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# Quantifying Conservativeness of Water-Soluble Chloride Testing

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*Proponents of water-soluble chloride testing argue that only chlorides in the pore solution contribute to corrosion and that this testing is more representative of free chlorides and therefore should be required. Proponents of acid-soluble chloride testing argue that although water-soluble testing may be more representative of free chlorides in the pore solution at early ages, bound chlorides can become unbound with time, making the water-soluble test unconservative for predicting later-age free chlorides. However, water-soluble testing likely unbinds some admixed chlorides during testing. If the number of chlorides released as part of the water-soluble test exceeds the number of chlorides released at later ages (that is, from carbonation), the water-soluble test should be sufficiently conservative. This research quantifies the release of admixed chlorides as a result of testing and carbonation. Results indicate that water-soluble testing is sufficiently conservative in most cases for assessing admixed chloride contents in various cementitious systems.*

**Keywords:** admixed chlorides; bound chlorides; carbonation; chloride release; chloride testing; specialty cements.

## INTRODUCTION

The presence of chlorides in sufficient quantities in a cementitious system can disrupt the passive layer on embedded steel reinforcement, which protects this reinforcement from corrosion. Chlorides in concrete can increase the risk of corrosion and reduce the service life of these structures. Chlorides can be present in the concrete constituent materials, intentionally added to the fresh mixture, or can be transported into the cementitious system from the surrounding environment.

Chlorides in the fresh mixture—that is, the admixed chlorides—can react during the cement hydration process, and some can become bound within the hydrated products. The binding of these chlorides can influence whether the concrete meets specifications for chloride limits and whether these chlorides can contribute to corrosion initiation of the reinforcing steel in the concrete. Bound chlorides that are physically (loosely) or chemically (tightly) bound in or on the hydrated cement products are initially unavailable for corrosion initiation and propagation. However, free chlorides—that is, chlorides that are present in the pore solution of the cementitious system—do contribute to corrosion initiation and propagation. The sum of the free and bound chlorides in the cementitious system represents the total admixed chlorides. Although the total admixed chlorides could be constant with time (assuming no external chloride exposure), the amount of free and bound chlorides could change with time and with exposure to CO<sub>2</sub> or sulfates. Knowing the

time variant, free and bound chlorides under different exposure conditions can assist users in selecting an appropriate test that will provide a representative estimate of later-age free chlorides, which will provide a better estimate of the future risk of corrosion and service life.

The free chlorides in the pore solution of the cementitious system are quantified by the extraction of the pore solution using high pressure. Longuet et al. (1973) developed the pore extraction method, and this process has been used by many researchers to extract pore solutions from cementitious systems (Barneyback and Diamond 1981; Page and Vennesland 1983; Arya et al. 1987; Dhir et al. 1990; Haque and Kayyali 1995; Pavlik 2000; Plusquellec et al. 2017). Longuet et al. (1973) provided a method to express the pore solution from crushed cement pastes. The general process reported is to crush a cementitious sample into manageable sizes, place this crushed cementitious material into the extraction equipment, place a load on the equipment to extract the pore solution, then collect and analyze this pore solution. One drawback of this method is that it is not yet standardized and statistics and error measures are needed.

ASTM C1218/C1218M-17 is a standardized test commonly reported to be an indicator of free chlorides. This test is performed by mixing 10 g (0.35 oz.) of powdered samples with 50 ± 1 mL (1.7 ± 0.034 fl oz.) of reagent water. The sample is then boiled for 5 minutes and allowed to stand for 24 hours for chloride extraction. After filtering residues from the sample, the filtrate is mixed with 3 mL (0.1 fl oz.) of 1:1 nitric acid and 3 mL (0.1 fl oz.) of 30% hydrogen peroxide. After 2 minutes, the sample is boiled again for several seconds, then after cooling to room temperature, is tested for chlorides using manual potentiometric titration following ASTM C114 requirements. Arya et al. (1990) distinguished between the pore solution and water-soluble chlorides and reported that although pore solution chlorides are more representative of the free chlorides, some loosely bound chlorides are released during water-soluble chloride testing. Shakouri et al. (2018) reported that the pore solution results are, on average, 77% of the water-soluble results. This finding is in line with the findings of Arya et al. (1990). Therefore, results from water-soluble chloride testing are generally higher than results from pore solution

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chloride testing, and water-soluble testing likely causes the unbinding of bound chlorides and thereby overestimates the number of free chlorides.

ASTM C1152/C1152M-04 is commonly reported to be an indicator of total chlorides. Shakouri et al. (2018), Trejo et al. (2019), and Trejo and Ahmed (2019) reported that ASTM C1152/C1152M detects, on average, approximately 94%, 93%, and 95% of the total admixed chlorides in ordinary portland cementitious (OPC) systems, respectively. These results indicate that acid-soluble chloride testing slightly underestimates the total chlorides, but even so, is likely a good indicator of total chlorides.

Water-soluble testing, following ASTM C1218/C1218M, is common practice for evaluating admixed chlorides in concrete. Several ACI documents also allow acid-soluble testing (ASTM C1152/C1152M). Some of these documents note that acid-soluble chloride testing is likely more appropriate because chlorides can be released at later ages because of carbonation, and that water-soluble testing may underestimate the number of chlorides released as a result of carbonation. Very little research has been performed to assess how much of the bound admixed chlorides are released during water-soluble chloride testing. In addition, very little research has been performed to quantify the number of chlorides that are released because of carbonation. The objective of this research is to quantify these chloride releases for different cementitious systems to determine if water-soluble testing is conservative or unconservative for estimating chlorides that can be unbound at later ages because of carbonation.

Dhir et al. (1990) performed acid- and water-soluble testing to evaluate the chloride content of OPC concrete specimens containing admixed chlorides. The authors reported that the acid extraction method yielded up to 70% more chlorides than the conventional water-soluble method (water-soluble to acid-soluble test ratio is  $\sim 0.6$ ). The authors also reported that water-soluble chlorides provided an immediate indication of corrosion risk and that acid-soluble chlorides can be used to evaluate the overall risk of corrosion of the cementitious systems when exposed to carbonation. However, if water-soluble testing extracts some of the bound chlorides as reported by Shakouri et al. (2018) and Arya et al. (1990), water-soluble chloride testing may be sufficiently conservative to evaluate “overall risks,” as referred to by Dhir et al. In addition, the ACI 222 documents (ACI Committee 222 2010, 2019) report that the average content of water-soluble chlorides is approximately 75 to 80% of the acid-soluble chlorides; that is, the acid-soluble test yields 25 to 33% more chlorides than the water-soluble test. Trejo et al. (2019) reported that results from the water-soluble tests can range from 8 to 77% of the acid-soluble tests for various cementitious systems and reported that the range published in ACI 222R-01(10) was in most cases incorrect for admixed chlorides.

Knowing the amount of free and bound chlorides is important as this information can influence material acceptance and future corrosion performance. However, the amount of free and bound chlorides can change with time and knowing the free, bound, or total chlorides in new concrete provides limited information on these chlorides at

later ages. The concentration change in free and bound chlorides is related to the carbonation of cementitious systems. Because bound chlorides can be released under certain exposure conditions, researchers have recommended that acid-soluble chloride testing be used to assess the overall risk of corrosion (Vesikari 2009; Geng et al. 2016). However, this would be appropriate only if nearly all bound chlorides were released upon carbonation at later ages. If only a very small number of chlorides are released upon carbonation, using acid-soluble chloride testing could significantly overestimate the later-age free chlorides and could be overly conservative. What is more important in selecting an appropriate test method is whether the results from that test method are representative of the free chlorides at later ages after carbonation. If the number of bound chlorides released from water-soluble testing exceeds the number of chlorides released as a result of carbonation, the water-soluble test would be a more appropriate test to assess free chlorides at later ages and potential risk of corrosion (that is, after carbonation). Alternatively, if the number of free chlorides after carbonation exceeds the number of bound chlorides released from water-soluble testing, the acid-soluble test may be the more appropriate test. The objective of this research is to identify the most appropriate chloride test that minimizes corrosion risk for OPC and specialty cements.

One significant variable that affects the binding of chlorides in cementitious systems is the hydration products of the cementitious system. When chlorides are included in the fresh mixture, binding of chlorides occurs during the process of forming these hydration products. Page and Vennesland (1983) reported that the hydration products of OPC bind approximately 60% of the total admixed chloride content. The authors also reported that after the addition of chlorides to the fresh mixture, these chlorides can be bound through chemical substitution or physical sorption to the OPC hydration products. Hirao et al. (2005), Florea and Brouwers (2012), and Geng et al. (2016) also reported that when chlorides are intentionally added to a fresh OPC mixture, chlorides will react with monosulfate to form Friedel's salt ( $C_3A \cdot CaCl_2 \cdot H_{10}$ ), or these chlorides can be physically adsorbed onto the outer layers of calcium-silicate-hydrate (C-S-H) gel. Friedel's salt, in turn, can physically interact with chlorides through ion exchange, dissolution, and precipitation, and because of its large surface area, can further bind chlorides. Florea and Brouwers (2012) reported that C-S-H could bind between 25 and 28% of the total admixed chlorides and monosulfate hydrate can bind up to approximately 70% of the total admixed chlorides. The authors also noted that ettringite and calcium hydroxide exhibit minimal binding capacities. However, Arya et al. (1990) reported that chlorides could react with the ettringite to produce calcium chloroaluminate.

Calcium aluminate cement (CAC) systems and calcium sulfoaluminate cement (CSA) are two common specialty cement systems. These systems exhibit different hydration products than that of OPC; therefore, the chloride binding capacities of these cements could be different from OPC systems.

The primary hydration products of CAC are  $\text{CAH}_{10}$  and small amounts of  $\text{C}_2\text{AH}_8$  with  $\text{AH}_3$ . These products convert to  $\text{C}_3\text{AH}_6$  with time, depending on time and temperature, where high temperatures increase this conversion rate. Limited research has been performed to assess the binding of chlorides in CAC systems. Sanjuán (1997) studied the conversion of CAC with the presence of admixed chlorides. The author reported that Friedel's salt is formed when the hexagonal-shaped  $\text{CAH}_{10}$  converts to the cubic  $\text{C}_3\text{AH}_6$  through dissolution, and the formation of Friedel's salt could occur through the replacement of hydroxide anions in the cubic-shaped  $\text{C}_3\text{AH}_6$  with chloride anions. Ann et al. (2010a,b) reported that low-alumina CAC systems exhibit lower chloride-binding capacities than OPC systems and attributed this lower binding to the lower level of hydration products that bind chlorides. The authors also reported that CAC is resistant to the release of bound chlorides, even at low pH levels. Later, Ann and Cho (2014) investigated the binding of chlorides in OPC and CAC systems and concluded that the binding of chlorides in CAC is lower than that of OPC.

Zhang and Glasser (2002), Winnefeld and Lothenbach (2010), and Zajac et al. (2016) reported that the main hydration products of CSA cement are ettringite ( $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 32\text{H}_2\text{O}$ ) and calcium monosulfate ( $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot \text{CaSO}_4\cdot 12\text{H}_2\text{O}$ ), along with amorphous aluminium hydroxide ( $\text{AH}_3$ ). Calcium monosulfate hydrate forms in the presence of lower  $\text{CaSO}_4$  quantities, whereas ettringite forms in the presence of higher  $\text{CaSO}_4$  quantities.

CSA systems have been reported to exhibit higher chloride-binding capacities than OPC systems. Ioannou et al. (2015) assessed concrete samples with a CSA-fly ash cement blend and reported that the binding of chlorides increased in the ettringite-rich environment. Monosulfate quantities in the CSA system are higher than that of OPC and therefore these systems can exhibit higher binding capacities. Hirao et al. (2005), Florea and Brouwers (2012), and Geng et al. (2016) all reported that calcium monosulfate, even in small quantities, exhibits high binding capacities. Therefore, the high binding capacities reported for CSA systems seem to be attributed mostly to the presence of calcium monosulfate.

This literature review indicates that CSA systems could initially bind more chlorides than OPC systems, while CAC systems likely initially bind less chlorides than OPC systems. The binding of chlorides is a critical parameter because the number of chlorides that are bound could influence whether certain concrete mixtures meet allowable chloride limits, and the number of free chlorides could influence future corrosion activity. Because the number of free chlorides could be a time-variant function (that is, it changes when carbonation occurs), accurately measuring these free and bound early- and later-age chlorides is important. If a cementitious system can bind all chlorides at early ages but all these chlorides are later released, the value of the results from early-age testing, which indicated no free chlorides, would be limited. It is well known that free chlorides are responsible for corrosion initiation and propagation. The water-soluble test method is a derived method that is believed to measure the free chlorides. However, some bound chlorides are released during testing.

The conservativeness of this test for predicting later-age free chlorides and eventual risk of corrosion is unknown, especially when the number of free chlorides increases when the cementitious system is exposed to carbonation. Knowing the amount of released chlorides after exposure to carbonation can help in determining the most appropriate testing to assess the later-age free chlorides.

The carbonation of OPC systems is a chemical reaction between gaseous  $\text{CO}_2$  and calcium-bearing phases such as  $\text{Ca}(\text{OH})_2$  and C-S-H.  $\text{CO}_2$  gas can be transported into the cementitious system matrix and change the chemical makeup by attacking the soluble  $\text{Ca}(\text{OH})_2$  to form calcium carbonate,  $\text{CaCO}_3$ , and water. Geng et al. (2016) assessed the release of bound chlorides in OPC under the exposure of carbonation and reported that carbonation of OPC resulted in the release of bound chlorides due to the decomposition of Friedel's salt and C-S-H gel, leading to an increase of free chlorides.

Pérez et al. (1983), Blenkinsop et al. (1985), and Vasudevan and Trejo (2022) reported that CAC exhibits a higher rate of carbonation than OPC because of the lower pH of the CAC pore solution. It has been reported that carbonation of CAC can rapidly decrease the pore solution pH. Fernández-Carrasco et al. (2001) reported that the carbonation of CAC decreases the porosity through the formation of the  $\text{CaCO}_3$  polymorphs, vaterite, and aragonite in the pores. In addition to the formation of  $\text{CaCO}_3$ , conversion is inhibited because the carbonation rate of hexagonal calcium aluminates,  $\text{CAH}_{10}$  and  $\text{C}_2\text{AH}_8$ , is faster than that of the cubic aluminate,  $\text{C}_3\text{AH}_6$ . Therefore, carbonation can inhibit the conversion of CAC systems by reducing the number of aluminates that can be converted. Goñi and Guerrero (2003) studied the influence of accelerated carbonation on the stability of Friedel's salt and the number of free chlorides in the pore solution of the CAC system and reported that the carbonation of Friedel's salt did not increase the free chlorides in the pore solution.

The hydration products of CSA systems have also been reported to decompose when exposed to  $\text{CO}_2$ . Mesbah et al. (2012) reported that under increasing  $\text{CO}_2$  concentrations, calcium monosulfate hydrate can react to form calcite. Nishikawa et al. (1992) reported that when CSA is exposed to  $\text{CO}_2$ , ettringite dissolves into gypsum, calcium carbonate, and alumina gel. Robl et al. (1996) reported that calcite replaces gypsum when exposed to  $\text{CO}_2$ . Therefore, carbonation can result in the decomposition of the hydration products in CSA cementitious systems, possibly resulting in the release of bound chlorides.

Mesbah et al. (2012) reported that Friedel's salt forms from the reaction of chlorides and monosulfate in CSA cementitious systems. Suryavanshi and Swamy (1996) reported that chlorides can be disassociated from Friedel's salt upon exposure to carbonation, and this could increase free chloride levels and elevate the risk of corrosion. Canonico et al. (2012) reported that the carbonation rate of CSA could be higher than that of OPC because of the low pH of the CSA pore solution. The literature indicates that the decomposition of the hydration products of CSA because of carbonation can release bound chlorides. However, how much bound chlorides are released is not known.

A review of the literature indicates that carbonation can increase the number of free chlorides in the pore solution of OPC cementitious systems. The review also indicates that the carbonation rates of CAC and CSA systems are typically higher than OPC systems and these higher rates could influence the rate and degree of release of bound chlorides. Knowing the number of bound chlorides that are released when exposed to CO<sub>2</sub> is important in assessing the risk of corrosion and service life of a structure. The objective of this paper is to first determine the number of bound chlorides that are released during water-soluble and acid-soluble testing and then to compare the amount of released chlorides with the number of chlorides that are released upon carbonation. If the number of bound chlorides released due to carbonation is less than or near the number of bound chlorides released from water-soluble testing at early ages, water-soluble testing should be used for assessing allowable chloride limits. If the number of bound chlorides released as a result of carbonation is more than the number of bound chlorides released from water-soluble testing at early ages, acid-soluble testing should be used. The results from this research will be used to identify the appropriate test method (water-soluble or acid-soluble) that should be used to assess allowable chloride limits to minimize risk of corrosion.

This study contains three parts. First, the study will assess the amount of early-age free chlorides using results from pore extraction and water-soluble testing for OPC, CAC, and CSA systems and will quantify how much of the bound admixed chlorides are released because of the ASTM C1218/C1218M (water-soluble chloride test) procedure. Second, the study will quantify the number of free chlorides, using water-soluble testing, of carbonated OPC, CAC, and CSA systems. This will provide data on how much chlorides are released because of carbonation. Lastly, using the information from the first two objectives, this research will identify the test that is most representative of later-age free chlorides of carbonated cementitious systems. The authors anticipate that this research will provide information to resolve the long debate on whether water- or acid-soluble testing is more appropriate for assessing admixed chlorides in different cementitious systems.

### RESEARCH SIGNIFICANCE

Debate exists as to whether admixed chlorides should be quantified with water- or acid-soluble testing. Because free chlorides in cementitious systems change with time and degree of carbonation, selecting an appropriate test method influences the risk associated with later-age corrosion. When chlorides become unbound, the risk of corrosion increases. This study quantifies the number of admixed chlorides released because of standardized water-soluble testing and as a result of carbonation exposure for various cementitious systems. These data provide information to determine if water-soluble testing is sufficiently conservative and more appropriate for assessing admixed chlorides in new concrete.

### EXPERIMENTAL PROGRAM

A full factorial design was used to assess the influence of four testing parameters on chloride measurements. The four

testing parameters include the type of cementitious system, the percentage of total admixed chlorides by mass of cement ( $Cl_{total}$ ), the water-cement ratio ( $w/c$ ), and the status of the cementitious system (uncarbonated or carbonated). The concentration of water-soluble chlorides was evaluated as the dependent variable. OPC, CAC, and CSA systems were assessed. Four levels of  $Cl_{added}$  by mass of cement (0, 0.05, 0.25, and 1%) and three levels of  $w/c$  (0.35, 0.45, and 0.55) were evaluated. Because background chlorides were present in the constituent materials, the total chloride concentration,  $Cl_{total}$ , is defined as the sum of  $Cl_{background}$  and  $Cl_{added}$ . A total of 36 (three types of cementitious systems  $\times$  four  $Cl_{added}$  percentages  $\times$  three  $w/c$  levels) scenarios for uncarbonated and carbonated cementitious systems were assessed with five replicates for each scenario (total of 360 samples) using a modified ASTM C1218/C1218M (auto-titration was used instead of manual titration). All chloride concentration tested following ASTM standards used the equations in the standards to quantify chloride concentrations. The pore solution chlorides ( $Cl_{pore-uncarb}$ ) obtained through extraction for each  $w/c$  and  $Cl_{total}$  level were evaluated using one sample. Note that this study assumes that the pore extraction method represents the early-age free chlorides. It should be noted that pore extraction could result in the release of some bound chlorides but as reported, chloride concentrations in free water-soluble testing are generally significantly higher than chloride concentrations from pore solution extraction.

### Materials

The materials used to prepare paste mixtures in this study included an OPC, a standard-grade CAC, and a commercial CSA. The oxide compositions of the cements were determined using X-ray fluorescence (XRF) analysis and are reported by Ahmed and Trejo (2020). The manufacturers reported that the chemistry of the cements and other characteristics meet standard requirements.

Primary standard reagents, NaCl (>99.9% purity) and AgNO<sub>3</sub> ( $\geq$ 99.80% purity), were used to prepare chemical solutions. The same NaCl was also used as the admixed chlorides. The mixing water was Type II reagent water that met ASTM D1193 requirements. All chemical solutions were prepared with the same reagent water.

Background chloride quantities for each cementitious system and  $w/c$  are shown in Table 1. These background chlorides were determined following ASTM C1152/C1152M but using auto-titration instead of manual titration.

### Specimen preparation

A total of 180 cylindrical specimens with diameters and heights of 34.3 x 52.1 mm (1.35 x 2.05 in.), respectively, were prepared. Two test samples were cut from each cast specimen. In addition to these specimens, three cube specimens with dimensions of 50.8 x 50.8 x 50.8 mm (2 x 2 x 2 in.) were prepared from each mixture to determine the chloride content and pH of the pore solution using the pore extraction test. Prior to mixing, NaCl was premixed with the mixing water at the predefined levels.

Cement pastes were prepared following the procedure prescribed by ASTM C305-14. Cement paste mixtures

were mixed in the laboratory under an ambient temperature of 22°C (73°F). To prevent bleeding of the paste mixtures, cement pastes were cast in sealed vials and rotated along their longitudinal axis at 30 rpm for 10 hours. The addition of NaCl retarded the final setting time of CAC pastes. Therefore, the CAC specimens with 0.25% and 1% admixed chloride levels were removed from the vials after 48 hours. OPC and CSA specimens were removed from the vials after 24 hours. All specimens were moist-cured at 22°C (73°F) for 28 days after casting.

At the end of the curing period, specimens were cut into two disc samples with thicknesses of 6 mm (0.24 in.) for carbonation exposure assessment. This disc thickness was selected to ensure that sufficient material was available for chloride testing and to ensure that these discs could be fully carbonated in a reasonable time. Specimens and disc samples were air-dried for 24 hours in the laboratory to remove surface moisture prior to CO<sub>2</sub> exposure.

Disc samples were subjected to accelerated carbonation in an environmental chamber with 20% CO<sub>2</sub>, ±65% relative humidity (RH), and 20°C (68°F). The RH was maintained using saturated salt solution in accordance with ASTM E104-02. The remaining samples from the cut specimens were tightly sealed with plastic wrap and stored in the laboratory (~22°C [73°F]) to prevent carbonation. The carbonated and uncarbonated samples were then ground into

powders passing a No. 20 (850 μm) sieve and evaluated for water-soluble chlorides.

Carbonated samples were tested for water-soluble chloride concentration after the entire depth of the disc was carbonated. The depth of carbonation was determined in accordance with CPC-18 (1988). Disc samples were split along the longitudinal axis to expose the fractured section and sprayed with phenolphthalein solution to confirm complete carbonation.

The pore solution was extracted using the pore extraction method. A cube specimen was removed from curing, sealed with plastic wrap, placed in a sealed plastic bag, and stored in a freezer to inhibit hydration until the extraction of pore solution. In this test, another cube specimen from each mixture was dried to a constant weight in a laboratory oven at 105°C (221°F) to determine the amount of evaporable water. The amount of evaporable water was then used to determine the percentage of free chlorides in the pore solution by the mass of cement. Samples were then crushed for pore solution extraction. The pH of the expressed pore solution was measured within 1 hour after extraction. The pH measurements were performed using a benchtop pH meter with a pH electrode.

## RESULTS AND DISCUSSION

In this study, different cementitious systems were subjected to full carbonation. The time to complete carbonation is shown in Fig. 1. The results indicate that the rate of carbonation for the OPC system is lower than the carbonation rates for the CAC and CSA systems. The results also indicate that the rate of carbonation is influenced by the *w/c* and the  $Cl_{total}$  level. Interestingly, higher admixed chloride concentrations seem to reduce the rate of carbonation. Lower carbonation rates are observed at lower *w/c* values and higher  $Cl_{total}$  levels in all systems. This is because systems with a lower *w/c* have lower porosity values and increased tortuosity. In addition, it has been reported that cementitious systems with higher levels of  $Cl_{total}$  can have higher early-age strengths and lower porosities (Abrams 1924), which could reduce carbonation rates.

Results and discussion from the experimental program will be separated into early-age (pre-carbonated) and later-age (post-carbonated) analyses. A comparison of these results will then be performed to assess the applicability of the test

**Table 1—Background chlorides for different systems**

| Cementitious system | <i>w/c</i> | Background chlorides, % by mass of cement |
|---------------------|------------|---|
| OPC                 | 0.35       | 0.007                                     |
|                     | 0.45       | 0.002                                     |
|                     | 0.55       | 0.008                                     |
| CAC                 | 0.35       | 0.008                                     |
|                     | 0.45       | 0.007                                     |
|                     | 0.55       | 0.006                                     |
| CSA                 | 0.35       | 0.056                                     |
|                     | 0.45       | 0.045                                     |
|                     | 0.55       | 0.026                                     |

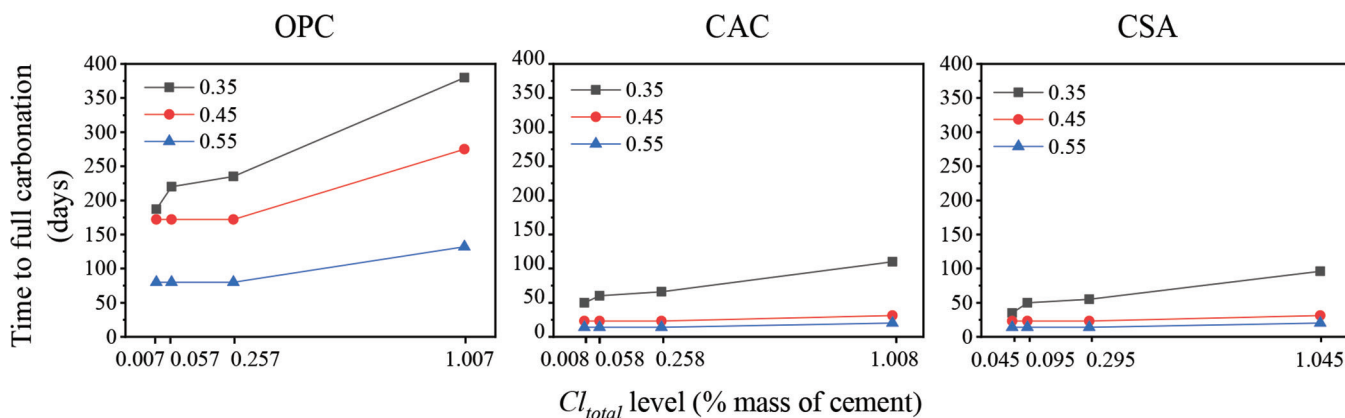


Fig. 1—Time to full carbonation as function of  $Cl_{total}$  level and *w/c* for different cementitious systems.

methods. Linear regression statistical analysis will be used to compare the test results (as percent by mass of cement).

### Chloride testing of uncarbonated specimens

To assess the number of free chlorides in uncarbonated specimens, the chloride concentrations from the pore press method (that is,  $Cl_{pore-uncarb}$ ) and the water-soluble test method before carbonation ( $Cl_{ws-uncarb}$ ) are compared. Figure 2 shows the  $Cl_{pore-uncarb}$  and the  $Cl_{ws-uncarb}$  for the different cementitious systems as a function of the  $w/c$  and  $Cl_{total}$  levels. Here,  $Cl_{pore-uncarb}$  and  $Cl_{ws-uncarb}$  are represented as a percentage of the total chloride concentration ( $Cl_{total}$ ), where  $Cl_{total}$  is the sum of  $Cl_{added}$  and  $Cl_{background}$  in the cementitious samples. Results indicate that the percentages of  $Cl_{pore-uncarb}$  and  $Cl_{ws-uncarb}$  generally increase with increasing  $w/c$  and  $Cl_{total}$  levels for the OPC system. Results also indicate that the percentages of

$Cl_{pore-uncarb}$  and  $Cl_{ws-uncarb}$  generally decrease with an increase in  $w/c$  and  $Cl_{added}$  levels for the CAC and CSA systems. This reduction in chloride concentrations could be attributed to the increased hydration of the mixtures with higher  $w/c$  values. Results indicate that  $Cl_{pore-uncarb} < Cl_{ws-uncarb}$  for all cases. A two-sample  $t$ -test indicates that there is a significant difference between  $Cl_{pore-uncarb}$  and  $Cl_{ws-uncarb}$  for OPC, CAC, and CSA. The two-sample  $t$ -test  $p$ -values at a 0.05 significance level for all systems were less than 0.0001.

The number of bound chlorides released as a result of water-soluble testing,  $Cl_{released-ws\ testing}$ , can be estimated as follows

$$Cl_{released-ws\ testing} = Cl_{ws-uncarb} - Cl_{pore-uncarb} \quad (1)$$

The values of  $Cl_{released-ws\ testing}$  are shown in Fig. 3. The results indicate that the chloride concentrations determined

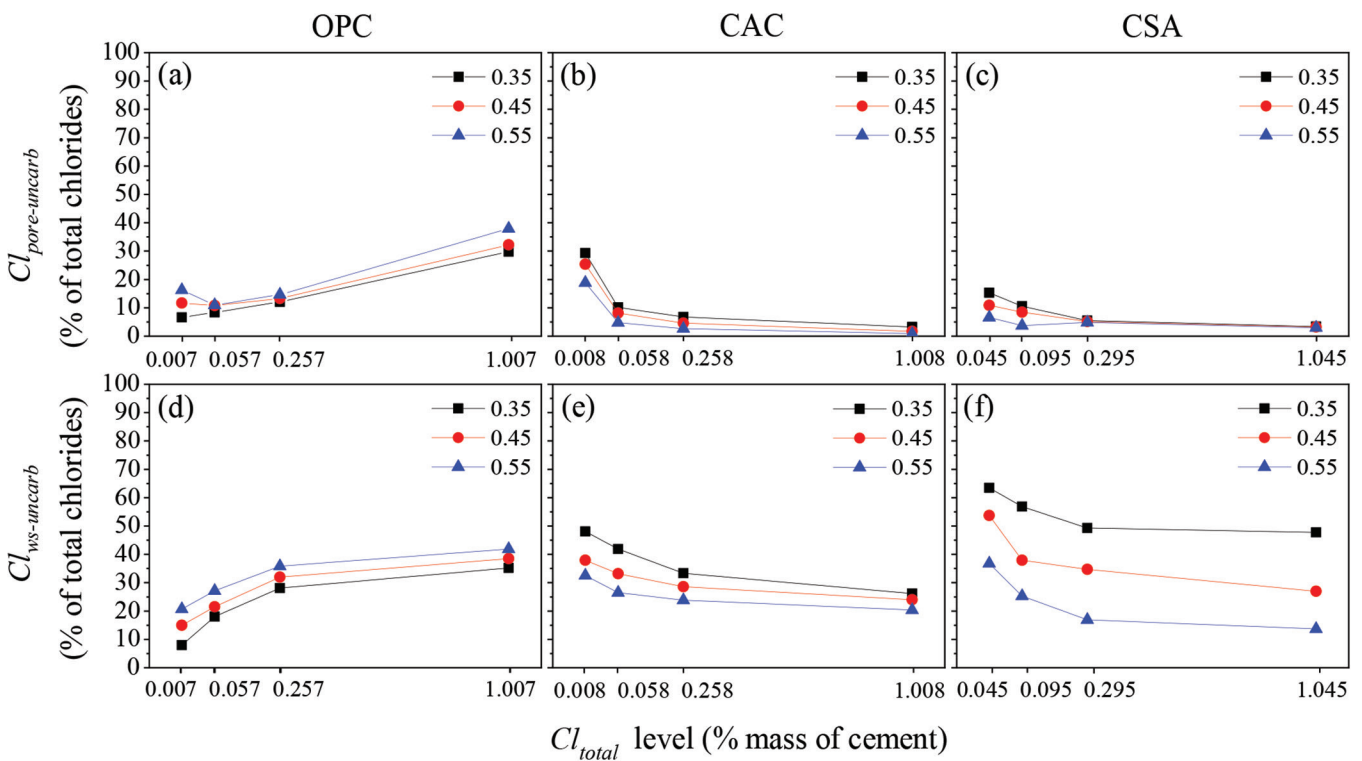


Fig. 2—Comparison of pore solution chlorides ( $Cl_{pore-uncarb}$ ) and water-soluble chlorides ( $Cl_{ws-uncarb}$ ) for different uncarbonated cementitious systems.

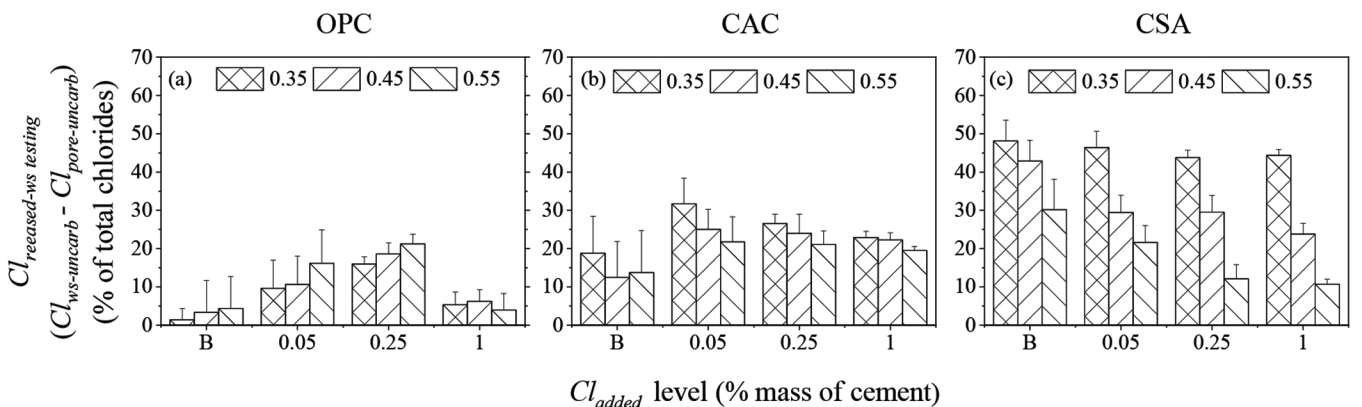


Fig. 3—Amount of bound admixed chlorides released as result of water-soluble testing.

using the water-soluble test are significantly higher than the free chloride results using the pore extraction test. For OPC systems, the water-soluble chloride test results overestimate the free chlorides as measured by pore extraction testing by up to approximately 20% of total admixed chlorides. For the CAC systems, the water-soluble test overestimates the free chlorides by up to approximately 30% of total admixed chlorides, and for CSA systems, the water-soluble chloride test overestimates the free chlorides (as measured with the pore solution extraction) by up to approximately 50%. These results indicate that the water-soluble testing regime extracts more bound chlorides in the CSA and CAC systems when compared to the OPC system. In addition, water-soluble testing overestimates the number of free chlorides, as measured by pore extraction testing, for all systems. Note that the results in Fig. 2 and 3 are shown as a percentage of the total admixed chlorides.

Regression results indicate that  $Cl_{pore-uncarb}$  measurements are on average 86, 7.2, and 7.8% of  $Cl_{ws-uncarb}$  measurements, with 95% upper confidence level values (95% UCL) of 92, 10, and 11% for OPC, CAC, and CSA, respectively. These results are shown in Fig. 4. Note that the regression results are reported here as a percentage by mass of cement and not as a percentage of total admixed chlorides.

To determine how much of the bound chlorides are released as a result of water-soluble testing, the  $\beta$  values from Fig. 4 can be used in Eq. (1) as follows

$$Cl_{released-ws\ testing} = (1 - \beta_A) \times Cl_{ws-uncarb} \quad (2)$$

Using this equation, it is determined that 14, 92, and 93% of the water-soluble chlorides measured using ASTM C1218/C1218M were bound chlorides released as part of the water-soluble test procedure for the OPC, CAC, and CSA cementitious systems, respectively.

In general, results indicate that the number of admixed chlorides that are released from water-soluble chloride testing in CAC and CSA systems are significantly greater than the number of admixed chlorides that are released during water-soluble testing in OPC systems. If the number of admixed chlorides released as a result of carbonation

is less than the number of chlorides released from the water-soluble testing, water-soluble testing is likely sufficiently conservative for assessing admixed chlorides in concrete. The following section presents results on the amount of bound admixed chlorides released because of carbonation.

### Chloride testing of carbonated specimens

After the chloride testing of uncarbonated samples, the number of free chlorides for carbonated OPC, CAC, and CSA systems was assessed using water-soluble testing. The number of chlorides released as a result of carbonation,  $Cl_{released-carb}$ , can be estimated as follows

$$Cl_{released-carb} = Cl_{ws-carb} - Cl_{ws-uncarb} \quad (3)$$

where  $Cl_{ws-carb}$  is the number of water-soluble chlorides for carbonated samples. This difference represents the number of chlorides released as a result of carbonation. Figure 5 shows the  $Cl_{ws-uncarb}$  and  $Cl_{ws-carb}$  values for the OPC, CSA, and CAC cementitious systems for different  $w/c$  and  $Cl_{total}$  levels.

Figure 5(a) shows that the percentage of  $Cl_{ws-uncarb}$  for the OPC mixtures increases slightly with an increase in  $w/c$ . Analysis indicates this increase is not statistically significant. This figure also shows that the percentage of  $Cl_{ws-uncarb}$  increases with increasing  $Cl_{total}$  levels. In general, at lower total chloride concentrations, the binding of these chlorides is expected to be high (in other words, the number of chlorides as measured using water-soluble testing would be expected to be low); as the total chloride concentration increases, the binding capacity of the system is reached and the percentage of binding stabilizes. Lower variability in  $Cl_{ws-uncarb}$  is associated with higher  $Cl_{total}$  concentrations; this is likely a result of testing at lower concentrations. Figure 5(d) shows the  $Cl_{ws-carb}$  values for the OPC samples. The  $Cl_{ws-carb}$  values for the OPC samples are higher than those of the uncarbonated OPC samples, indicating that chlorides are being released due to carbonation. The water-soluble chlorides increase as the  $w/c$  level increases, which is likely a result of increased carbonation of the specimens with higher  $w/c$  values. However, at

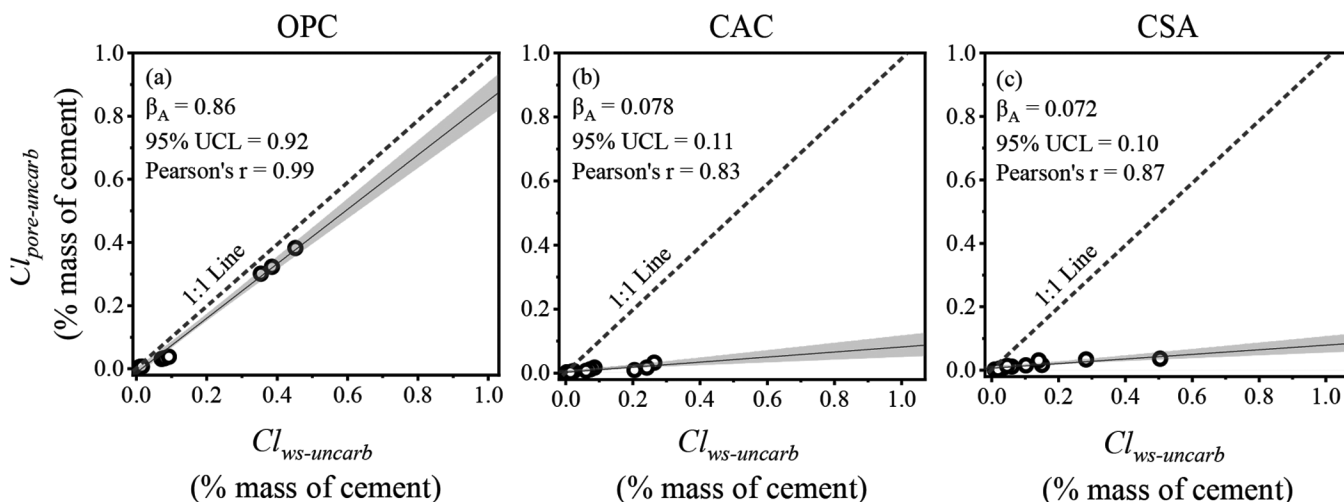


Fig. 4—Relationship between  $Cl_{pore-uncarb}$  and  $Cl_{ws-uncarb}$  for different uncarbonated cementitious systems.

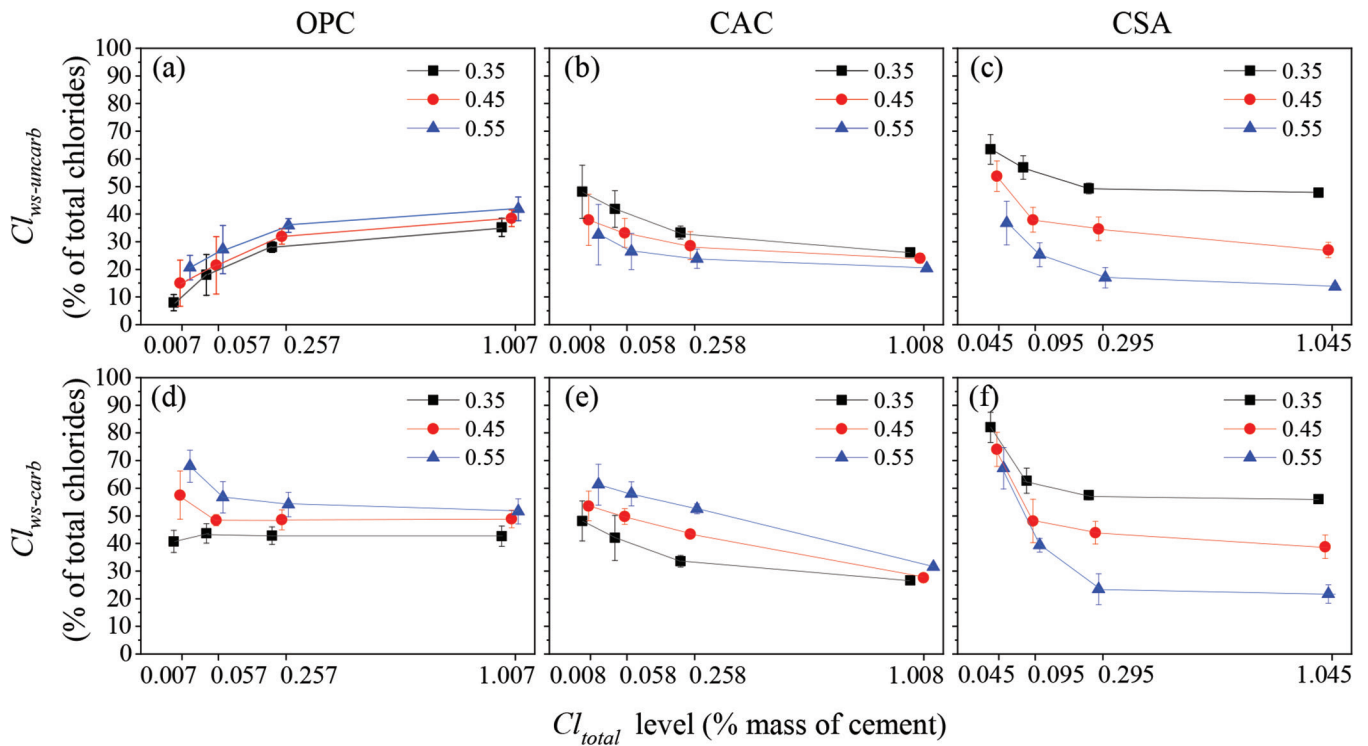


Fig. 5—Comparison of water-soluble chlorides for different uncarbonated and carbonated cementitious systems (values offset to distinguish error bars).

the higher  $Cl_{total}$  levels, the mean  $Cl_{ws-carb}$  changes negligibly, indicating that above some  $w/c$  value, increased carbonation does not occur. The variability in the measured  $Cl_{ws-carb}$  is generally similar for different  $w/c$  and  $Cl_{total}$  levels.

Figure 5(b) shows the  $Cl_{ws-uncarb}$  values for the CAC. Higher  $Cl_{ws-uncarb}$  values are observed at lower  $w/c$ , and the  $Cl_{ws-uncarb}$  decreases with increasing  $Cl_{total}$  levels. The  $Cl_{ws-uncarb}$  values for the CAC specimens exhibit higher variability at lower  $Cl_{total}$  levels and lower variability at higher  $Cl_{total}$  levels. Figure 5(e) shows the  $Cl_{ws-carb}$  values for the CAC. The  $Cl_{ws-carb}$  values do not significantly differ from the  $Cl_{ws-uncarb}$  values for the CAC with a  $w/c$  of 0.35. However, the  $Cl_{ws-carb}$  values for the carbonated CAC are higher than that of the uncarbonated CAC with  $w/c$  values of 0.45 and 0.55. This indicates that the  $w/c$  likely has a significant influence on the release of bound chlorides in CAC systems when exposed to  $CO_2$  and carbonated. In general, at each  $Cl_{total}$  level, the  $Cl_{ws-carb}$  is lower at lower  $w/c$  values. The variability in chloride measurements is higher at the lower  $Cl_{total}$  levels and lower at higher  $Cl_{total}$  levels.

Figure 5(c) shows the measured  $Cl_{ws-uncarb}$  for the CSA specimens. The  $Cl_{ws-uncarb}$  decreases with an increase in  $w/c$  and a decrease in  $Cl_{total}$  levels. The variability in  $Cl_{ws-uncarb}$  measurements for the CSA samples decreases with increasing  $Cl_{total}$  levels. Figure 5(f) shows the  $Cl_{ws-carb}$  for the CSA samples. The  $Cl_{ws-carb}$  values are higher than that of the uncarbonated CSA samples, again indicating that chlorides are released due to carbonation. The  $Cl_{ws-carb}$  percentages of the carbonated CSA samples exhibited similar trends as the  $Cl_{ws-uncarb}$ .

The differences in chloride measurements using the water-soluble testing methods before and after carbonation

indicate that chlorides are being released because of carbonation. The difference between pre- and post-carbonated samples,  $Cl_{released-carb}$ , is shown in Fig. 6 for the different cementitious systems.

Figure 6(a) shows the number of bound chlorides that are released in the OPC system after carbonation. Higher percentages of bound chlorides are released at lower  $Cl_{total}$  levels, and the  $w/c$  influences the release of bound chlorides at these lower  $Cl_{total}$  levels. The mean number of chlorides released after carbonation ranges from approximately 7.5 to 47.3% of the total chlorides.

Figure 6(b) shows the concentrations of bound chlorides that are released after carbonation in the CAC system. The unbinding of chlorides due to carbonation in the CAC system increases with increasing  $w/c$  and is negligible for all  $Cl_{total}$  levels at a  $w/c$  value of 0.35. For the background, 0.05, and 0.25  $Cl_{added}$  levels, approximately 0 to 31.4% of the total chlorides are released because of carbonation. These changes in chloride concentrations are less than the values observed for OPC systems.

Figure 6(c) shows the concentration of bound chlorides released in the CSA system because of complete carbonation. The results indicate that lower amounts of chlorides are released from the CSA system when compared with the OPC system. For the background and 0.05  $Cl_{added}$  levels (that is, the lower  $Cl_{total}$  levels), the change in concentration of chlorides increases at higher  $w/c$  values. For most cases, the change in concentration of released chlorides decreases with increasing  $Cl_{total}$  levels. The  $w/c$  negligibly affects the release of bound chlorides at the 0.25 and 1%  $Cl_{added}$  levels (that is, higher  $Cl_{total}$  levels) for CSA systems. The mean amount of change in chlorides after carbonation ranges from



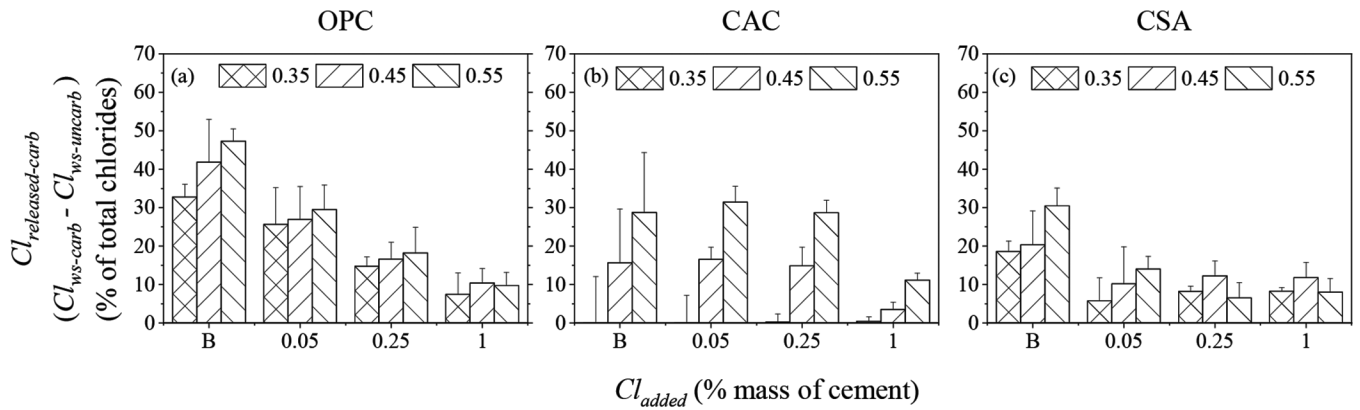


Fig. 6—Amount of bound chlorides released as result of carbonation.

approximately 5.8 to 30.4% of the total chlorides. Note that these changes in values are lower than the changes observed in the OPC system.

Linear regression can be performed to investigate the relationship between  $Cl_{ws-uncarb}$  and  $Cl_{ws-carb}$  for the different cementitious systems. This regression output is shown in Fig. 7 and indicates that  $Cl_{ws-uncarb}$  and  $Cl_{ws-carb}$  are strongly and positively correlated. This relationship is confirmed by the Pearson correlation coefficient of 0.99 for OPC and CSA, and 0.96 for CAC.  $Cl_{ws-uncarb}$  provided  $\beta$  coefficients with 95% UCL of 0.85 and 0.88 for OPC, 0.8 and 0.96 for CAC, and 0.81 and 0.87 for CSA. Regression analysis results are reported by percent mass of cement because the published allowable chloride limits are reported using these units.

The relationship between the concentration of water-soluble chlorides before and after carbonation indicates that bound chlorides, likely tighter-bound chlorides, can be released and become unbound in the pore solution because of complete carbonation. Thus, carbonation increases the number of free chlorides in the cementitious system. In addition,  $w/c$  and  $Cl_{total}$  levels influence the measured water-soluble chloride values after carbonation. In general, Fig. 7 indicates that the  $Cl_{ws-carb}$  measurements are, on average, 15, 20, and 19% higher than the  $Cl_{ws-uncarb}$  results (that is,  $\% \Delta Cl_{ws-carb} = ((1/\beta) - 1) \times 100$ ) for the OPC, CAC, and CSA, respectively. This indicates that 15, 20, and 19% of the bound chlorides for the different cementitious systems can be released because of carbonation.

### Selecting appropriate chloride test

As already noted, both ASTM C1218/C1218M (water-soluble chloride testing) and ASTM C1152/C1152M (acid-soluble chloride testing) are allowed to assess chloride concentrations of concrete in ACI documents. It is argued that acid-soluble chloride testing is likely the more appropriate test because chlorides can be released at later ages because of carbonation, and that water-soluble testing may underestimate the number of chlorides released as a result of carbonation. Limited research has been performed to assess how much of the bound admixed chlorides are released during water-soluble chloride testing and how much of the bound chlorides are released because of carbonation. The objective of this research is to quantify these chloride releases for different cementitious systems to determine if water-soluble

testing is sufficiently conservative. ACI documents assume that water-soluble chlorides are approximately 75 to 80% of the acid-soluble chlorides. However, Trejo et al. (2019) reported that the range published in ACI 222R-01 was in most cases incorrect for admixed chlorides. Because of this, only one test should be specified in ACI documents.

This research generated data on how much of the bound admixed chlorides are released because of water-soluble testing ( $Cl_{released-ws}$ ) and how much of the admixed chlorides are released when specimens are completely carbonated ( $Cl_{ws-carb}$ ). The number of admixed chlorides released as part of the water-soluble testing (ASTM C1218/C1218M) was determined to be 14, 92, and 93% of the water-soluble results ( $Cl_{ws-uncarb}$ ) for the OPC, CAC, and CSA cementitious systems, respectively. The number of admixed chlorides released because of carbonation (not testing) was determined to be 15, 20, and 19% of the water-soluble test results ( $Cl_{ws-uncarb}$ ) for the OPC, CAC, and CSA cementitious systems, respectively.

If the amount of bound admixed chlorides that are released because of water-soluble testing extraction is greater than the amount of bound admixed chlorides released as a result of carbonation, then it could be concluded that water-soluble testing is sufficiently conservative and can account for the release of bound chlorides as a result of carbonation. Alternatively, if the ratio of these variables is greater than unity—that is, if

$$\frac{Cl_{released-ws}}{Cl_{released-carb}} > 1 \quad (4)$$

then the water-soluble test method following ASTM C1218/C1218M could be considered sufficiently conservative.

Using Eq. (1) and (3) and substituting these into Eq. (4) provides the following

$$\frac{Cl_{ws-uncarb} - Cl_{pore-uncarb}}{Cl_{ws-carb} - Cl_{ws-uncarb}} - 1 > 0 \quad (5)$$

From the chloride testing of uncarbonated samples, regression results indicate a significant relationship between  $Cl_{pore-uncarb}$  and  $Cl_{ws-uncarb}$  values for OPC, CAC, and CSA ( $p$ -value < 0.001). The relationship between  $Cl_{pore-uncarb}$  and  $Cl_{ws-uncarb}$  values for different  $w/c$  values and  $Cl_{total}$  levels can be represented by

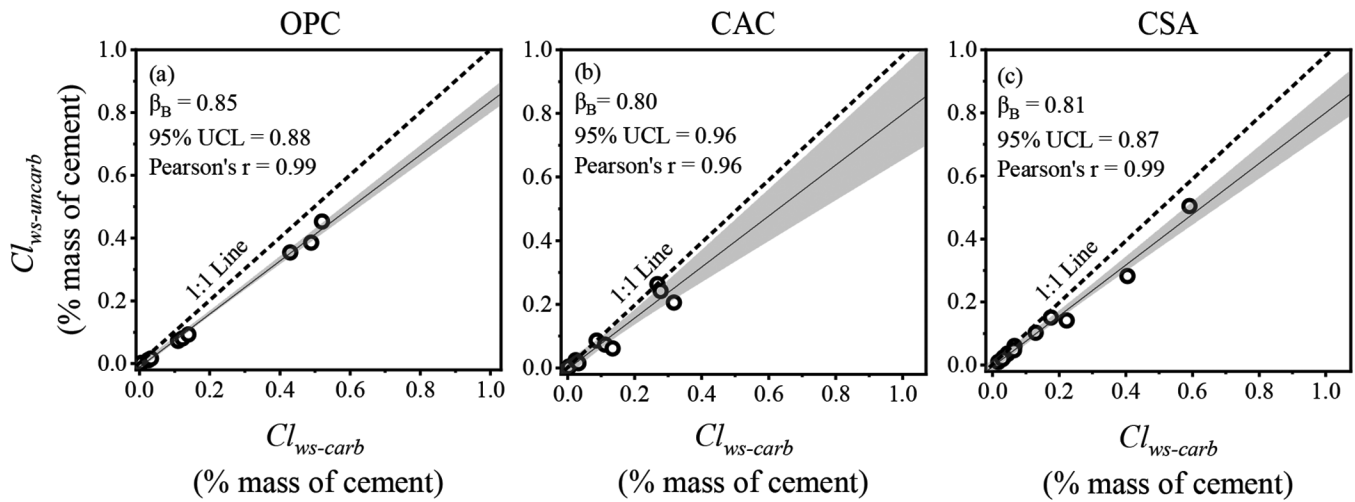


Fig. 7—Relationship between uncarbonated and carbonated water-soluble chloride results for different cementitious systems.

$$Cl_{\text{pore-uncarb}} = \beta_A \times Cl_{\text{ws-uncarb}} \quad (6)$$

From the testing of carbonated samples, regression results indicate a significant relationship between  $Cl_{\text{ws-uncarb}}$  and  $Cl_{\text{ws-carb}}$  values for all cementitious systems at varying  $w/c$  values and  $Cl_{\text{total}}$  levels ( $p$ -value < 0.001). This relationship is represented by

$$Cl_{\text{ws-uncarb}} = \beta_B \times Cl_{\text{ws-carb}} \quad (7)$$

Equation (7) can also be written as follows

$$Cl_{\text{ws-carb}} = \frac{Cl_{\text{ws-uncarb}}}{\beta_B} \quad (8)$$

Substituting Eq. (6) and (8) into Eq. (5) gives

$$\frac{Cl_{\text{ws-uncarb}} - (\beta_A \times Cl_{\text{ws-uncarb}})}{\frac{Cl_{\text{ws-uncarb}}}{\beta_B} - Cl_{\text{ws-uncarb}}} - 1 > 0 \quad (9)$$

and simplifying Eq. (9) gives

$$\frac{(1 - \beta_A)}{\left(\frac{1}{\beta_B} - 1\right)} - 1 > 0 \quad (10)$$

The left part of the equation can be referred to as a measure of the conservativeness of the water-soluble test method for assessing later-age free chlorides and will be referred to here as the conservative factor for the water-soluble test method,  $CF_{\text{ws}}$ . Table 2 shows the values of  $\beta_A$ ,  $\beta_B$ , and  $CF_{\text{ws}}$ .

These results indicate that the  $CF_{\text{ws}}$  value for OPC is less than zero and would be considered unconservative for most admixed chloride levels. However, the largest difference between the chlorides released because of carbonation and testing was for the background conditions, where the release of chlorides due to carbonation only exceeded the release of chlorides due to testing for the two lower chloride concentrations. The  $CF_{\text{ws}}$  values for both CAC and CSA are significantly greater than zero and thus water-soluble testing

would be considered very conservative for both systems. It should be noted that specimens in this research project were completely carbonated to pH levels less than 9, which is considered severe. Although the  $CF_{\text{ws}}$  for OPC is less than zero, the severity of the test condition in this research likely makes this value slightly negative.

## SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

The study determined that water-soluble testing, following ASTM C1218/C1218M, extracts some bound chlorides. The results indicate that 14, 92, and 93% of the water-soluble chlorides are likely bound chlorides in the ordinary portland cement (OPC), calcium aluminate cement (CAC), and calcium sulfoaluminate cement (CSA) systems, respectively. This research also assessed how much chlorides are released because of complete carbonation of the cementitious systems. The results indicate that 15, 20, and 19% of the bound admixed chlorides in the OPC, CAC, and CSA systems can be released because of carbonation.

This research also assessed whether the water-soluble test is sufficiently conservative to assess later-age free chloride concentrations in OPC, CAC, and CSA systems after carbonation. The number of chlorides released because of carbonation in the OPC system was determined to be greater than the number of chlorides released as part of the ASTM water-soluble test method. This indicates that the water-soluble test may not be sufficiently conservative to estimate later-age free chlorides. However, because the samples were completely carbonated and this occurred mostly at lower admixed chloride concentrations, the water-soluble test method following ASTM C1218/C1218M can be sufficiently conservative. This indicates that water-soluble testing likely not only assesses “immediate” risks of corrosion, but also is sufficient to assess the “overall” risk of corrosion. Testing indicates that ASTM C1218/C1218M is sufficiently conservative to allow for the chlorides released due to carbonation in CAC and CSA systems; the amount of bound admixed chlorides released because of testing is significantly greater than the amount of bound admixed chlorides released because of complete carbonation.

**Table 2—Values of  $\beta_A$ ,  $\beta_B$ , and  $CF_{ws-test}$** 

| Cementitious system | $\beta_A$ | $\beta_B$ | $CF_{ws}$ |
|---------------------|-----------|-----------|-----------|
| OPC                 | 0.86      | 0.85      | -0.21     |
| CAC                 | 0.078     | 0.80      | 2.69      |
| CSA                 | 0.072     | 0.81      | 2.96      |

The findings of this research result in the following recommendations:

1. For OPC systems, there is a small risk that the amount of bound admixed chlorides released because of carbonation may exceed the amount of bound admixed chlorides released because of the ASTM water-soluble testing protocol. However, because past research has shown little correlation between the ASTM water-soluble and acid-soluble test results (Trejo et al. 2019) and the water-soluble testing accounts for chloride binding within the different systems, the authors believe the risk is relatively small and water-soluble testing following ASTM C1218/C1218M should be required in the ACI documents that specify allowable chlorides.

2. For the CAC and CSA systems assessed in this research, it is determined that ASTM C1218/C1218M is sufficiently conservative and the amount of bound admixed chlorides released as part of the ASTM test protocol significantly exceeds the amount of admixed bound chlorides released because of complete carbonation. This is an important finding as Ahmed and Trejo (2020) reported that acid-soluble testing following ASTM C1152 results in the formation of a gel-like structure in the test solution which likely binds chlorides. This binding of chlorides in the acid-soluble testing can result in an underestimation of total chlorides. In the same context, Ahmed and Vaddey (2021) reported that the concentration of acid-soluble chlorides in fully carbonated OPC, CAC, and CSA paste samples is lower than the concentration of acid-soluble chlorides in uncarbonated paste samples; this indicates some binding of acid-soluble chlorides after carbonation.

3. Three findings suggest that water-soluble testing should be the required testing for background chlorides in concrete as a result of the following: i) there is a lack of correlation between water-soluble and acid-soluble test results and binding varies significantly; ii) the challenges associated with acid-soluble testing of CAC and CSA systems; and iii) the results from this research indicate that the ASTM C1218/C1218M test procedure (water-soluble chloride testing) will in most cases be sufficiently conservative for assessing free chlorides at later ages.

Based on these findings, the authors recommend that ACI documents specify only water-soluble testing for assessing admixed chlorides. If the ASTM standard could be modified to extract slightly more of the bound admixed chlorides (for example, longer boiling time), the test standard may be sufficiently conservative for all cementitious types evaluated in this research.

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