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RELATIONSHIPS BETWEEN FREE AND WATER-SOLUBLE CHLORIDE CONCENTRATIONS IN CONCRETE

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Abstract: Corrosion of metals embedded in concrete is pivotal when studying durability of reinforced concrete structures. Chloride ions present in the vicinity of steel reinforcements tend to initiate and/or accelerate their corrosion. Chloride ions are either bound physically or chemically to the cementing material or free in the pore solution, and only the latter can be transported. Free chloride concentration C_f was measured by pore solution expression method however it is found to be very difficult in low water to cement ratios. Water extraction method is used to measure water-soluble chloride concentration C_w in concrete. However, the results are found to be highly dependent on liquid to solid ratio, temperature, size of particles, and extraction method. The aim of this study is to experimentally evaluate current standard test method for acid-soluble chloride (ASTM C1152-04 (2012a)) and water-soluble chloride (ASTM C1218-15 (2017)) in mortar and concrete, and the relationships between C_w and C_f . Six concrete mixes containing Portland-limestone (CSA type GUL) cement with and without supplementary cementing materials including silica fume or ground granulated blast-furnace slag were subjected to a non-steady state migration experiment. The acid-soluble and water-soluble chloride concentrations at different depths within the sample were determined at 84 days. Freundlich isotherm was employed along with total chloride concentration data to determine the concentration of free chloride C_f values. Linear relationship between C_w and C_f was observed with a significant dependency on the binder composition. Measurements of water-soluble chloride concentration are not equivalent to free chloride concentration.

1 INTRODUCTION

In studying durability of reinforced concrete structures exposed to marine environments or de-icing salts, the entry of chloride ions into concrete and corrosion of embedded metals is known to be one of the major deterioration modes (Basheer, Chidiac, and Long 1996, Shi et al. 2012). Chloride ions enter the concrete surface by capillary action or diffusion depending on the degree of saturation and then diffuse inside the concrete core. The total concentration of chlorides in concrete consists of free chlorides that are dissolved in the pore solution and bound chlorides which are either physically adsorbed to calcium hydrate silicate (CSH) or chemically reacted with various hydration products of cementing materials (Ishida, Miyahara, and Maruya 2008, Florea and Brouwers 2012). Only the free chlorides are free to diffuse through the pore solution and are the culprit behind the initiation and propagation of corrosion. Bound chlorides can significantly delay chloride penetration process and add to the resistance of concrete to the chloride attack (Saillio, Baroghel-Bouny, and Barberon 2014, Thomas et al. 2012, Ishida, Miyahara, and Maruya 2008). Pore solution expression method proposed by Barneyback and Diamond (1981) is known to be the most accurate and common method for measuring the free chloride content. However, this method is found to be difficult to use when dealing with low water to cement ratios as it is found impossible to extract pore solution from thin layers of concrete (Yuan 2009). As such, the water extraction method which measures

the chloride water-soluble concentration in concrete has become the recommended method. In studying the relationship between free and total chloride contents in concrete, Mohammed and Hamada (2003) defined the free chloride as water-soluble concentration. However, the results from water extraction method are found to yield higher chloride ions concentration in comparison to pore solution (Yuan 2009, Otsuki, Nagataki, and Nakashita 1993, Ishida, Miyahara, and Maruya 2008, Haque and Kayyali 1995). Moreover, different relationships and proportionality coefficients were reported, indicating that some of the physically bound chloride ions can be released by water extraction method. It should be noted that the results of water extraction method are found to be highly dependent on testing parameters such as liquid to solid ratio, temperature, size of particles, and extraction method (Yuan 2009, Pavlík 2000), hence it is necessary to follow a standard test method. ASTM C1152-04 (2012a) and ASTM C1218-15 (2017) are current standard test methods for determination of acid-soluble chloride ions (total chloride content) and water-soluble chloride ions in mortar and concrete, respectively. This study aims to experimentally evaluate the relationships between C_w and C_f . Toward this objective, six concrete mixes containing Portland-limestone (CSA type GUL) cement with and without supplementary cementing materials (SCM) including silica fume (SF) or ground granulated blast-furnace slag (GGBFS) were prepared and subjected to a non-steady state migration experiment. The acid-soluble and water-soluble chloride concentrations at different depths within the sample were determined at 84 days. The results were used to investigate the relationship between free and bound chloride concentrations.

2 Experimental program

Concrete mixes were designed with three variables, namely GGBFS and SF cement replacement levels and water to cementing material ratio (w/cm). Total cementing content is 450 kg/m³ with GGBFS and SF cement replacement level of 0% to 30% and 0% to 8%, respectively. Water to cementing material ratio ranges from 0.32 to 0.40. High-range water-reducing admixture (HRWRA) and viscosity modifying admixture (VMA) were added to the mixtures. The concrete mixture proportions are summarized in Table 1. Three samples per concrete mix were cast and tested.

Table 1: Concrete mixture proportions

Mix #	w/cm	cm [kg/m ³]	cm composition [%wt cm]			V_a [m ³ /m ³]
			GUL	SF	GGBFS	
1	0.32	450	100	0	0	0.65
2	0.32	450	70	0	30	0.65
3	0.32	450	92	8	0	0.65
4	0.40	450	100	0	0	0.62
5	0.40	450	70	0	30	0.61
6	0.40	450	92	8	0	0.61

2.1 Materials

The chemical and physical properties of cementing materials used for this study are summarized in Table 2. The Portland-limestone (CSA type GUL) cement and GGBFS were supplied by LafargeHolcim in Canada, and SF by BASF (BASF 2014b). The chemical admixtures used in this study, HRWRA Glenium© 7700 (BASF 2014a) and VMA MasterMatrix© VMA 362 (BASF 2014c), were provided by BASF. As for the coarse aggregate, the nominal maximum aggregate size, specific gravity, bulk density and absorption are 14 mm, 2.74, 1544 kg/m³, and 1.58%, respectively. The fineness modulus, specific gravity, bulk density, and absorption of fine aggregate are 2.71, 1746 kg/m³, 2.88, and 1.28%, respectively. The bulk density, specific gravity, and absorption of coarse and fine aggregate were determined in accordance with ASTM C127-15 (ASTM 2015a) and ASTM C128-15 (ASTM 2015b), respectively.

Table 2: Chemical and physical properties of cementing materials

Oxides / Compounds	Composition [wt%]		
	GUL	GGBFS	SF
CaO	61.3	36.9	
SiO ₂	18.0	36.2	> 85
Al ₂ O ₃	4.4	10.4	
Fe ₂ O ₃	2.8	0.6	
MgO	2.9	11.9	
K ₂ O	0.5	0.5	
Na ₂ O	0.2	0.4	
Na ₂ O _{eq}	0.6	0.8	
SO ₃	3.6	2.7	
TiO ₂	0.3	1.1	
MnO	2.9	0.5	
Free CaO	1.1		
Limestone	11.5		
Loss on Ignition	5.5	0.8	< 3.0
Total	96.8	101.2	
C ₃ S	47		
C ₂ S	16		
C ₃ A	7		
C ₄ AF	8		
Blaine [m ² /kg]	468	475	
Specific gravity	3.15	2.92	2.20

2.2 Mixing, placement and curing procedure

The concrete mixes were prepared, placed and consolidated by employing a consistent procedure and using a vertical-axis pan mixer. The materials used in each mixture were proportioned and stored in the laboratory at 20±2 °C for 24 hours. For each concrete mix, three cylinders with 100 mm diameter by 50 mm high, were cast following the procedure described in ASTM C1758-15 (ASTM 2015c). The cylinders were sealed and stored at a temperature of 20±2 °C for 24 hours before being de-moulded and cured in saturated limewater at 22±2 °C for 84 days.

2.3 Testing procedure

At the age of 84 days, in order to determine the chloride diffusion coefficient of concrete samples, a non-steady state migration test was implemented using three 50 mm cylinders for each mix. The migration test configuration follows that of ASTM C1202-12 (ASTM 2012b). First, concrete samples were removed from limewater, the surfaces were towel dried and the dimensions of the samples were measured and recorded. Then, electrical tape was used to seal the side surface of each cylinder. The solutions used to fill the upstream and downstream cells were 3% NaCl and 0.3 N NaOH solutions, respectively. The applied voltage and duration of the test for each mix were determined based on NT Build 492 (NT-BUILD 1999) procedure. Current passing through the sample and temperature of the downstream were monitored during the test to ensure that the sample was appropriately sealed (van Noort, Hunger, and Spiesz 2016) and to check that the temperature did not change.

After the migration test was completed, the samples were flushed under running water then towel dried. Then, the concrete specimens were ground in layers of 3 to 4 mm parallel to the exposure surface, using

Profile Grinder 1100. The collected powder was used to determine both acid-soluble (total) and water-soluble chloride content of concrete at different depths by means of potentiometric titration (Metrohm 836 Tirando) and in accordance with ASTM C1152-04 (ASTM 2012a) and ASTM C1218-15 (ASTM 2017), respectively. Additionally, the volume of water-accessible porosity and density of the concrete samples were determined in accordance with ASTM C642-13 (ASTM 2013).

The analyses of the migration test results followed the model proposed by Spiesz et al. (2012). The corresponding Equations, Eqs 1 to 3, were used to first determine the concrete chloride diffusion coefficient and subsequently for determining the free chloride profile.

$$[1] \varphi \frac{\partial c}{\partial t} + (z F U) / (R T L) D_{Cl} \frac{\partial c}{\partial x} = -k [c - (C_b / K_b)^{1/n}]$$

$$[2] (1 - \varphi) \rho_s \frac{\partial C_b}{\partial t} = k [c - (C_b / K_b)^{1/n}]$$

$$[3] C_t = [\varphi c + (1 - \varphi) \rho_s C_b] / \rho_c$$

where C_b is the concentration of bound chloride, K_b and n are empirical coefficients known as chloride binding capacity and binding intensity for Freundlich binding isotherm, k is the chloride mass transfer coefficient, φ is water-accessible porosity of concrete, and ρ_c and ρ_s are density of liquid-saturated concrete and density of solid state in concrete, respectively. The model accounts for non-linear binding isotherm by employing Freundlich isotherm which is experimentally shown to be accurate for chloride concentrations between 0.01 to 1 M (Tang 1996). Moreover, the non-equilibrium condition between free and bound chloride concentrations for migration test (Tang 1996, Spiesz, Ballari, and Brouwers 2012) is accounted for by introducing the binding rate k . The chloride diffusion coefficients were determined by fitting the numerical solution of Eqs. 1-3 to the experimental total chloride concentration profiles. Subsequently, the free chloride concentration profiles were determined.

3 Experimental results and discussion

Table 3 summarizes the mixes' mean and the coefficient of variance COV values for water-accessible porosity and density. The mean and COV values of effective chloride diffusion coefficient and binding parameters, including binding capacity and binding intensity, are given in Table 4. The coefficients of determination (R^2) for fitting Eqs. 1-3 to the measured chloride concentration profiles were found to be between 0.92 and 1.00. Moreover, the maximum COV values for water-accessible porosity, density, chloride diffusivity and binding parameters are respectively 4.5%, 0.3%, 5.7%, and 7.4%, which reveals good precisions and comparable to those reported in the literature and standards (ASTM 2016, NT-BUILD 1999, Tang and Sørensen 2001).

Table 3: Water-accessible porosity and density at 84 days

Mix #	Air void		Density	
	Mean [%]	COV [%]	Mean [kg/m ³]	COV [%]
1	12.5	1.4	2543	0.1
2	12.0	4.2	2470	0.2
3	12.8	3.1	2406	0.2
4	15.6	1.5	2250	0.1
5	15.5	4.4	2217	0.3
6	15.6	4.5	2144	0.3

Table 4: Chloride diffusion coefficient, binding capacity and binding intensity at 84 days

Mix #	D_{Cl}		K_b		n	
	Mean [$\times 10^{-12}m^2/s$]	COV [%]	Mean [$\times 10^{-3}dm^{3n}/g^n$]	COV [%]	Mean [-]	COV [%]
1	1.67	3.3	0.58	4.3	0.30	0.0
2	0.93	1.5	0.75	0.6	0.59	3.2
3	0.57	5.1	0.55	2.6	0.55	7.4
4	3.22	1.1	0.60	0.8	0.46	2.2
5	1.47	0.6	0.86	6.8	0.48	2.6
6	0.91	5.7	0.62	2.0	0.55	3.8

Experimental results show that at a constant water to cement ratio, the mix without SCM had the highest chloride diffusivity, followed by mixes containing GGBFS and SF, respectively. Decrease in transport properties of concrete is attributed to the refinement of pore structure of concrete due to pozzolanic reaction of SCMs. Furthermore, from Tables 3 and 4 one can observe that both water-accessible porosity and chloride diffusion coefficient of concrete decrease with decrease of w/cm ratio for mixes having the same cementing material composition. The chemical composition of cementing materials, more specifically C_3A and GGBFS contents due to high alumina content (Dhir, El-Mohr, and Dyer 1997), is known to significantly affect the binding capacity of cement pastes (Zibara 2001, Loser et al. 2010, Yuan et al. 2009). One can observe that binding capacity of concrete mixes increases significantly in presence of GGBFS, while SF with 8% cement replacement level does not have significant effect on K_b . In the literature, a slight decrease in K_b is reported as a result of presence of SF, which can be attributed to either lower binding capacity of CSH with lower Ca/Si ratio (Beaudoin, Ramachandran, and Feldman 1990), or to the reduction of pH of pore solution and decrease of C_3A content of cementing materials (Yuan et al. 2009). Moreover, by comparing two mixtures with the same cementing material composition, it can be seen that K_b increases with increase of w/cm, which can be attributed to higher amount of CSH formed. The observed trends and values for chloride diffusion coefficient D_{Cl} and binding capacity K_b are consistent with the literature (Delagrave et al. 1997, Frederiksen et al. 1997, Oh and Jang 2004, Tang 1996, Yang and Wang 2004, Youm et al. 2016). It should be noted that in order to compare K_b values of cement paste with those of mortar and concrete, it should be normalized to the volume fraction of paste to remove the effect of aggregates.

The free chloride concentrations at each layer were calculated by using Eqs. 1-3 along with measured total (acid-soluble) chloride concentration profiles. Figure 1 shows the free chloride versus water-soluble chloride concentrations at different depths for each mix, which reveals a linear relationship between C_w and C_f values with a coefficient of determination (R^2) higher than 0.95 except for one mix. The proportionality coefficient for mixes in this study ranges between 1.43 to 2.81. From Figure 1, one can observe that at a constant water to cement ratio, the lowest proportionality coefficient corresponds to the mix without SCM, while the mix containing GGBFS had the highest coefficient. Moreover, experimental results show that for mixes without SCM and mixes containing SF the proportionality coefficient increases with increase of water to cement ratio (see Figures 1a, 1c, 1d, and 1f), while the inverse is true for mixes containing GGBFS. Furthermore, one observes that for mixes without SCM and mixes containing SF, the proportionality coefficient increases with increase of binding capacity. For the mixes without SCM, the increase of K_b is attributed to the increase of CSH content which adds to the physical binding capacity. Also, for mixes containing SF, while decrease of C_3A leads to decrease of chemical binding capacity, it is compensated for by increase of CSH content which adds to the physical binding capacity. Therefore, for both cases, the proportionality coefficient is increased with increase of binding capacity of the mixture. On the other hand, for the mixes containing GGBFS, the increase of binding capacity is attributed to the high alumina content and adds to the chemical binding capacity. Therefore, the proportionality coefficient decreases with increase of K_b in mixes containing GGBFS.

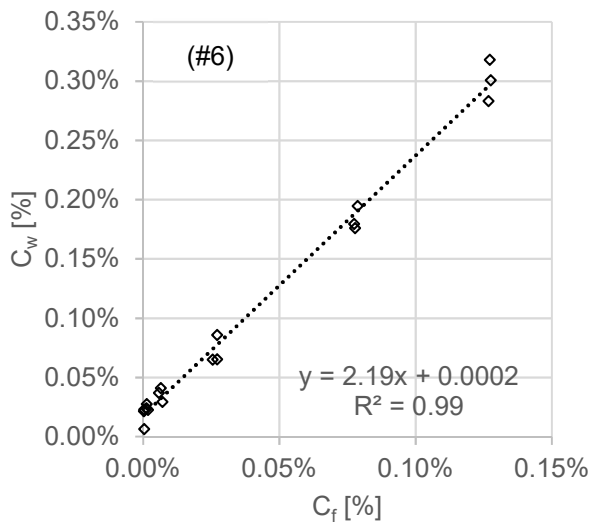
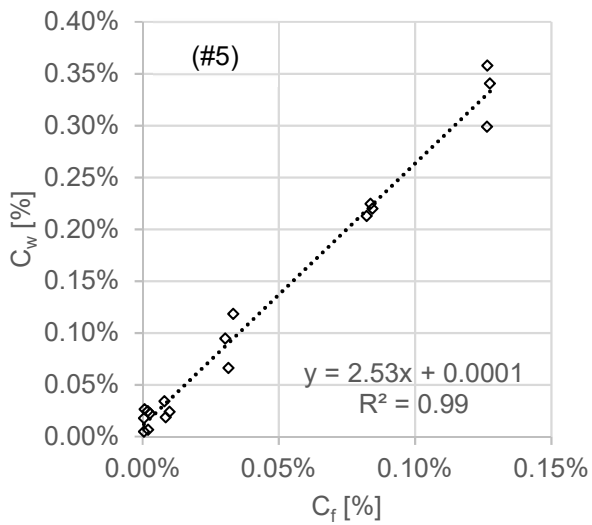
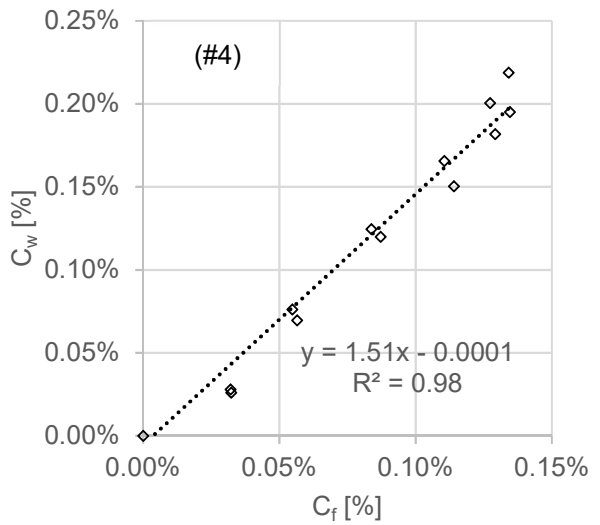
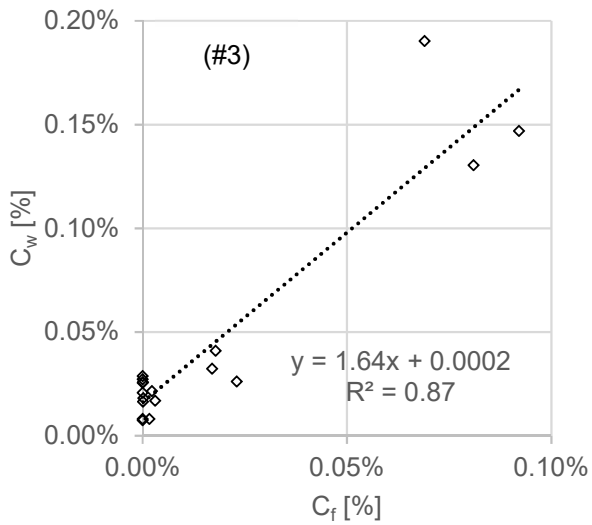
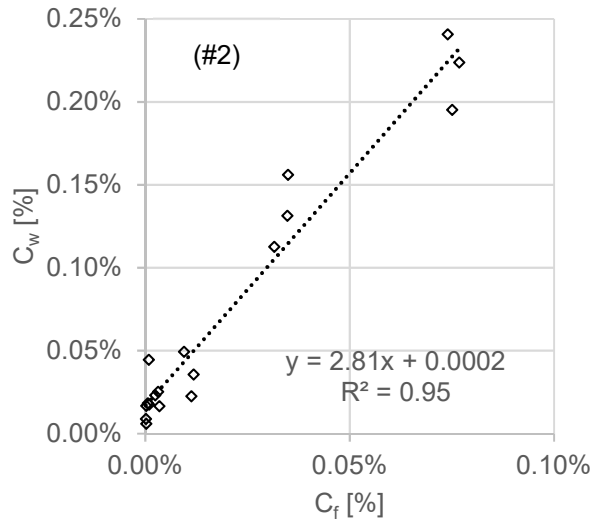
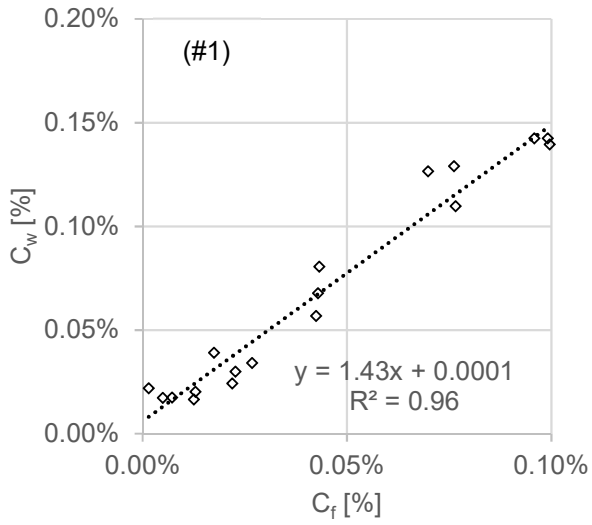


Figure 1: Free VS water-soluble chloride concentrations in concrete mixes #1 to #6

The percent differences between the free chloride concentrations and water-soluble chloride concentrations were calculated and found to have a minimum value of 40% and a maximum value greater than 300%. These results and those shown in Fig. 1 clearly indicate that measurements of water-soluble chloride concentration are not equivalent to free chloride concentration. Additional steps as described in this paper are necessary for determining the values of free chloride concentrations using measurements of water-soluble chloride concentrations.

4 Conclusions

The following conclusions can be drawn from this study:

- Water extraction method which measures the water-soluble chloride concentration in concrete, releases a part of physically bound chloride, and therefore, gives higher values compared with free chloride content.
- Water-soluble and free chloride concentrations are linearly proportional, with proportionality coefficient depending on composition and chemical properties of binder.
- At a constant w/cm ratio, mixes without SCM have the lowest proportionality coefficient, while mixes containing GGBFS have the highest proportionality coefficient.
- For mixes without SCM and mixes containing SF, the proportionality coefficient increases with increase of w/cm ratio, while the inverse is true for mixes containing GGBFS.
- For mixes without SCM and mixes containing SF, the proportionality coefficient increases with increase of binding capacity K_b , while the inverse is true for mixes containing GGBFS.
- Measurements of water-soluble chloride concentration are not equivalent to free chloride concentration.

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