposed to a 30% mass CaCl_2 solution. The current threshold at which deterioration is considered mitigated in cementitious paste due to CAOXY is 15 g/100 g paste (15 oz/100 oz paste). In this study, results indicate that a partial replacement of cement with fly ash reduces the damage due to CAOXY formation. In specimens stored in a 30% CaCl_2 solution, there is an increased mass gain in specimens with lower fly ash levels corresponding to more damage. Mass change results indicate that a 20% cement replacement with fly ash may be enough to mitigate CAOXY damage and that CAOXY levels up to 19 g/100 paste (19 oz/100 oz paste) were required to limit mass gain.

It was further shown that $\text{Ca}(\text{OH})_2$ and CAOXY levels in cementitious paste are inversely related to fly ash content, with $\text{Ca}(\text{OH})_2$ and CAOXY levels decreasing as fly ash content increases. Specimen mixtures having lower fly ash content experienced reduced compressive strength as compared to higher fly ash content mixtures when submerged in a 30% mass CaCl_2 solution. This indicates that higher levels of $\text{Ca}(\text{OH})_2$ and CAOXY lead to exacerbated damage. Compressive strength results indicate damage was observed in all test specimens. Compressive strength reductions corresponding to CAOXY levels of 13.8, 5.2, and 2.5 g/100 g paste (oz/100 oz paste) are in good agreement with the flexural strength results of CAOXY documented in Qiao et al³⁴, somewhat confirming the current threshold of 15 g/100 g paste (15 oz/100 oz paste). Therefore, given the lack of known “acceptable” paste/concrete deterioration correlation, this work supports the current CAOXY threshold of 15 g/100 g paste (15 oz/100 oz paste). However, as noted in the future research section, an “acceptable” deterioration level is needed to fully verify this value.

6. REFERENCES

1. Smolczyk, H. G., "Chemical Reactions of Strong Chloride Solutions with Concrete," *Proceedings of the 5th International Symposium on the Chemistry of Cement*, Tokyo, Japan, 1968, pp. 274-280.
2. Zhou, Y.; Gencturk, B.; Willam, K.; and Attar, A., "Carbonation-Induced and Chloride-Induced Corrosion in Reinforced Concrete Structures," *Journal of Materials in Civil Engineering*, V. 27, No. 9, 2015, 04014245.
3. Wu, Z.; Shi, C.; Gao, P.; Wang, D.; and Cao, Z., "Effects of Deicing Salts on the Scaling Resistance of Concrete," *Journal of Materials in Civil Engineering*, V. 27, No. 5, 2015, pp. 1-11.
4. Farnam, Y.; Bentz, D. P.; Sakulich, A. R.; Flynn, D. R.; and Weiss, J., "Measuring Freeze and Thaw Damage in Mortars Containing Deicing Salt Using a Low Temperature Longitudinal Guarded Comparative Calorimeter and Acoustic Emission," *Advances in Civil Engineering Materials*, V. 3, No. 1, 2014, pp. 316-337.
5. Chatterji, S.; and Jensen, A. D., "Studies of the Mechanism of Calcium Chloride Attack on Portland Cement Concrete," *Nordisk Betong*, V. 19, 1975, pp. 5-6.
6. Berntsson, L.; and Chandra, S., "Damage of Concrete Sleepers by Calcium Chloride," *Cement and Concrete Research*, V. 12, No. 1, 1982, pp. 87-92.
7. Mori, H.; Kuga, R.; Ogawa, S.; and Kubo, Y., "Chemical Deterioration of Hardened Cement Pastes Immersed in Calcium Chloride Solution," *Proceedings of the 3rd International Conference on Sustainable Construction Materials and Technologies*, Kyoto, Japan, 2013, Paper 329.
8. Darwin, D.; Browning, J. A.; Gong, L.; and Hughes, S. R., "Effects of Deicers on Concrete Deterioration," *ACI Materials Journal*, V. 105, No. 6, 2008, pp. 622-627.
9. Mesbah, A.; François, M.; Cau-dit-Coumes, C.; Frizon, F.; Filinchuk, Y.; Leroux, F.; Ravaux, J.; and Renaudin, G., "Crystal Structure of Kuzel's Salt $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\frac{1}{2}\text{CaSO}_4\cdot\frac{1}{2}\text{CaCl}_2\cdot 11\text{H}_2\text{O}$ Determined by Synchrotron Powder Diffraction," *Cement and Concrete Research*, V. 41, No. 5, 2011, pp. 504-509.
10. Birnin-Yauri, U. A.; and Glasser, F.P., "Friedel's Salt, $\text{Ca}_2\text{Al}(\text{OH})_6(\text{Cl},\text{OH})\cdot 2\text{H}_2\text{O}$: Its solid Solutions and Their Role in Chloride Binding," *Cement and Concrete Research*, V. 28, No. 12, 1998, pp. 1713-1723.
11. Monosi, S.; Alvera, I.; and Colleparidi, M., "Chemical Attack of Calcium Chloride on the Portland Cement Paste," *Il Cemento*, V. 2, 1989, pp. 97-104.
12. Monosi, S.; and Colleparidi, M., "Research on $3\text{CaO}\cdot\text{CaCl}_2\cdot 15\text{H}_2\text{O}$ Identified in Concretes Damaged by CaCl_2 Attack," *Il Cemento*, V. 87, 1990, pp. 3-8.

13. Sutter, L.; Van Dam, T.; Peterson, K. R.; and Johnston, D. P., "Long-Term Effects of Magnesium Chloride and Other Concentrated Salt Solutions on Pavement and Structural Portland Cement Concrete Phase I Results," *Transportation Research Record*, V. 1979, 2006, pp. 60-68.
14. Peterson, K.; Julio-Betancourt, G.; Sutter, L.; Hooton, R. D.; and Johnston, D., "Observations of Chloride Ingress and Calcium Oxychloride Formation in Laboratory Concrete and Mortar at 5°C," *Cement and Concrete Research*, V. 45, No. 1, 2013, pp. 79-90.
15. Colleparidi, M.; Coppola, L.; and Pistolesi, C., "Durability of Concrete Structures Exposed to CaCl₂ Based Deicing Salts," *Durability of Concrete-Proceedings of the 3rd CANMENT/ACI International Conference*, Nice, France, SP-145, American Concrete Institute, Farmington Hills, MI, 1994, pp. 107-120.
16. Suraneni, P.; Qiao, C.; Azad, V.; Farnam, Y.; Monical, J.; Unal, E.; Villani, C.; Isgor, B.; and Weiss, J., "A Review of Recent Work on Deicing Salt Damage to Concrete Pavements and Its Mitigation," *International Conference on Advances in Construction Materials and Systems*, Chennai, India, 2017, pp 1-15.
17. Chatterji, S., "Mechanism of the CaCl₂ Attack on Portland Cement Concrete," *Cement and Concrete Research*, V. 8, No. 4, 1978, pp. 461-467.
18. Galan, I.; Perron, L.; and Glasser, F. P., "Impact of Chloride-Rich Environments on Cement Paste Mineralogy," *Cement and Concrete Research*, V. 68, 2015, pp. 174-183.
19. Wang, X.; Sadati, S.; Taylor, P.; Li, C.; Wang, X.; and Sha, A., "Material Characterization to Assess Effectiveness of Surface Treatment to Prevent Joint Deterioration from Oxychloride Formation Mechanism," *Cement and Concrete Composites*, V. 104, 2019, 103394.
20. Farnam, Y.; Dick, S.; Wiese, A.; Davis, J.; Bentz, D.; and Weiss, W. J., "The Influence of Calcium Chloride Deicing Salt on Phase Changes and Damage Development in Cementitious Materials," *Cement and Concrete Composites*, V. 64, No. 1, 2015, pp. 1-15.
21. Qiao, C.; Suraneni, P.; and Weiss, W. J., "Phase Diagram and Volume Change of the Ca(OH)₂-CaCl₂-H₂O System for Varying Ca(OH)₂/CaCl₂ Molar Ratios," *Journal of Materials in Civil Engineering*, V. 30, No. 2, 2018, 04017281.
22. Qiao, C.; Suraneni, P.; and Weiss, W. J., "Measuring Volume Change Caused by Calcium Oxychloride Phase Transformation in a Ca(OH)₂-CaCl₂-H₂O System," *Advances in Civil Engineering Materials*, V. 6, No. 1, 2017, pp. 157-169.
23. Julio-Betancourt, G. A., "Effect of De-icer and Anti-icer Chemicals on the Durability, Microstructure and Properties of Cement Based Materials," Ph.D. Thesis, University of Toronto, Toronto, Ontario, CN, 2009, 930 pp.

24. Jones, W.; Farnam, Y.; Imbrock, P.; Spiro, J.; Villani, C.; Golias, M.; Olek, J.; and Weiss, W. J., “An Overview of Joint Deterioration in Concrete Pavement: Mechanisms, Solution Properties, and Sealers,” Purdue University Report, West Lafayette, IN, 2013, 69 pp.
25. Ghantous, R. M.; Farnam, Y.; Unal, E.; and Weiss, W. J., “The Influence of Carbonation on the Formation of Calcium Oxychloride,” *Cement and Concrete Composites*, V. 73, 2016, pp. 185–191.
26. Taylor, P.; Sutter, L.; and Weiss, W. J., “Investigation of Deterioration of Joints in Concrete Pavements,” InTrans Project Reports 91, Ames, IA, 2012, 212 pp.
27. Suraneni, P.; Azad, V. J.; Isgor, O. B.; and Weiss, W. J., “Calcium Oxychloride Formation in Pastes Containing Supplementary Cementitious Materials: Thoughts on the Role of Cement and Supplementary Cementitious Materials Reactivity,” *RILEM Technical Letters*, V. 1, 2016, pp. 24–30.
28. Farnam, Y.; Zhang, B.; and Weiss, W. J., “Evaluating the Use of Supplementary Cementitious Materials to Mitigate Damage in Cementitious Materials Exposed to Calcium Chloride Deicing Salt”, *Cement and Concrete Composites*, V. 81, 2017, pp. 77-86.
29. Suraneni, P.; Azad, V. J.; Isgor, O. B.; and Weiss, W. J., “Use of Fly ash to Minimize Deicing Salt Damage in Concrete Pavements,” *Transportation Research Record*, V. 2629, 2017, pp. 24–32.
30. Farnam, Y.; Wiese, A.; Bentz, D.; Davis, J.; and Weiss, W. J., “Damage Development in Cementitious Materials Exposed to Magnesium Chloride Deicing Salt,” *Construction and Building Materials*, V. 93, No. 5, 2015, pp. 384-392.
31. Suraneni, P.; Monical, J.; Unal, E.; Farnam, Y.; and Weiss, W. J., “Calcium Oxychloride Formation Potential in Cementitious Pastes Exposed to Blends of Deicing Salt,” *ACI Materials Journal*, V. 114, No. 4, 2017, pp. 631–641.
32. Monical, J.; Unal, E.; Barrett, T.; Farnam, Y.; and Weiss, W.J., “Reducing Joint Damage in Concrete Pavements: Quantifying Calcium Oxychloride Formation,” *Transportation Research Record*, V. 2577, No. 1, 2016, pp. 17–24.
33. AASHTO T 365-20, “Standard Method of Test for Quantifying Calcium Oxychloride Amounts in Cement Pastes Exposed to Deicing Salts,” American Association of State Highway and Transportation Officials, Washington D.C., 2020, 10 pp.
34. Qiao, C.; Suraneni, P.; and Weiss, W. J., “Flexural Strength Reduction of Cement Pastes Exposed to CaCl₂ Solutions,” *Cement and Concrete Composites*, V. 86, 2018, pp. 297-305.
35. Jones, C.; Ramanathan, S.; Suraneni, P.; and Hale, W. M., “Calcium Oxychloride: A Critical Review of the Literature Surrounding the Formation, Deterioration, Testing procedures, and Recommended Mitigation Techniques,” *Cement and Concrete Composites*, 2020, 103663.

36. Suraneni, P.; Azad, V. J.; Isgor, O. B.; and Weiss, W. J., “Deicing Salts and Durability of Concrete Pavements and Joints,” *Concrete International*, V. 38, No. 4, 2016, pp. 48-54.
37. Suraneni, P.; Azad, V. J.; Isgor, O.B.; and Weiss, W. J., “Role of Supplementary Cementitious Material Type in the Mitigation of Calcium Oxychloride Formation in Cementitious Pastes,” *Journal of Materials in Civil Engineering*, V. 30, No. 10, 2018, pp. 1-10.
38. ASTM C618-19, “Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete,” ASTM International, West Conshohocken, PA, 2019, 5 pp.
39. ASTM C114-18, “Standard Test Methods for Chemical Analysis of Hydraulic Cement,” ASTM International, West Conshohocken, PA, 2018, 33 pp.
40. ASTM C311/C311M-18, “Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use in Portland-Cement Concrete,” ASTM International, West Conshohocken, PA, 2018, 11 pp.
41. ASTM C305-14, “Standard Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars,” ASTM International, West Conshohocken, PA, 2014, 3 pp.
42. ASTM C511-19, “Standard Specification for Mixing Rooms, Moist Cabinets, Moist Rooms, and Water,” ASTM International, West Conshohocken, PA, 2019, 3 pp.
43. ASTM C1872-18e2, “Standard Test Method for Thermogravimetric Analysis of Hydraulic Cement,” ASTM International, West Conshohocken, PA, 2018, 7 pp.
44. Kim, T., and Olek, J., “Effects of Sample Preparation and Interpretation of Thermogravimetric Curves on Calcium Hydroxide in Hydrated Pastes and Mortars,” *Transportation Research Record*, V. 2290, 2012, pp. 10-18.
45. ASTM C109/C109M-20a, “Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or [50-mm] Cube Specimens),” ASTM International, West Conshohocken, PA, 2020, 11 pp.