Synergistic Effects of Air Content and Supplementary Cementitious Materials in Reducing Damage Caused by Calcium Oxychloride Formation in Concrete

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Abstract

Pavement damage occurs in cold-region concrete exposed to high concentrations of calcium chloride ($CaCl_2$). The damage is caused by a combination of conventional freeze-thaw damage and the formation of a deleterious phase known as calcium oxychloride from a reaction between $CaCl_2$ and calcium hydroxide in the concrete. Much research has focused on calcium oxychloride mitigation in cement pastes, but not on concrete damage due to calcium oxychloride. In this study, the synergistic roles of air and supplementary cementitious materials (SCMs) in reducing damage in concrete exposed to high concentrations of $CaCl_2$ and freeze-thaw conditions is studied. Concrete mixtures were made with different SCM replacement levels and air contents ranging from 1.8 to 8.0% and immersed in 25% $CaCl_2$ solutions and subject to freeze-thaw cycles (-8 °C to 25 °C) for 600 days. Bulk resistivity and visual assessment of damage were found to be excellent descriptors of the damage progression. Damage was reduced as the SCM content and air content was increased. Mixtures which had 20% SCM and 8% air and mixtures which had 35% SCM and more than 4% air showed strong durability against damage due to calcium oxychloride formation.

Keywords: Deicing salt; calcium oxychloride; freeze-thaw; non-destructive testing; supplementary cementitious materials.

1. Introduction

Premature deterioration along pavement joints has been a major issue limiting service life in many cold regions in the U.S. [1-7]. While concrete pavements generally demonstrate adequate long-term performance, joint deterioration can severely affect the service life, in addition to being laborious and expensive to repair [1-3]. The deterioration is caused in part by freeze-thaw and in part due to the formation of a deleterious phase known as calcium oxychloride. This phase forms from a reaction between calcium chloride ($CaCl_2$) or magnesium chloride ($MgCl_2$) deicers and calcium hydroxide in the concrete [1-3,8,9]. As the intensity of deicing and the use of stronger deicers such as $CaCl_2$ and $MgCl_2$ increases, it stands to reason that the incidence of such deterioration will increase [10]. Several authors have investigated freeze-thaw damage in concrete, and while the mechanisms are not completely understood, freeze-thaw damage can generally be mitigated by having adequate amounts of well-distributed and appropriately sized air voids in the concrete [2,11]. The effects of $CaCl_2$ on concrete are more complex due to interactions with various hydrate phases [12]. Calcium oxychloride forms when higher concentrations of $CaCl_2$ are used [8,13]. The most commonly suggested form of calcium oxychloride in concrete has the chemical formula $3Ca(OH)_2 \bullet CaCl2 \bullet 12H_2O$ [14] and the chemical reaction showing its formation is shown in Eq. 1 [8].

$$CaCl_2 + 3Ca(OH)_2 + 12H_2O \rightarrow 3Ca(OH)_2 \bullet CaCl_2 \bullet 12H_2O \quad (1)$$

Supplementary cementitious materials (SCMs) are natural or industrial by-product materials that improve the performance, durability, and sustainability of concrete mixtures [15,16]. The use of SCMs in cement pastes causes a reduction in the amount of calcium hydroxide and calcium oxychloride due to dilution and pozzolanic reactions [3,17-19]. The reduced calcium hydroxide and calcium oxychloride contents are reflected in reduced damage in cement pastes exposed to high concentration $CaCl_2$ solutions [19-22]. Calcium hydroxide and calcium oxychloride contents are reduced as SCM reactivity and replacement are increased [18]. Based on the studies listed above and certain other studies [18,19,22-25], specifications to limit damage induced by calcium oxychloride formation in concrete pavements were introduced in the United States (performance based specification AASHTO PP 84). Two suggestions are used in this specification for pavement concretes, which are 30% SCM replacement, or limiting measured calcium oxychloride amounts in cement pastes to below 0.15 g/g cement paste. The AASHTO PP 84 specifications are mainly based on the work done on cement pastes [18,19,22-25], and they have not been validated for a range of concrete mixtures. Studies of concrete damage due to calcium oxychloride are somewhat limited, but these studies suggest that the damage reduces as the air content and SCM replacement increases [26-29]. While little research has been performed on the damage to concrete exposed to both freeze-thaw and concentrated $CaCl_2$ solutions, two important studies merit mention. Ghazy et al. showed that fly ash and nanosilica could mitigate calcium and magnesium oxychloride damage under such conditions [26]. Julio-Betancourt showed that pessimum concentrations of $CaCl_2$ for damage were dependent on exposure temperature, and increased as the temperature increased [28]. However, neither of these studies dealt with mixtures in which both air and SCM contents were significantly varied.

Realistic concrete pavement mixtures for cold regions are air entrained and have SCMs at different replacement levels. The synergistic effects of these two parameters in reducing damage due to calcium oxychloride in freezing conditions is not clearly understood. The objective of this study is to critically evaluate the synergies between air and SCM contents in reducing damage due to calcium oxychloride formation in concrete. Through this study, we seek to further examine the SCM replacement criteria in AASHTO PP 84 that deal with concrete pavement joint damage in the presence of $CaCl_2$. This study is the first part of a larger project where the performance of concretes immersed in $CaCl_2$ solutions and subjected to a variety of temperature conditions with and without freezing are studied.

Concrete mixtures with fly ash and slag replacement levels of 0, 20, and 35% by mass with air contents ranging from 1.8 to 8.0% were made. The concretes were characterized using extensive fresh and hardened concrete testing. At 28 days, the cylinders were immersed in 25% $CaCl_2$ solution and were subjected to freeze-thaw cycles (-8 °C to 25 °C), and monitored using mass loss, bulk resistivity, surface resistivity, ultrasonic pulse velocity, and visual assessment up to 600 days.

2. Materials

Type I/II OPC was used in all mixtures in this study. Class F fly ash and ground granulated blast furnace slag (also known as slag here, but simply termed slag throughout the text here) were used as SCMs. The chemical compositions of the cementitious materials obtained from the manufacturer or through X-ray fluorescence testing performed on beads using a calibrated device are provided in Table 1.

Table 1. Chemical compositions of the cement, fly ash, and slag (weight %).

Oxide	**Cement***	**Fly ash**	**Slag**
SiO_2	19.90	56.01	32.09
Al_2O_3	4.55	21.71	12.88
Fe_2O_3	3.77	12.98	0.75
CaO	63.96	4.81	42.44
MgO	1.17	1.03	6.53
SO_3	2.35	0.37	3.03
K_2O	0.37	2.57	0.27
Na_2O	0.18	0.30	0.13

* The cement has a limestone content of 3.8%, an LOI of 2.5%, and a Blaine fineness of 386 m^2/kg.

The chemical admixtures used for testing include a commercial superplasticizer and an air entraining agent. The aggregates used for testing include coarse aggregates (oolitic limestone, nominal maximum size 25.4 mm, 3.75% absorption capacity) and fine aggregates (siliceous sand, nominal maximum size 4.75 mm, 2.84% absorption capacity). Aggregates were corrected for water content before mixing. Commercial deicing $CaCl_2$ with >95% purity was used to prepare solutions with 25% concentration of $CaCl_2$ by mass by mixing the salt with tap water.

3. Experimental methods

3.1. Mixing and curing procedures

Concrete mixture designs were made with water-to-cementitious materials ratio (w/cm) of 0.40 and with fly ash and slag replacement levels of 0, 20, and 35% (by mass) and are shown in Table 2. Mixtures were designed to have a slump between 20 mm to 120 mm and targeted air contents of 2 ± 1%, 5 ± 1%, and 8 ± 1% which were achieved using the air entraining agent. The tolerances in the air content values are somewhat smaller than the 1.5% which is common in field conditions. These mixtures are modified variants of a realistic base mixture design, which was obtained in consultation with a ready mix concrete producer.

Mixing was conducted using a rotating drum mixer. First, aggregates were added, and mixed for one minute. Then, the cementitious materials were added and mixed for two minutes. Finally, water and admixtures were added. Small amounts of superplasticizer were added in four cases for stiff mixtures (as shown in Table 2). The total mixing time was about 15 minutes and fresh concrete properties (slump and air content) were tested for each mixture. Actual, measured air contents ranged from 1.8% to 8.0%. The design slump was not achieved for two mixtures and the target air content of 5 ± 1% was not obtained for one mixture. After mixing, six 100 × 200 mm concrete cylinders were cast for each mixture and moist cured for 28 days. Three of the concrete cylinders were tested destructively at 28 days for evaluating their compressive strength, whereas the rest were tested non-destructively at 28 days and during the freeze-thaw cycles up to failure or for 600 days.

Table 2. Concrete mixtures tested for this study. OPC is ordinary portland cement, FA is fly ash, SL is slag, and (SP) is superplasticizer.

Mixture	**TAC* (%)**	**w/cm**	**Cement (kg/m^3)**	**Fly ash (kg/m^3)**	**Slag (kg/m^3)**	**Sand (kg/m^3)**	**Coarse aggregate (kg/m^3)**	**Air entrainer (%)**	**SP (%)**
OPC-2.6	2	0.40	372	–	–	757	1051	–	0.30
OPC-6.6	5	0.40	372	–	–	757	1051	0.10	–
OPC-7.9	8	0.40	372	–	–	757	1051	0.38	–
FA20-2.1	2	0.40	298	74	–	757	1051	–	0.11
FA20-5.6	5	0.40	298	74	–	757	1051	0.24	0.09
FA20-7.9	8	0.40	298	74	–	757	1051	0.66	–
FA35-1.8	2	0.40	242	130	–	757	1051	–	–
FA35-4.5	5	0.40	242	130	–	757	1051	0.30	–
FA35-8.0	8	0.40	242	130	–	757	1051	0.75	–
SL20-2.8	2	0.40	298	–	74	757	1051	–	0.26
SL20-4.9	5	0.40	298	–	74	757	1051	0.08	–
SL20-8.0	8	0.40	298	–	74	757	1051	0.20	–
SL35-1.9	2	0.40	242	–	130	757	1051	–	–
SL35-4.0	5	0.40	242	–	130	757	1051	0.10	–
SL35-7.5	8	0.40	242	–	130	757	1051	0.30	–

*TAC: Target Air Content.

3.2. Test methods

3.2.1. Slump and air content of concrete

After five to ten minutes of mixing, the concrete was tested for slump according to ASTM C143 and air content in accordance with ASTM C231.

3.2.2. Compressive strength

At the age of 28 days, concrete cylinders were tested for compressive strength in accordance with ASTM C39. All cylinders were capped with sulfur prior to testing. The coefficient of variation (COV) values of strength ranged from 0.26 to 7.9% and averaged 4.5%. At 600 days, after the end of the exposure duration, the remaining cylinders which did not fail were tested for compressive strength and compared with their initial values at 28 days.

3.2.3. Freeze-thaw cycles

At 28 days, three concrete cylinders from each mixture design were submerged in 25% $CaCl_2$ solutions in a sealed container (liquid-solid ratio of 0.7 by mass) and were then moved into a freezer for 24 hours. After 24 hours in the freezer, the container was taken out of the freezer and placed under ambient conditions for 24 hours after which the procedure was repeated. Using this method, each cycle took 48 hours. Residue and spalled material in the containers were removing on average every 30 cycles. The $CaCl_2$ solution was replaced with fresh solution every 100 cycles. Solution replenishment guidelines for such exposures are unavailable, and the frequency was limited by the amount of effort and solution volumes needed. Temperature monitoring was performed for ambient conditions, the $CaCl_2$ solution, and the core of the concrete cylinders during the cycles and the average values are shown in Figure 1. The temperature in the freezer varied somewhat depending on the location, and the average ambient temperature is shown in Figure 1. The average ambient temperature was -8 ± 2 °C. The lowest average temperature for the cylinders and the solution were measured to be -4 ± 2 °C in the freezer. In each cycle, the cylinders spend about 10 hours at freezing temperatures. On the thawing side, the ambient temperature reached 25 ± 2 °C while the sample and solution reached 24 ± 2 °C before they were moved back inside the freezer. In order to account for the varying temperatures in the different locations in the freezer, the sealed containers were placed in a randomized manner inside the freezer. The test conditions are somewhat realistic in terms of temperature exposure in cold regions, however, the test is an accelerated test, as immersion in 25% $CaCl_2$ solutions is a harsh exposure condition compared to field conditions.

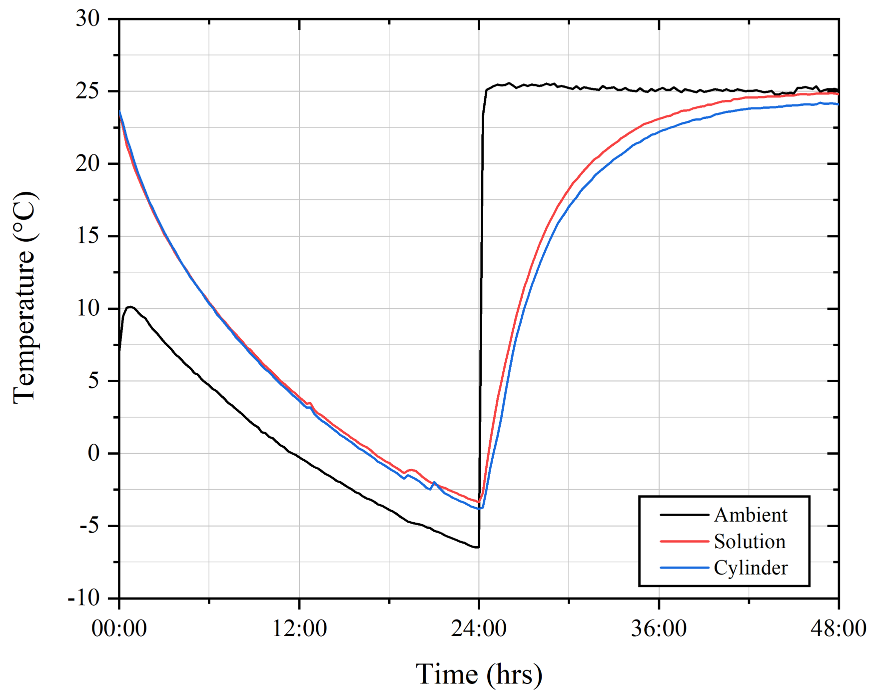


Figure 1. Measured temperature for ambient conditions, $CaCl_2$ solution, and concrete cylinders during a full freeze-thaw cycle.

3.2.4. Mass change

The mass of the concrete cylinders was measured at 28 days and after approximately every ten cycles during the first 150 cycles of experiment and approximately every 30 cycles on average for the rest of experiment up to 300 cycles. The slowdown in the measurements was because many mixtures showed damage which did not change substantially with time in the duration of 150 to 300 cycles. The surface of the concrete was air dried for 2 hours in the laboratory at 25 ± 2 °C before mass was measured. The mass and dimensions were used to calculate density at 28 days.

The COV values of the density measurements at 28 days ranged from 0.9 to 2.3% and averaged 1.4%.

3.2.5. Bulk resistivity

The bulk resistivity of the concrete cylinders was measured at 28 days and after approximately every 10 cycles for the first 150 cycles and every 30 cycles for the rest of the experiment based on ASTM C1760 at a frequency of 1 kHz. The saturation state of the concrete is unknown and variable, therefore interpretation of resistivity numbers is somewhat complexity, however, as discussed later in the text, the resistivity proved to be an accurate indicator of the concrete quality during exposure and damage. The COV values of bulk resistivity measurements at 28 days ranged from 1.7 to 9.6%, and averaged 4.9%.

3.2.6. Surface resistivity

The surface resistivity of the concrete cylinders was measured at 28 days and after approximately every 10 cycles for a limited number of cycles based on ASTM WK37880. Due to the excellent correlations that were observed between surface and bulk resistivity, the surface resistivity measurements were discontinued. Measurements were made using the four-point Wenner probe method at a frequency of 40 Hz. The COV values of surface resistivity measurements at 28 days ranged from 4.1 to 11.8% and averaged 6.5%.

3.2.7. Ultrasonic pulse velocity (UPV)

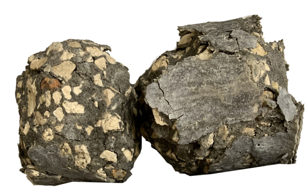
The UPV of the concrete cylinders was measured at 28 days and after approximately every 10 cycles for the first 150 cycles of the experiment and on average every 30 cycles for the rest of the experiment in accordance with ASTM C597 using a pulse voltage equal to 250 V. A couplant was used to ensure adequate contact between the transducers and the concrete. The COV values of UPV measurements at 28 days ranged from 0.3 to 2.4% and averaged 1.3%.

3.2.8. Visual damage monitoring

Based on the damage observed in the concrete during the first 30 cycles, a visual damage classification scheme was developed and is shown in Table 3. Each cylinder was carefully observed and assigned one classification for each measurement. As the visual damage is only assessed periodically, the condition of the concrete in between cycles is unknown. Here, an averaging assumption is made – in the first half of the period between cycles, the condition of the concrete is the same as the prior visual assessment, and in the second half of the period, the condition of the concrete is the same as the post visual assessment.

Table 3. Visual damage classification.

Damage classification	Description	Representative image
None	No signs of cracks on the ends or the sides of the cylinders.	
Minor	Short and thin cracks on the ends but no damage on the sides of the cylinders.	

Moderate	Long and deep cracks on the ends; some cracking on the sides of the cylinders.	
Severe	Large amount of spalling at the ends of the cylinder; some cracking on the sides and middle but middle is still intact.	
Failure	More than half of the cylinder has spalled; cracks throughout the volume	

3.2.9. Post-cycle measurements

For each cylinder that failed prior to the end of the 600 days test duration, cylinders were crushed and small, representative, pieces from the core were extracted and oven dried at 100 °C for 72 hours to evaluate the solution absorption. At the end of experiment, mixtures which did not fail were tested for their compressive strength and then solution absorption was evaluated in a manner similar to the failed mixtures.

4. Results and discussion

4.1. Fresh and hardened initial properties of concrete

Table 4 shows the fresh and hardened properties of the concrete tested at the time of mixing and at 28 days. Measured slump ranged from 0 to 165 mm and air contents ranged from 1.8 to 8.0%. Loss of air content over time and the quality of the air void system is not considered in this study but these important parameters and how they impact damage due to calcium oxychloride formation should be studied in the future.

Table 4. Fresh and hardened properties for the concrete mixtures.

Mixture	Slump (mm)	Air content (%)	Density (kg/m^3)	Strength (MPa)	UPV (m/s)	Bulk resistivity (Ohm-m)	Surface resistivity (Ohm-m)
OPC-2.6	0	2.6	2339.5	41.2	4538.5	38.1	71.8
OPC-6.6	75	6.6	2163.6	29.1	4231.7	43.8	72.3
OPC-7.9	50	7.9	2165.2	25.6	4314.5	52.0	93.8
FA20-2.1	65	2.1	2310.9	37.2	4439.2	46.6	75.7
FA20-5.6	50	5.6	2209.3	31.1	4294.5	51.5	83.8
FA20-7.9	75	7.9	2127.1	18.8	4186.3	50.8	86.2
FA35-1.8	65	1.8	2285.6	28.8	4423.3	53.4	97.1
FA35-4.5	115	4.5	2228.4	20.0	4414.2	63.2	106.2
FA35-8.0	165	8.0	2022.1	8.38	3796.7	63.4	124.4
SL20-2.8	75	2.8	2275.5	37.9	4565.7	57.3	101.9
SL20-4.9	35	4.9	2220.7	36.0	4377.8	56.7	96.9
SL20-8.0	90	8.0	2162.5	21.1	4284.2	66.4	114.4
SL35-1.9	25	1.9	2311.5	37.2	4672.3	92.9	153.6
SL35-4.0	40	4.0	2261.4	34.8	4545.7	109.5	197.7
SL35-7.5	110	7.5	2114.8	16.9	4286	106.7	188.4

Figure 2 illustrates the compressive strength for different concrete mixtures as a function of the corresponding air content at 28 days. The compressive strength values range from 8.4 MPa (FA35-8.0) to 41.2 MPa (OPC-2.6). The strength decreases as the air content and SCM amounts increase [30-32]. Fly ash causes a greater decrease in the strength than slag at the same replacement levels. The mixture with 35% fly ash shows poor strength performance at high air contents, consistent with literature [32]. However, the fly ash is a Class F fly ash, which reacts slowly, especially at early ages, so the strength of several mixtures is expected to improve over time. Exposure at later-ages is being evaluated in a companion study.

The compressive strength roughly decreases linearly as the air content increases, though in certain mixtures with SCM, the behavior may be considered to be bilinear, with greater slope at higher air contents. The slope (the dependence of strength on air content) does not depend strongly on SCM amount or type and is 3 ± 1 MPa for each percentage of air for the mixtures tested. These findings, while in line with literature, highlight a potential issue with increased amounts of SCMs that are being suggested in AASHTO PP84 – significant decreases in strength may result, with some fly ashes. These decreases, which may be prominent at early ages, will then have to be compensated through the use of lower w/cm and chemical admixtures, which could potentially increase the concrete cost.

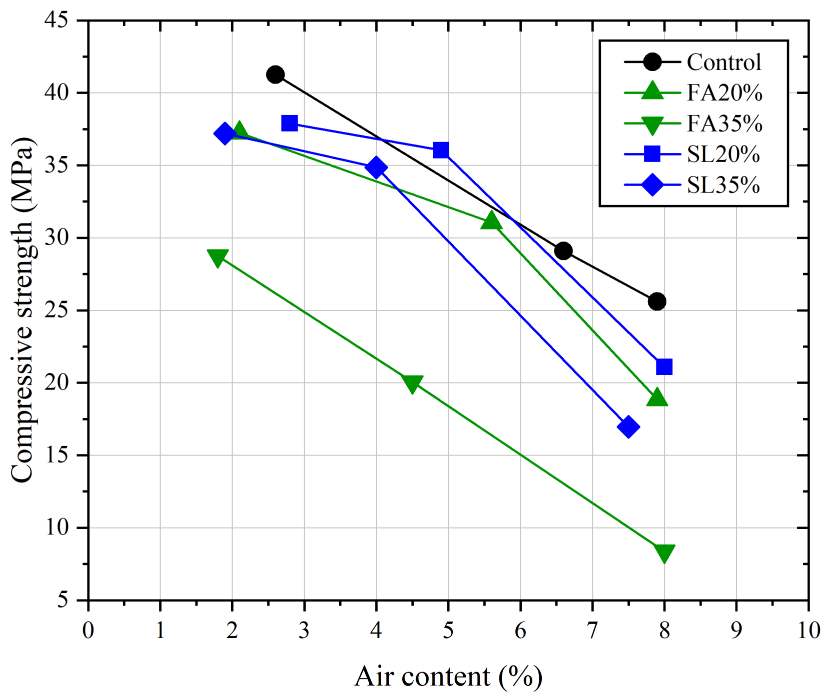


Figure 2. Compressive strength at 28 days plotted against air content.

Bulk resistivity values measured at 28 days as a function of air content are plotted in Figure 3. The bulk resistivity increases as the SCM replacement increases, which is well known from literature [33]. The highest bulk resistivity is measured for the mixtures with 35% slag. A longer curing duration is anticipated to further increase the bulk resistivity of the fly ash mixtures. The general effect of increasing air content is to increase the bulk resistivity. However, different SCM types and amounts produce different results, and at higher air contents, the resistivity is not strongly affected by air content. Comparing Figure 2 and Figure 3 suggests that no obvious correlation can exist between the two measurements; in fact, many of the strongest mixtures (OPC) have low bulk resistivity values.

While not discussed in detail, analysis of the other initial hardened properties showed a strong linear relationship between surface resistivity and bulk resistivity (discussed later in the text), and a moderate linear relationship between compressive strength and UPV (consistent with literature [34,35]).

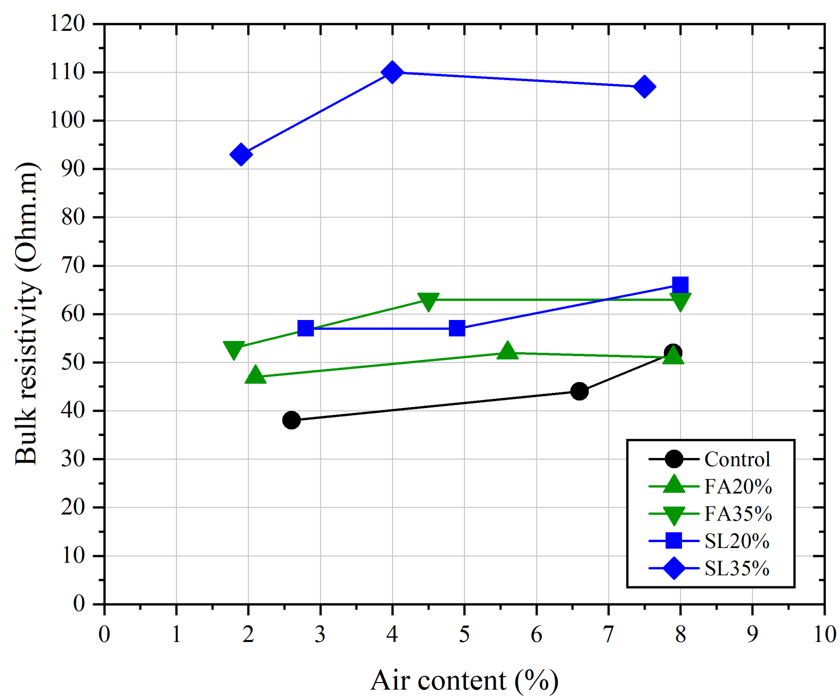


Figure 3. Bulk resistivity values at 28-days for all concrete mixtures.

4.2. Visual monitoring during exposure

Figure 4 shows the number of cycles for each mixture to reach the designated damage classification. Other studies monitoring concrete cylinders exposed to deicing salt and freeze-thaw cycles have reported similar schemes of damage classification [36-38].

Increasing air contents and increasing SCM amounts significantly reduce the damage at any given cycle and the increase the time to failure. The improvement of calcium oxychloride durability with air is due to two reasons. The first reason is a reduction in the degree of saturation that is provided by the presence of air voids at any given exposure duration compared to mixtures without air [3,29]. The second reason is the air voids provide space which can accommodate the crystal growth or expansion of the calcium oxychloride [3]. Both these mechanisms are similar to the role that air plays in reducing freeze-thaw damage. SCMs improve calcium oxychloride durability because they reduce the amount of calcium oxychloride that forms (Eq. 1) through dilution and pozzolanic reaction [19,23,39]. Greater SCM replacement levels and use of more pozzolanic SCMs will further reduce the amount of calcium oxychloride that forms. SCMs are also likely to modify the transport of $CaCl_2$ into concrete, but a detailed discussion of transport phenomena is out of the scope of this work.

Mixtures which have high amounts of air but no SCM, such as OPC-6.6 or OPC-7.9 fail rapidly. While the air does provide space for expansion, the large amount of calcium hydroxide in these concretes enables continuous formation of calcium oxychloride, which ultimately leads to failure. Therefore, the usage of SCM to reduce damage due to calcium oxychloride formation in concrete is essential. However, using only SCM but low amounts of air does not confer adequate durability either, as seen in mixtures FA20-2.1 and SL20-2.8. While 20% SCM reduces the amount of calcium oxychloride that forms, from paste studies, it is known that substantial amounts of calcium oxychloride can still form at such replacement levels [9,19]. The lack of air to reduce expansion/crystallization stresses leads to rapid damage. Therefore, visual observations confirm that the use of air to reduce damage due to calcium oxychloride formation, in addition to the use of SCMs which reduces the amount of calcium oxychloride formed, is essential.

As the air content and SCM replacement increase, the time duration spent in each damage classification stage increases, meaning the increase in the time to failure with use of air and SCMs is substantial. OPC-2.6 fails less than 40 cycles, FA20-5.6 fails at 160 cycles, whereas FA20-7.9 does not show any damage after 300 cycles. When 20% SCM is used, the highest air contents (8%) show limited or no damage. When 35% SCM is used, even mixtures with 4% air do not fail during exposure. Six of the mixtures with the qualities specified above did not fail during the duration of the exposure. Based on these results, we can state that there is an interplay between air content and SCM replacement. Specifications should take such an interplay into account, as suggesting 30% SCM replacement or more may limit freedom for mixture designs. Considering that typical mixture designs in cold regions call for 6.5% air content, mixtures with 35% SCM are not likely to suffer damage due to calcium oxychloride formation under such conditions. However, it is unclear whether mixtures with 20% SCM will show adequate performance, especially when tolerances and variability in air content measurements are taken into account. In addition, considering the considerable differences between FA20-5.6 and FA20-7.9, mixtures with 20% SCM and 5% air content may show very different performance from mixtures with 20% SCM and 7% air content. The exact type of SCM used and the nature of the air void system are further parameters which will influence behavior. Many of these parameters and their effects on calcium oxychloride resistance have never been studied in literature; our findings suggest that such studies are warranted.

OPC and fly ash mixtures became soft and mushy as damage increased and the mixtures approached failure. However, in concretes containing slag, a similar softening phenomenon was not observed. Instead, cylinders appeared to maintain their hardness, but showed spalling with pieces fracturing with sharp faces. OPC and fly ash mixtures showed spalling with rounded edges.

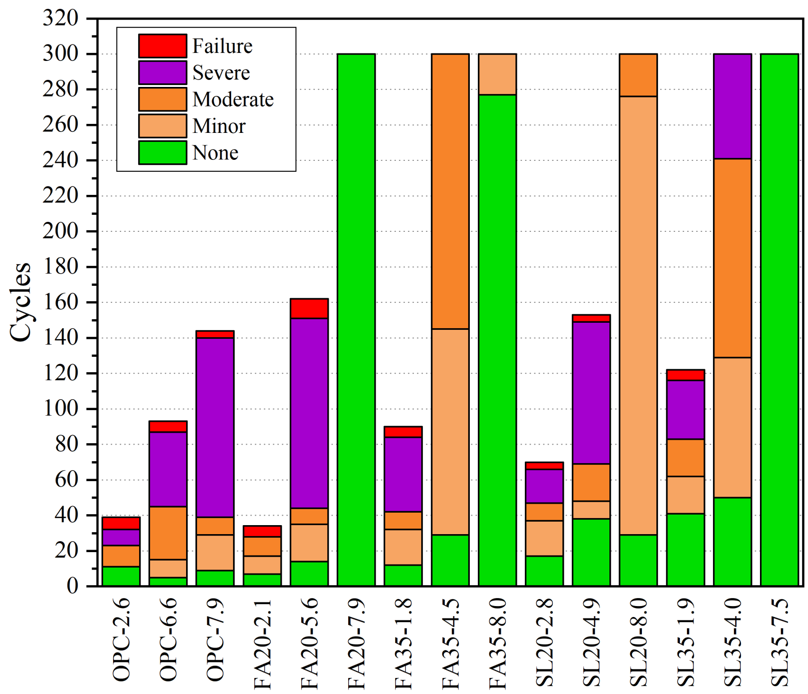


Figure 4. Visual damage classification plotted against number of cycles.

4.2. Surface resistivity and UPV changes during exposure

Figure 5 shows the relationship between surface resistivity and bulk resistivity. For all concretes tested, initially, and after exposure to several freeze-thaw cycles, there is a strong linear relationship between surface resistivity and bulk resistivity. Similar relationships for concrete have been reported by other studies [40,41]. Therefore, surface resistivity is not further explored in this study. The conclusions that have been drawn for bulk resistivity are also valid for surface resistivity, considering the linear nature of their relationship.

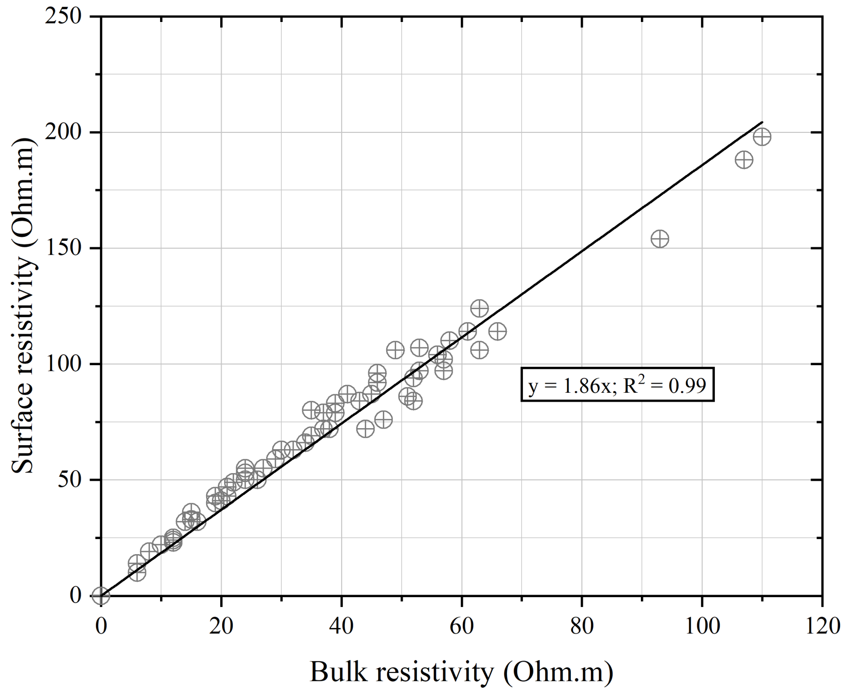
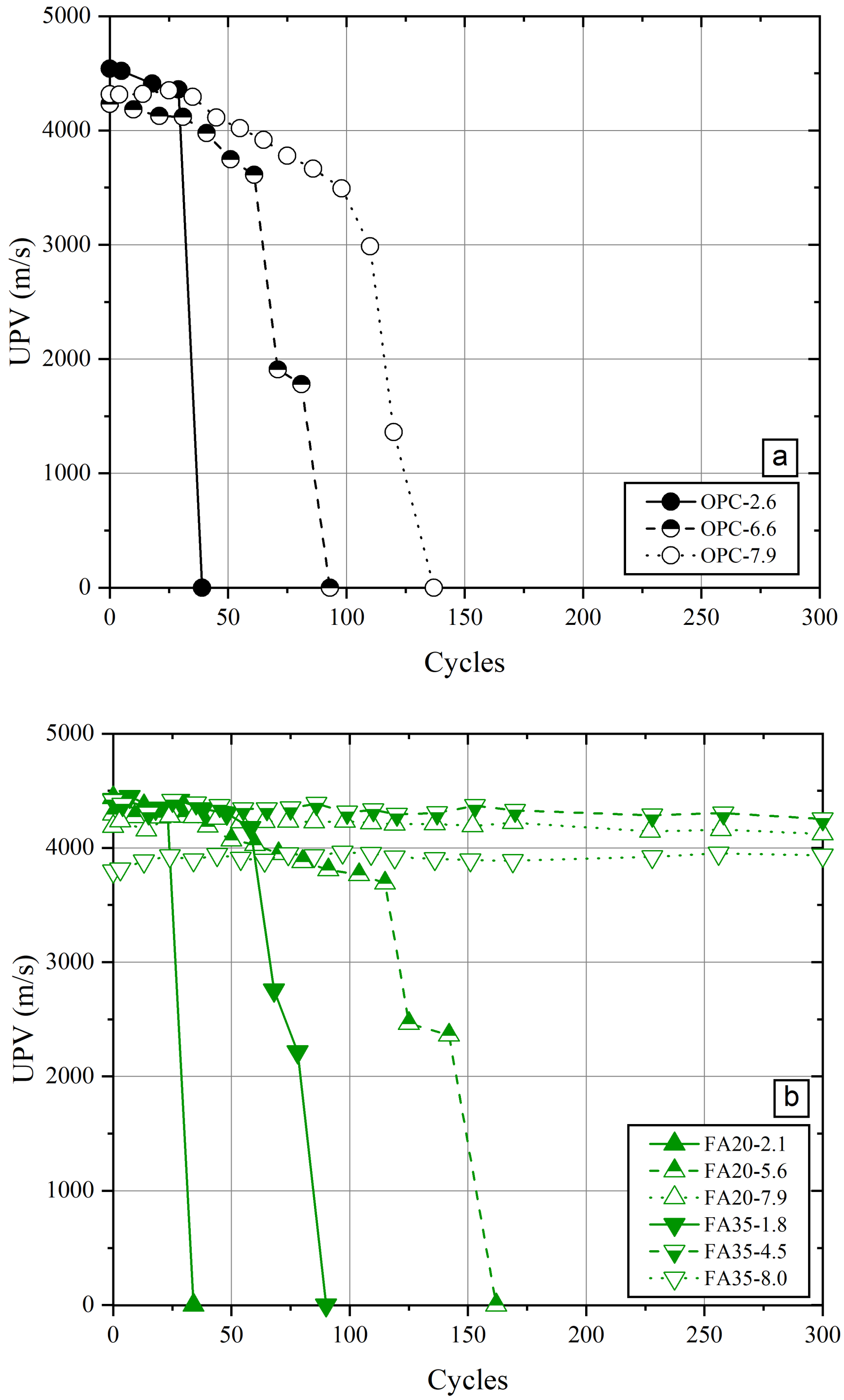


Figure 5. Relationship between surface resistivity and bulk resistivity for hardened concrete and hardened concrete immersed in 25% $CaCl_2$ solution and subject to freeze-thaw cycles.

Figure 6 shows the variation of the UPV during the exposure for concrete cylinders. The UPV values reduce as the mixtures undergo damage. The OPC cylinders (Figure 6a) manifest damage early, which leads to sharp reductions in the UPV values. As the air content in the OPC mixtures increases, damage is manifested later (time to failure is increased). When the mixture fails (based on Table 3 and Figure 4), UPV values reach zero. The reduction in the UPV values is somewhat sudden and not continuous. As the SCM content increases, the time to failure increases (Figure 6b and Figure 6c). Similarly, as the air content increases, the time to failure increases, consistent with visual observations. Mixtures with high SCM and air contents, for example FA35-8.0 appear to not manifest any damage over the 300 cycles, as the UPV does not change over time. The effect of air and SCMs is considerable – the OPC-2.6 mixture fails at less than 50 cycles, whereas the FA35-8.0 mixture appears to not be damaged over 300 cycles. Therefore, air and

SCMs are essential in mixtures exposed to conditions in which calcium oxychloride formation can occur. The UPV observations are in line with the visual observations. These findings suggest that strength does not in any way control damage due to calcium oxychloride formation, as OPC-2.6 is the strongest mixture based on compressive strength. Therefore, increasing strength is not a valid strategy to improve durability against calcium oxychloride; whereas increasing air content and SCM replacement are valid strategies. The decrease in UPV of concretes as they are damaged has been studied for exposure to freeze-thaw cycles and salt scaling conditions [42,43], but studies appear to be limited for conditions in which calcium oxychloride can form. Curve fitting to explore the UPV behavior was explored but simple curves which explain the UPV changes were not discovered.

Based on Table 3 and Figure 4, the number of cycles when the cylinders reach a visual classification of severe is known. An attempt was made to define a UPV level or a reduction in UPV values which correspond to a severe damage classification. For the OPC mixtures, a 4% decrease in UPV values corresponded to the severe damage classification. However, this "threshold" UPV reduction ranged from 2.5% to 8.1% for different mixtures, as it showed a strong dependence on the air content and SCM replacement. While in certain mixtures a 5% UPV reduction was reflected as severe damage (for example the OPC mixtures), other mixtures (SL35-7.5) did not show any damage even when the mass change exceeded 5%. Therefore, defining a general threshold for damage based on UPV level is not trivial. UPV values drastically drop when damage exceeds the severe classification, but the exact behavior again depends on air and SCM.


a
OPC-2.6
OPC-6.6
OPC-7.9
UPV (m/s)
Cycles
0
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200
250
300
b
FA20-2.1
FA20-5.6
FA20-7.9
FA35-1.8
FA35-4.5
FA35-8.0
UPV (m/s)
Cycles

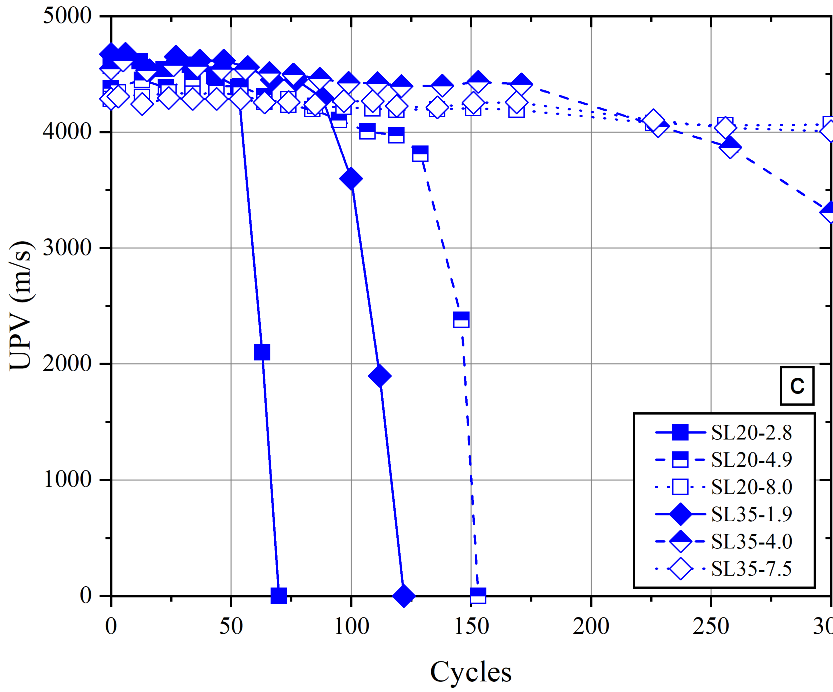


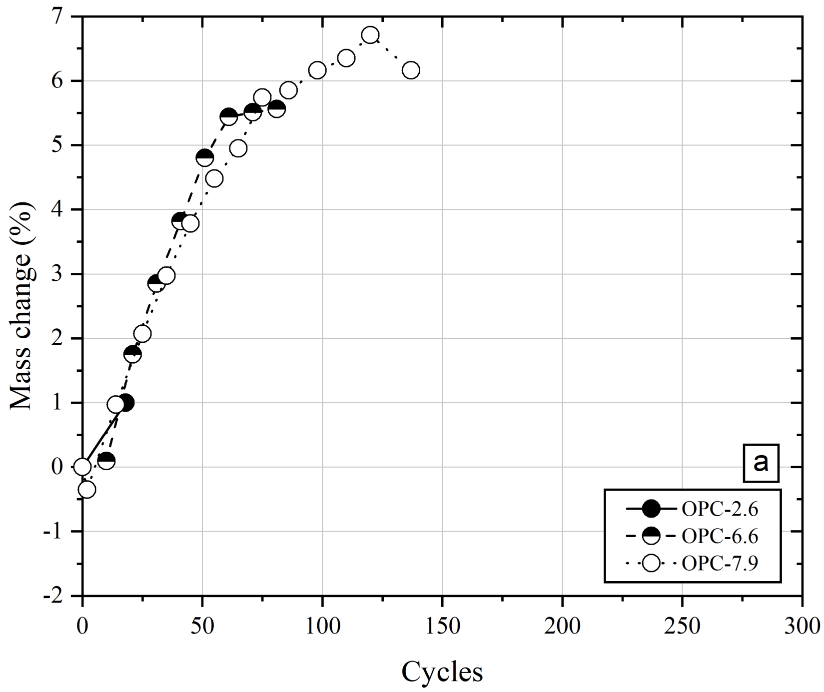
Figure 6. UPV plotted against number of cycles for mixtures a) OPC, b) fly ash, c) slag.

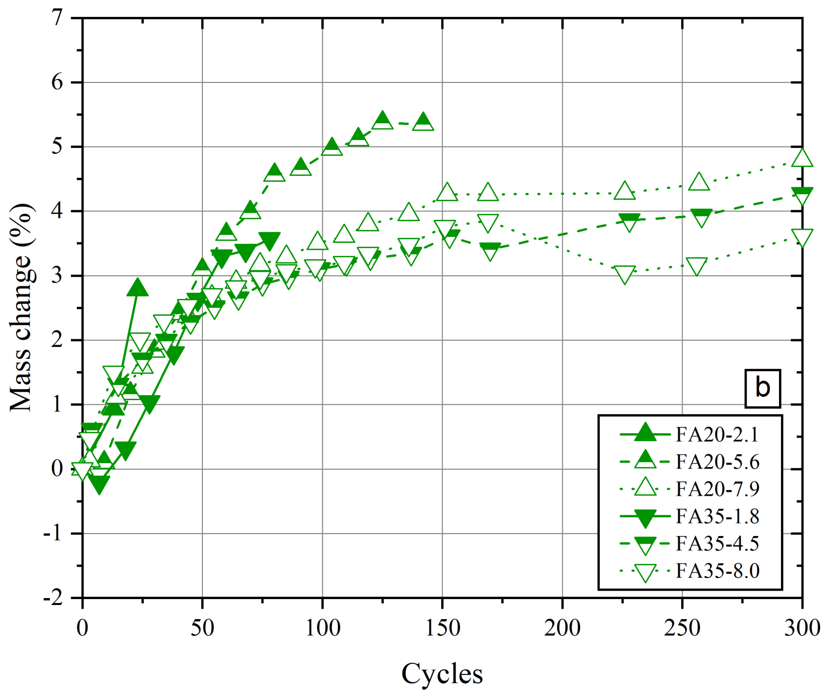
4.3. Mass changes during exposure

The mass change values for the control, fly ash and slag mixtures are plotted in Figure 7. During the freeze-thaw cycles, all concrete mixtures demonstrate a generally increasing trend in their mass as they absorbed $CaCl_2$ solution. Increases in mass during exposure to freeze-thaw and salt scaling conditions are known [42]. The OPC mixtures, which showed early failure, show rapid increase in mass. This increase was especially seen in OPC-2.6, which failed after very few measurements. For OPC-6.6 and OPC-7.9, the mass increases rapidly to values greater than 5%, before failure occurs. Mass change measurements are complex because mixtures leach calcium hydroxide and show spalling, in addition to solution sorption. Other studies have observed similar complexities and have suggested measurement of the spalled material separately in addition to the specimen mass to better evaluate mass changes [44]. When large-sized chunks of the concrete are spalled, then the mass is reduced, which is reflected as a sharp drop in the curves in Figure 7.

“Final” values of mass change are not shown, as often mixtures are broken into pieces by this time and the mass change measurement does not have any meaning when mixtures are in this condition. Similar to the UPV, the use of air entrainment and SCM, causes slower increases in mass. The slope of the curves in the initial portion appears to be reduced as SCM replacement is increased. However, the curves are not particularly linear, which makes a quantification of the slope somewhat complex. Mixtures with both air and SCM commonly show a two-stage behavior where the mass loss increases only slightly after a certain point, but this is not the case for all mixtures. It appears that mixtures with greater amounts of air and SCM show a lower mass change (increase) at a given numbers of cycles. The mass change needed to induce failure increases with air content: OPC-6.6 failed at 4.6% mass change whereas OPC-7.9 failed at 6.2% mass change. Corresponding values for FA20-2.1 and FA20-5.6 are 2.8% and 6.1%, respectively.

A mass change “threshold” for severe damage/failure cannot be defined as it depends on air content and SCM replacement. Some mixtures (FA20-2.1) show failure at mass change values below 3%, but other mixtures (SL35-7.5) show no damage even at mass change values of 4% or greater.


Mass change (%)
Cycles
a
OPC-2.6
OPC-6.6
OPC-7.9


Mass change (%)
Cycles
b
FA20-2.1
FA20-5.6
FA20-7.9
FA35-1.8
FA35-4.5
FA35-8.0

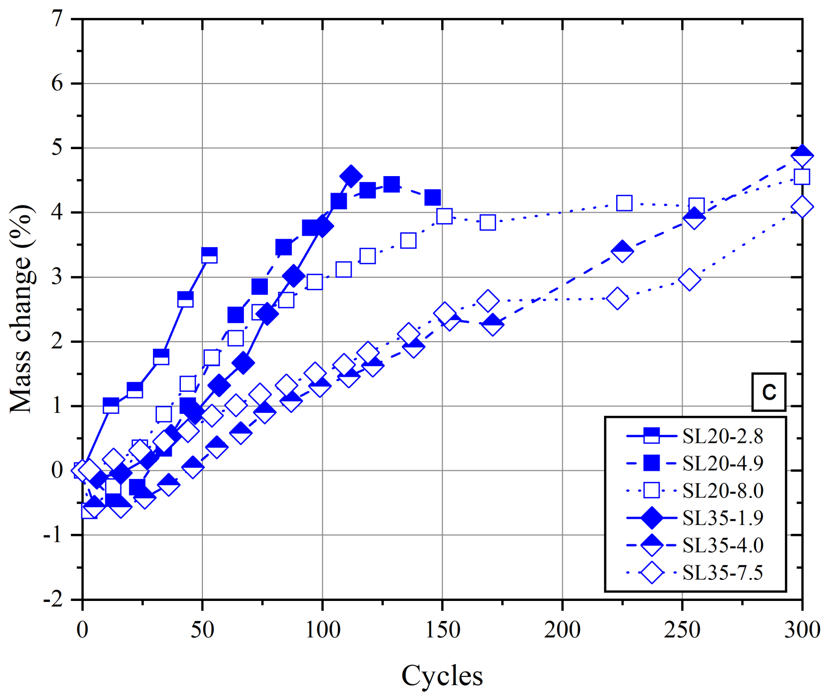


Figure 7. Mass change vs. number of cycles a) OPC, b) fly ash, c) slag.

4.4. Bulk resistivity changes during exposure

Bulk resistivity values for the control, fly ash and slag mixtures are shown in Figure 8. In all mixtures, the bulk resistivity reduces as the number of cycles increases and the $CaCl_2$ ingresses into the concretes. The bulk resistivity of the concretes increases with air content and SCM replacement, which is consistent with visually better-quality concretes (after a fixed number of cycles) and the results obtained from UPV and mass change. It is evident from the different tests that air and SCM improve the performance of concrete undergoing damage due to calcium oxychloride formation for reasons discussed in Section 4.2.

As the mixtures are exposed to $CaCl_2$ solution and freeze-thaw cycles, the bulk resistivity values decrease. The initial decrease is rapid, likely because the solution ingress changes the pore solution conductivity and the degree of saturation [3,6]. For concretes which show poor performance (for example OPC-2.6), cracking and spalling initiate early, and the concrete sorbs large amounts of the ionic solution, leading to very low values of bulk resistivity before failure. As the amount of air increases, for example, in the mixtures OPC-6.6 and OPC-7.9, the bulk resistivity decreases rapidly, but then the rate of decrease reduces. However, the bulk resistivity in these mixtures continues to reduce, as they suffer damage and ultimately fail. As the amount of air and SCM replacement increases, the initial bulk resistivity at 28-days increases. The bulk resistivity reduces during exposure, but at a given number of cycles, the bulk resistivity is higher in mixtures with greater amounts of air and SCM replacement. In addition, many mixtures with greater amounts of air and SCM (for example FA35-8.0) have bulk resistivity values that are unchanged after an initial reduction. The lack of a further reduction in the bulk resistivity is consistent with a lack of damage in these mixtures from visual observations (Figure 4).

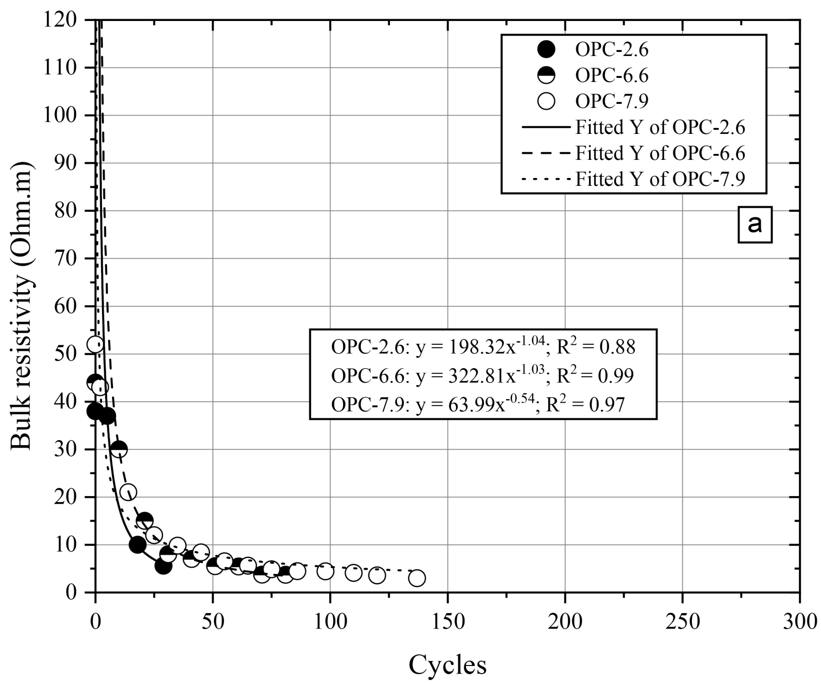
The initial bulk resistivity should in principle be a strong predictor of calcium oxychloride durability, as bulk resistivity increases as SCM replacement increases. However, the bulk resistivity does not depend strongly on air content, so a function which combines the bulk resistivity and air content is likely to be a reliable indicator of mixture resistance to damage due to calcium oxychloride formation. This is a powerful finding, because air content and bulk resistivity are relatively simple measurements to perform on any concrete. However, in our study, the initial bulk resistivity is not always an accurate indicator of calcium oxychloride durability. For example, the initial bulk resistivity values of OPC-7.9 and FA20-7.9 are similar, although the former fails at 140 cycles whereas the latter shows no damage even at 300 cycles. This discrepancy is because the fly ash reaction extent is low at 28-days [45,46]. The bulk resistivity of FA20-7.9 would have continued to increase as the fly ash reaction increases, although bulk resistivity values of OPC mixtures typically plateau at 28-days. Therefore, mature measurements of bulk resistivity (56- or

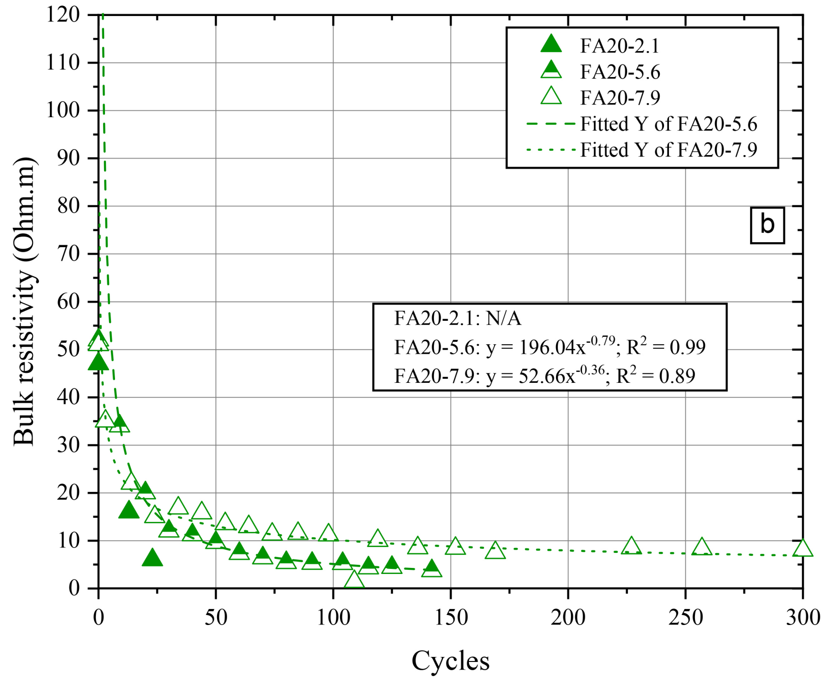
91-days) would be better predictors of calcium oxychloride durability. Using bulk resistivity would be an attractive and practical option as the measurements are relatively simple to perform and could be performed in a routine manner by concrete producers. The use of surface resistivity (which correlates with bulk resistivity) would be especially attractive as it could be used to rapidly assess the threat of calcium oxychloride damage in existing pavements.

While UPV and mass change did not appear to show the same type of behavior for all mixtures, bulk resistivity appears to be more consistent in this regard. For the bulk resistivity, most mixtures appear to show a power law type decay in their response when exposed to the 25% $CaCl_2$ solution. Saturation functions that describe the behavior of partially saturated concrete have been suggested to follow a power law [47]. The reduction in bulk resistivity in mixtures exposed to 25% $CaCl_2$ solution is driven by both increase in the degree of saturation and a decrease in pore solution resistivity. As the behavior observed here is similar to the power law saturation function, one interpretation is that the changes in degree of saturation may dominate the changes in the pore solution resistivity.

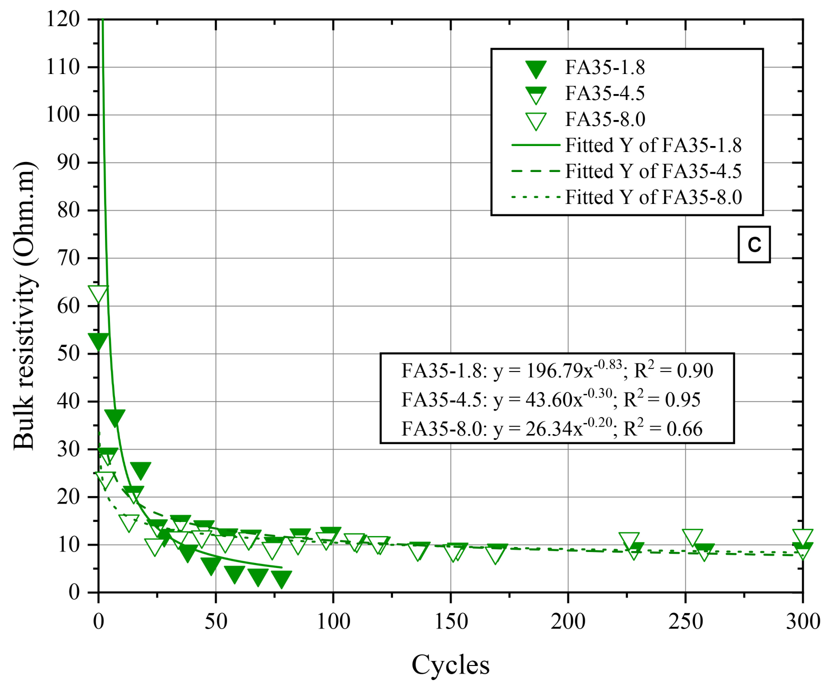
While threshold values of UPV and mass change were not found, for the bulk resistivity, by comparing to the visual damage (Figure 4), it appears that when the bulk resistivity is reduced to a value below 4 Ohm.m, the cylinders reach a severe/failure damage classification. Therefore, one can tentatively consider a value of 4 Ohm.m of bulk resistivity as a failure threshold when concrete is damaged by calcium oxychloride formation. A corresponding threshold for minor/moderate damage is not evident, and such a threshold may depend on mixture design. A correlation between the degree of saturation and damage due to calcium oxychloride formation has not been established, but it is reasonable that mixtures which reach high degree of saturation values quicker will also fail sooner. This thinking is consistent with freeze-thaw damage, where concrete fails rapidly after exceeding a critical degree of saturation [6]. For freeze-thaw, the air content strongly affects the time needed to reach a critical degree of saturation. For calcium oxychloride, if a critical degree of saturation exists, in addition to the air content, it would also depend on the SCM replacement.

Since the bulk resistivity appears to show a consistent response, and a threshold value for failure could be defined, curve fitting for the bulk resistivity was performed using power law fits, as shown in Figure 8. All mixtures, except two mixtures which showed rapid failure (FA20-2.1 and SL20-2.8) were fit using power laws. The fits appear to largely have good R^2 values. As a result, bulk resistivity may be used to predict failure in concrete in such conditions. While saturation driven reductions in the bulk resistivity are feasible [47], the exact physical significance of such fitting is not clear. Nevertheless, the fits are important as they can in principle be used to predict the time to failure for mixtures which have not failed.





FA20-2.1
FA20-5.6
FA20-7.9
Fitted Y of FA20-5.6
Fitted Y of FA20-7.9
b
FA20-2.1: N/A
FA20-5.6: y = 196.04x^-0.79; R^2 = 0.99
FA20-7.9: y = 52.66x^-0.36; R^2 = 0.89
Bulk resistivity (Ohm.m)
Cycles
0
10
20
30
40
50
60
70
80
90
100
110
120
0
50
100
150
200
250
300



FA35-1.8
FA35-4.5
FA35-8.0
Fitted Y of FA35-1.8
Fitted Y of FA35-4.5
Fitted Y of FA35-8.0
c
FA35-1.8: y = 196.79x^-0.83; R^2 = 0.90
FA35-4.5: y = 43.60x^-0.30; R^2 = 0.95
FA35-8.0: y = 26.34x^-0.20; R^2 = 0.66
Bulk resistivity (Ohm.m)
Cycles
0
10
20
30
40
50
60
70
80
90
100
110
120
0
50
100
150
200
250
300

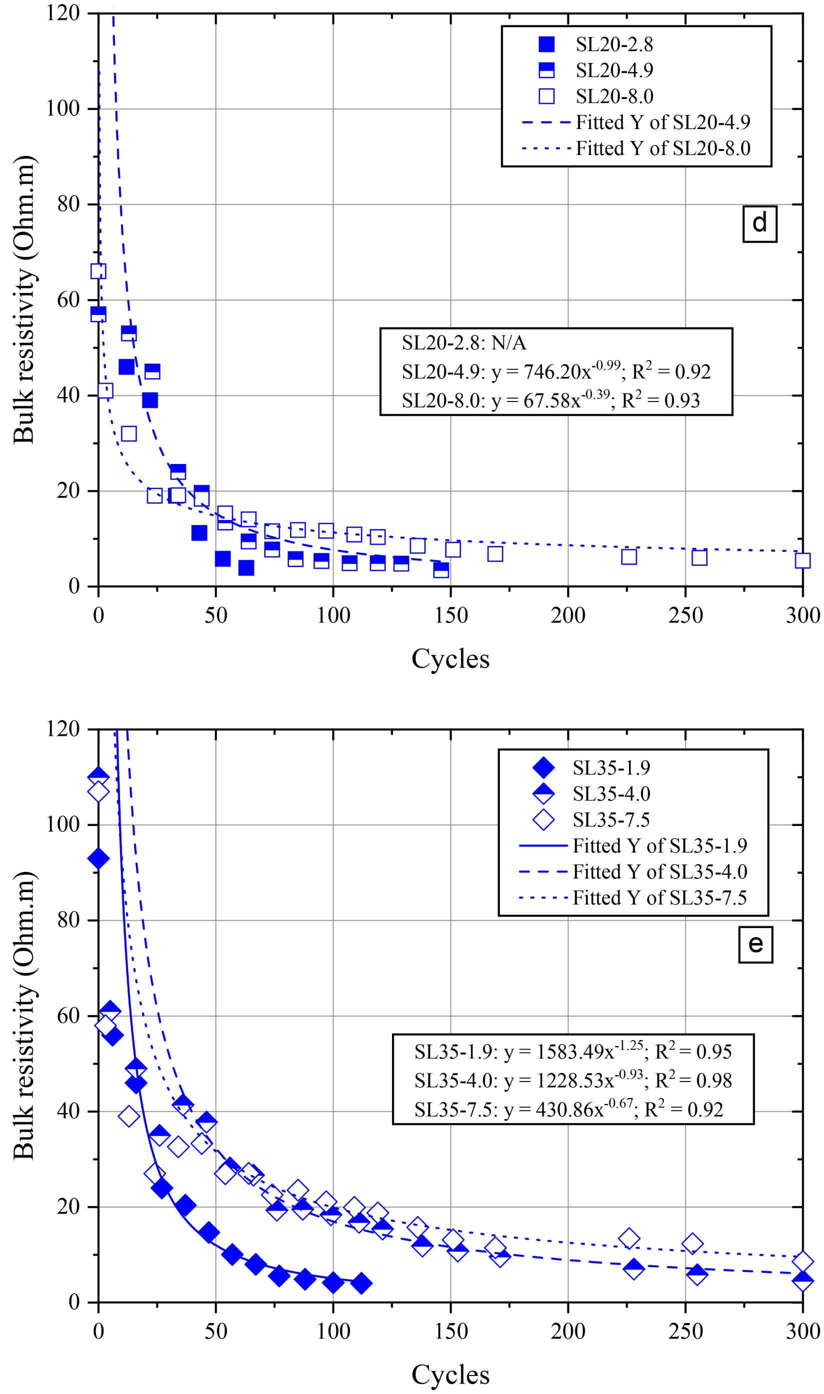


Figure 8. Bulk resistivity values and fitted lines for a) OPC, b) 20% fly ash, c) 35% fly ash, d) 20% slag, e) 35% slag.

The predicted time to failure for all mixtures is shown in Table 5. Assuming the failure threshold of 4 Ohm.m for samples as point of failure, the expected number of cycles to failure was evaluated for all mixtures where fitting was performed. The prediction error is also shown in Table 5. The predicted error ranges from -12% to +30%, depending on the mixture design, with average of 10%. Considering the wide variety of mixtures tested, these numbers appear to be rather reasonable. The table demonstrates quantitatively that the time to failure is increased very significantly as the air and SCM contents are increased, consistent with results obtained other measurements.

4.5. Post-exposure measurements

After 300 cycles, the cylinders from the six remaining mixture designs which failed were tested in compression. Cylinders were left to air dry for 24 hours before the test. The measured strength values and corresponding 28-day values are shown in Table 6. The table shows that all mixtures experienced some level of damage during exposure, except FA35-8.0. Mixtures with higher air contents and SCM replacements show lesser damage, as evidenced by smaller strength reductions. Fly ash in some mixtures may have continued to react during exposure as the 28-day curing was not adequate for full fly ash reaction [45,46,48].

The measured solution absorption is shown for all mixtures in Figure 9. There appears to be a relationship between the durability of the concrete and the absorption values. Specifically, mixtures which fail early appear to have absorbed a greater amount of solution. This is unsurprising as the solution sorption is what ultimately leads to failure. The cylinders which did not fail all show absorption below 8%, whereas almost all mixtures which failed show sorption greater than 8%. Absorption values decrease as SCM replacement and air content increases.

Table 5. Measured and predicted number of cycles to failure using power law fits for the bulk resistivity (N/A: For FA20-2.1 and SL20-2.8, fitting was not possible due to early failure).

Mixture name	Measured cycles to failure	Damage status at 300 cycles	Predicted cycles to failure	Prediction error (%)
OPC-2.6	33	Failure	43	30%
OPC-6.6	88	Failure	71	-19%
OPC-7.9	141	Failure	170	21%
FA20-2.1	29	Failure	N/A	-
FA20-5.6	152	Failure	138	-9%
FA20-7.9	-	None	1287	-
FA35-1.8	85	Failure	109	28%
FA35-4.5	-	Moderate	2871	-
FA35-8.0	-	Minor	12382	-
SL20-2.8	67	Failure	N/A	-
SL20-4.9	150	Failure	197	31%
SL20-8.0	-	Moderate	1406	-
SL35-1.9	117	Failure	103	-12%
SL35-4.0	-	Severe	473	-
SL35-7.5	-	None	1080	-

Table 6. Changes in compressive strength of mixtures after 300 cycles (SD is the standard deviation of the compressive strength measurements).

Mixture name	0 Cycles		300 Cycles		Change (%)	Damage Status
	Compressive Strength (MPa)	SD (MPa)	Compressive Strength (MPa)	SD (MPa)		
FA20-7.9	18.85	1.28	15.69	0.33	-17%	None
FA35-4.5	20.04	0.05	17.13	1.50	-15%	Moderate
FA35-8.0	8.38	0.13	13.06	0.13	56%	Minor
SL20-8.0	21.08	0.58	13.72	2.15	-35%	Moderate
SL35-4.0	34.85	2.58	4.94	0.36	-86%	Severe
SL35-7.5	16.95	0.68	14.78	0.31	-13%	None

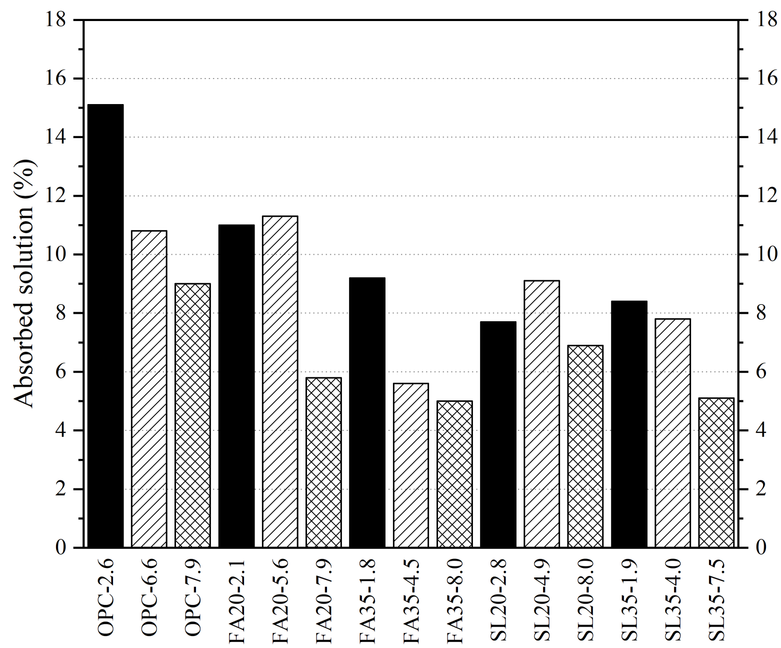


Figure 9. Solution absorption of the various mixtures.

As discussed earlier, the bulk resistivity and air content should in principle be able to predict concrete durability when exposed to calcium oxychloride formation. As exposure was performed at early ages, here, SCM replacement level is used as a proxy for the bulk resistivity. Figure 10 shows a plot of cycles to failure (from Table 5, measured values used where available, predicted values used otherwise) plotted against the multiplied SCM replacement level in (wt. %) and air content (volume %) with the number cycles to failure. The cycles to failure increase as the SCM replacement level multiplied by the air content increases, especially beyond a threshold level. Depending on the cycles to failure, each mixture is classified into one of two performance groups as defined below:

- Poor durability: Concrete is expected to fail in less than 300 cycles.
- High durability: Concrete is expected to fail after more than 300 cycles.

According to this classification, if concrete mixture SCM replacement multiplied by air content is more than 125, mixtures would be highly durable when exposed to high concentrations of $CaCl_2$. Some error in such assessments is likely, but this finding appears to be a good starting point for further evaluation of realistic field mixtures. Concrete mixtures with 20% SCM and more than 7.9% air or 35% SCM and more than 4.0% air fall into the highly durable group. Using SCM replacement multiplied by air content, we are able to theoretically predict the time to failure for other mixtures. Minimum levels of air needed for adequate durability at different SCM levels are: 15% SCM (8.3% air), 20% SCM (6.25% air), 25% SCM (5% air), and 30% SCM (4.2% air). Recommended air contents in ACI documents vary depending on aggregate size, but for severe exposure, they are usually around 6.5%. However, field tolerance on air content is typically 1.5%. For an 8% air mixture, 15% SCM would be adequate, but for a 5% air mixture, 25% SCM would be adequate.

When one considers the AASHTO PP84 guidelines, the 30% SCM replacement appears to be on the higher side. However, our calculations do not have an inbuilt factor of safety and are based on limited data in the air content range of 5% to 8%. Therefore, at this time, we suggest that the 30% SCM replacement in AASHTO PP84 is reasonable. Further data on impacts of the curing duration, effects of SCM chemistry, later-age bulk resistivity evolution, air void system, and performance of realistic mixtures (5% to 8% air and SCM replacements between 15% and 30%) are needed before implementation of changes in the AASHTO PP84 replacement level. Developing suitability criteria for concrete that will be exposed to deicing salts based on a combination of air contents, SCM replacements, and bulk resistivity measurements will an important and implementable advantage. If such relationships can be developed, the other

AASHTO PP84 provision, which calls for the quantification of calcium oxychloride in cementitious pastes, a rather complex measurement, could potentially be simplified.

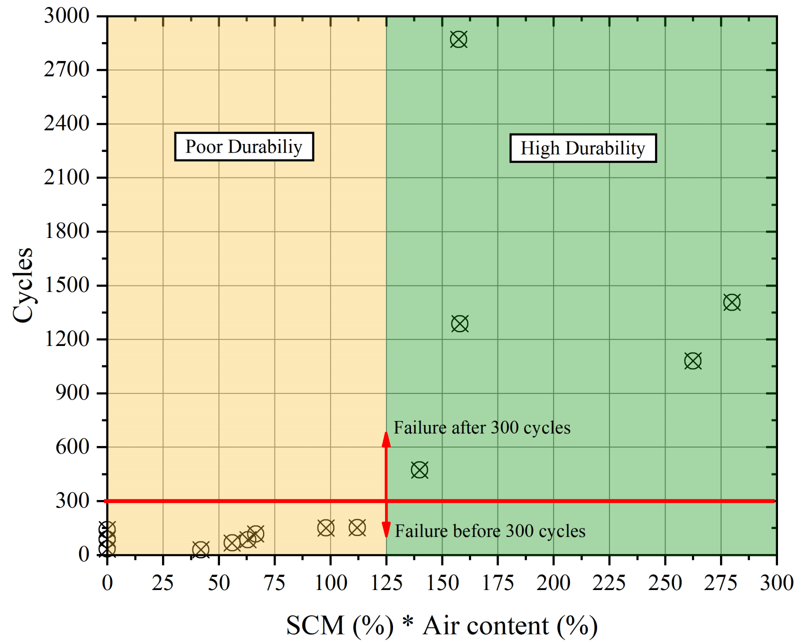


Figure 10. Performance classification of mixture designs based on air content and SCM replacement.

4. Conclusions

This study investigated the synergistic roles of air and supplementary cementitious materials (SCMs) in reducing concrete damage when exposed to concentrated $CaCl_2$ solutions and freeze-thaw cycles. The following conclusions can be drawn based on the monitoring of damage over 600 days and post-exposure measurements:

- The use of air entrainment and SCMs reduces the damage at any given cycle. Damage is reduced as the SCM replacement increases.
- Bulk resistivity, surface resistivity, and visual assessment appear to be clear indicators of damage progression over time. UPV and mass change are also damage indicators, however, they are somewhat more complex to interpret.

- Mixtures which had 20% SCM and 8% air and mixtures which had 35% SCM and more than 4% air showed strong durability against damage caused by calcium oxychloride formation.
- Based on power law fits for bulk resistivity, time to failure can be estimated for mixtures which have not failed.
- SCM content multiplied by air content can differentiate mixtures which show poor and high durability under such exposure conditions, with a threshold value of 125 between the two behavior types.
- Further testing of realistic field mixtures and establishment of thresholds based on air content, SCM replacement, and bulk resistivity is an important step in better designing mixtures for cold regions.

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