

Analysis of the Impact of Deicing Salts on Transport Properties of Concrete – Preliminary Results

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ABSTRACT

The ingress of deicing chemical solutions into the pore system of hardened concrete can profoundly affect its physical and chemical properties. It is a known fact that salt solutions are highly conductive in comparison with pure water and as a result when they penetrate into concrete they alter its electrical resistivity as well as other transport properties. In this study, the influence of three deicing salts on transport properties measured in four different ways: (1) surface resistivity (SR), (2) rapid chloride permeability (RCPT), (3) sorptivity, and (4) apparent chloride diffusion, of specimens exposed to sodium chloride, calcium chloride, and magnesium chloride is investigated. The feasibility of using these test methods to evaluate in service structures is discussed. It was observed that transport properties, measured by the several test methods, appear to be influenced by different factors when in presence of salts. There is a correlation between SR and RCPT, but in these preliminary results there is no good correlation between the other tests.

INTRODUCTION

It is well documented that deicing chemicals such as sodium, potassium and magnesium chloride can inflict significant damage to concrete pavements and structures reducing their durability and performance. Nevertheless, the application of deicing salts cannot be eliminated for safety reasons, despite the fact that they are one of the main sources of concrete deterioration through scaling, spalling, physical and chemical salt attack, and the corrosion of embedded steel.

Depending on the environmental conditions, concrete structures can be subjected to simultaneous mechanisms of chloride ingress: capillary absorption, diffusion in pores and cracks, and permeation under hydraulic pressure, complicating the understanding and evaluation of transport properties in concrete. For example, since concrete is rarely fully saturated, pure diffusion is unlikely to be the only mechanism responsible for chloride ingress; instead, the non-uniform distribution of moisture is likely to cause capillary absorption, and in some cases ingress under pressure. The synergetic effect of diffusion and absorption leads to a much faster chloride penetration¹.

Coring structures in order to assess condition, chloride profile, and then estimating remaining service life is a common practice. Test results from cores are then used as inputs in available models, nevertheless, most service life models were developed using inputs obtained in the laboratory. It has been shown that

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chloride profiles from field cores, as well as absorption, may differ significantly from similar mixtures prepared in the laboratory, due to field condition and the exposure history^{2,3}.

Since apparent diffusion coefficient is the most popular input in service life models, several models have been developed over the years to correlate electrical measurements to apparent diffusion coefficient but it is still not clear if they are applicable to concrete with prior exposure to deicing salts.

RESEARCH SIGNIFICANCE

This study aims to evaluate the combined effect of diffusion and absorption on transport properties of concrete samples exposed to one of these common deicing salts (NaCl, CaCl₂ or MgCl₂), as well as limewater and assess if there is any correlation between absorption, conductivity and diffusion. Testing will be conducted after 28 days, 90 days, 6 months and 1 year of exposure. Results presented herein are preliminary, for 28 and 90 days exposure. Longer exposure testing is still underway.

MATERIALS AND TESTING

Materials and Mixtures

The cementitious materials used in this study included type I/II portland cement, Class F fly ash and grade 100 slag cement. The portland cement has a reported Blaine fineness of 397 m²/kg and a calculated Bogue phase composition of 62% C₃S, 9% C₂S, 7% C₃A, and 7% C₄AF, with a reported limestone content of 3.4%, all by mass. Both the slag cement and the Class F fly ash were used individually in the various concrete mixtures. The slag cement had a reported Blaine fineness of 592 m²/kg with a sulfide content, sulfate ion content of 0.7%, 0.1%, respectively. The fly ash had a calcium oxide content less than 1%. The coarse aggregate was a #57 limestone having a 25 mm (1 in.) nominal maximum size, a specific gravity of 2.72 and a water absorption of 0.3 %, while the fine aggregate was a natural sand having a specific gravity of 2.61, a water absorption of 0.87 % and a fineness modulus of 2.80. A total of six non-air entrained concrete mixtures were designed. The only admixture used was an ASTM C494 type F admixture to achieve a slump of 25 mm to 75 mm (1 in. to 3 in.).

Concrete mixtures were prepared in the laboratory in accordance with ASTM C192. Fresh concrete was evaluated for slump (ASTM C143), temperature (ASTM C1064), air content (ASTM C231), and unit weight (ASTM C138). Table 1 summarizes the mixture proportions, fresh properties, compressive strength and surface resistivity values before deicing chemical solution exposure.

Initial Curing and Subsequent Conditioning in Deicing Solution or Limewater

The plain portland cement concrete mixtures were initially cured in saturated limewater for 28 days, while the binary mixtures, containing either slag cement or fly ash, were kept in limewater for 56 days. After these initial curing periods, specimens were tested for compressive strength and surface resistivity. Then, all specimens were moved to a controlled drying environment at 22.8°C (73°F), 50%RH for 28 more days, prior to being exposed to deicing chemical solution, so that the combined effect of absorption and diffusion could be evaluated. At the end of 28 days of drying, cylinders for SR, RCP and Sorptivity testing had their sides sealed with epoxy (except for the top and bottom surfaces). Specimens for

apparent diffusion coefficient were cut into two halves (100 mm by 100 mm (4 in. by 4 in.) cylinders) and their sides and sawn faces were coated with epoxy. Then, samples were divided into four groups. Each group was placed on egg-crate panels and submerged in a different deicing chemical solution or in limewater until the time of testing.

The selected deicing chemicals were sodium chloride, calcium chloride, and magnesium chloride in a fixed concentration of 3.7 moles of chloride/L. The resulting solution concentrations were 17.8 %, 17.1 % and 15.0 % of the total mass solution, respectively for NaCl, CaCl₂, and MgCl₂. These concentrations were chosen to represent the dilution effect on the pavement⁴.

Table 1 - Mixture Proportions, Fresh Concrete Properties, Compressive Strength, and Surface Resistivity before Deicing Chemical Solution Exposure

	42PC*	50PC*	42FA30*	50FA30*	42SL50*	50SL50*
Batch Quantities						
Type I/II cement, kg/m ³ (lb/yd ³)	335 (564)	335 (564)	234 (395)	234 (395)	167 (282)	167 (282)
Fly ash, kg/m ³ (lb/yd ³)			100 (169)	100 (169)		
Slag cement, kg/m ³ (lb/yd ³)					167 (282)	167 (282)
SCM, %	0	0	30	30	50	50
w/cm	0.42	0.50	0.42	0.50	0.42	0.50
#57 Crushed Limestone, kg/m ³ (lb/yd ³)	1080 (1821)	1080 (1821)	1080 (1821)	1080 (1821)	1080 (1821)	1080 (1821)
Natural Sand, kg/m ³ (lb/yd ³)	866 (1459)	796 (1342)	830 (1399)	761 (1282)	854 (1440)	785 (1323)
Mixing Water, kg/m ³ (lb/yd ³)	141 (237)	167 (282)	141 (237)	167 (282)	141 (237)	167 (282)
ASTM C494 Type F, mL/100kg (oz/cwt)	587 (9)	65 (1)	365 (5.6)	98 (1.5)	456 (7)	130 (2)
Paste content (% of volume)	24.7	27.4	26.1	28.7	25.1	27.8
Fresh Concrete Properties						
ASTM C143, Slump, mm (inch)	31.8 (1.25)	69.9 (2.75)	76.2 (3)	114.3 (4.5)	76.2 (3)	88.9 (3.5)
ASTM C231, Air, %	2.4	2.1	2.8	1.7	2.7	2.0
ASTM C138, Density, kg/m ³ (lb/ft ³)	2446 (152.7)	2396 (149.6)	2387 (149)	2388 (149.1)	2411 (150.5)	2387 (149)
ASTM C1064, Temperature, °C (°F)	23.9 (75)	24.4 (76)	23.3 (74)	23.9 (75)	23.3 (74)	23.3 (74)
ASTM C39, Compressive Strength, MPa(psi)						
28 days	56.6 (8209)	40.6 (5892)				
56 days			51.4 (7453)	36.4 (5283)	60.2 (8727)	41.5 (6025)
AASHTO T358, Surface Resistivity, kΩ-cm and ion penetrability						
28 days	21 Low/Mod	11 High				
56 days			59 Very low	42 Very low	68 Very low	51 Very low

* The Mix ID is as follows: 42 and 50 refer to water to cementitious ratios of 0.42 and 0.50, respectively, followed by cementitious materials used (PC for Portland cement, FA for Fly Ash and SL for Slag Cement), and the cementitious materials replacement levels in percent. Note. The mixture design data are based on the target batch quantities. The yield adjusted batch quantities based on the measured density vary slightly from target values.

Testing

Compressive Strength

Compressive strength was determined according to ASTM C39 and the results represent the average of two cylinders.

Surface Resistivity

Surface resistivity was determined according to the AASHTO T358. When testing was carried out after samples have been exposed to salt solutions on their ends for 28 days and 90 days (the equivalent concrete ages were 84 and 146 days for the plain mixtures and 112 and 174 days for the binary mixtures), on the day of testing, about 25 mm (1 in.) wide stripes of the epoxy were stripped off the specimens at the testing locations (0, 90, 180, and 270 degrees). Special precautions were taken to avoid drying during removal of epoxy and cross contamination between specimens exposed to different deicing chemicals.

Sorptivity and RCP Testing

After the completion of surface resistivity readings, the epoxy was removed completely and two 50 mm (2 in.) thick slices were obtained from each cylinder: one from the exposed top and one from the exposed bottom. Specimens intended for sorptivity testing were prepared, conditioned and tested according to ASTM C1585.

RCP testing was carried out according to ASTM C1202, except that: a) specimens were not vacuum saturated, in order to prevent any possible salt dilution; and b) a sample from the bottom of the cylinder was also used as testing specimen. The surface of the sample that was previously exposed to the deicing salt solution (of all three types) was always tested facing the cell containing NaCl. The results are the average of the samples obtained from the top and bottom of the specimen.

Apparent Diffusion Coefficient

Specimens were tested according to ASTM C1556. The unsealed surface of the sample (either the original top or bottom faces of the cylinder) was exposed to the solutions for 90 days (the equivalent ages were 146 days for the plain mixtures and 174 days for the binary mixtures). Acid soluble chloride content was measured in accordance with ASTM C1152, from which an apparent chloride diffusion coefficient was calculated in accordance with ASTM C1556.

RESULTS AND DISCUSSIONS

Before Exposure to Deicing Chemical Solution

Compressive Strength

Table 1 shows that mixtures containing 50% of slag cement achieved at 56 days the same or higher strength than the plain mixtures at 28 days. On the other hand, mixtures containing 30% of fly ash by 56 days presented compressive strength about 10% lower than the plain mixtures. Nevertheless, even for the fly ash mixtures, average compressive strengths of 5300 to 7500 psi would be generally

acceptable since, for most concrete pavements applications and for many structures, compressive strengths of 31 MPa (4500 psi) are sufficient.

Surface Resistivity (SR)

Mixtures with lower w/cm presented higher surface resistivity, as expected. When comparing plain mixtures, 42PC showed about twice the surface resistivity as the 50PC mixture at the same age. When comparing binary mixtures, this difference was not as pronounced: 42FA30 presented 40% higher SR compared to 50FA30 while 42SL50 exhibited 33% higher SR than 50SL50.

Nevertheless, the effect of including supplementary cementitious materials in the mixtures appeared to be much more significant in increasing SR than the decrease of w/cm from 0.50 to 0.42: fly ash mixtures presented at 56 days 180% and 300% higher SR than plain mixtures at 28 days with the same w/cm (0.42 and 0.50, respectively) and slag cement mixtures yielded, at 56 days, 222% and 388% higher SR than plain mixtures at 28 days with the same w/cm (0.42 and 0.50, respectively). When comparing fly ash mixtures with slag cement mixtures, slag cement mixtures presented the highest SR but the SR difference between the two supplementary cementitious materials is less pronounced than when they are compared with plain mixtures (15% and 21% for 0.42 and 0.50 respectively).

Resistivity is affected by many materials characteristics, such as, the pore volume and their interconnectivity, the pore solution chemistry, the degree of hydration and the relative humidity of the sample⁵. As a result, the interpretation of the contribution of w/cm or presence of supplementary cementitious materials to the increase in SR is not as straightforward as it may appear. The use of SCM promotes the refinement of the pores and disruption of pore continuity, changes the chemistry of the pore solution, and decreases alkali leaching. On the other hand, due to their lower specific gravities, mixtures containing SCMs presented higher paste content (Table 1).

After Exposure to Deicing Chemical Solution

Surface Resistivity

Surface resistivity is the inverse of electrical conductivity. The electrical conduction in cementitious materials occurs primarily through the fluid phase, or the pore solution, and depends on the pore structure and on the electrical conductivity of the pore solution⁵.

The pore structure is a function of the pore volume and their connectedness of the pores (resulting from water/cement ratio and the presence of SCMs). Hence, as a general rule, the 42PC mixture is expected to have a higher resistivity than 50PC because of the lower w/c and lower resistivity than 42FA30 and 42SL50, for each individual exposure condition due to the SCMs. This was confirmed (Figure 1 (a) and (b)). Using the same rationale, 42FA30 was expected to present higher resistivity than 50FA30, and 42SL50 was expected to present higher resistivity than 50SL50. Nevertheless, in Figure 1(a) in 42FA30 samples exposed to $MgCl_2$ show lower resistivity than the in 50FA30 and there was no significant difference between the limewater samples of these two mixtures. Also, in Figure 1(b) there is no significant difference between 42SL50 and 50SL50 samples exposed to $MgCl_2$. In both cases, the lower resistivity, expected due to the higher porosity of mixtures with $w/cm = 0.50$, may have been counteracted by their pore solution conductivity. Figures 1(c) and (d) are discussed below in 4.2.2.

Pore solution conductivity is affected by the chemistry of the cementitious materials, the water content of the mixture, the degree of hydration of the cementitious materials⁵ and curing or exposure conditions⁶. Table 2 presents an estimation of the pore solution conductivity for specimens in limewater obtained according to Bentz⁷. According to Table 2, the conductivity of both binary mixtures with higher w/cm is lower than their lower w/cm counterpart mixtures, explaining why concrete specimens from 42FA30 and 42SL50 did not show higher resistivities than those from 50FA30 and 50SL50 and, respectively.

For specimens exposed to salts, there is also a contribution of the conductivity of each salt (Table 3) to the total conductivity of the pore solution. Despite the salt contribution to the conductivity of the pore solution, Figure 1(a) shows no significant difference for any of the exposure conditions in mixtures 42PC, 50PC and 50FA30 and in mixture 50SL50, the only significant different resistivity was for specimens in $MgCl_2$. Also unexpectedly, in mixture 42FA30, $NaCl$ and $CaCl_2$ exposed samples presented much higher resistivity than the limewater one. At 90 days, the same sort of unpredicted results was observed.

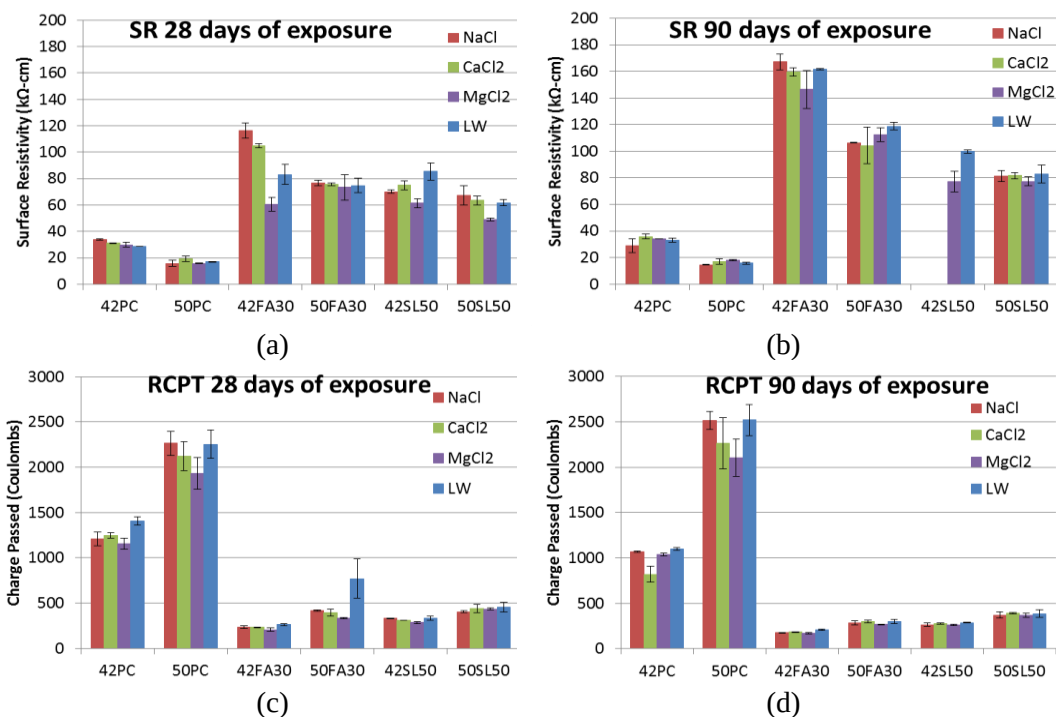


Figure 1 - (a) SR results after 28 days in salt solutions, (b) SR results after 90 days in salt solutions ($NaCl$, $CaCl_2$ for 42SL50 discarded due to high between replicate variability), (c) RCP results after 28 days in salt solutions and (d) RCP results after 90 days in salt solutions. LW stands for limewater. Note. Error bars indicate the range for the lowest and highest values.

When comparing Figure 1 (a) and (b), in all binary mixtures, the resistivity at 90 days was higher than at 28 days, for all exposure conditions. The highest increase was observed in mixture 42FA30, especially for $MgCl_2$ exposed samples, where the resistivity increase was about 240%. This was probably due to continuing hydration of the slower-reacting SCMs and potential leaching of ion species from the specimens. For plain mixtures, there was not a significant difference between the two ages, despite the continuous salt solution exposure. Also when comparing resistivity before and after exposure, the resistivity after 28

days exposure in salt solutions is higher than before any salt solution exposure, with exception of mixtures 42SL50 and 50SL50, exposed to MgCl_2 .

Table 2 – Estimated Pore Solution Composition and Conductivity for Specimens Exposed to Limewater at the End of Curing Period

Mixture	K^+ (M)*	Na^+ (M)*	OH^- (M)*	Electrical conductivity in S/cm
42PC	0.61	0.15	0.76	14.9
50PC	0.47	0.12	0.59	11.9
42FA30	0.75	0.18	0.53	17.9
50FA30	0.59	0.14	0.73	14.5
42SL50	0.29	0.07	0.36	7.7
50SL50	0.22	0.06	0.28	6.1

Note *: leaching of ions due to initial curing and during exposure, neither the presence of salts, were not considered in this estimation.

In order to explain the unanticipated results, the effects of several mechanisms on the resistivity need to be considered, which may be acting simultaneously, either causing synergetic or counter effects. At this point, it is not possible to determine which ones are present or are the most prevalent, but they are being investigated and will be reported in the future. Longer term exposure results will be available in about a year.

Table 3 – Electrical Conductivity of Solutions at 20°C⁸ and Estimated Surface Tension and Viscosity of the deicing solutions

	Surface Tension (10^{-6} N/mm)	Viscosity (cP)	(Surface Tension/Viscosity) ^{0.5}	Electrical conductivity in S/cm
NaCl	77	1.2	8.0	18.8
CaCl ₂	80	1.5	7.3	16.7
MgCl ₂	73	1.8	6.4	12.9
Water	72	1.0	8.5	7.9

Leaching behavior

Alkalis and calcium hydroxide can be leached out of concrete due to solution concentration gradients depending on the storage solution chemistry and volume in relation to sample size⁶. Leaching causes a decrease of ionic species in the pore solution and consequently an increase of its resistivity. Research⁶ suggests that the pore solution resistivity can vary by as much as 80% as a result of leaching.

The use of saturated limewater is normally intended to prevent $\text{Ca}(\text{OH})_2$ leaching from concrete, but it may not prevent the diffusion of alkalis out of the test specimen and into the storage solution. The impact of the storage solution on the alkalis leaching has been studied by Kandasamy and Shehata⁹, who found a decrease of up to 40% on the alkalis released into the storage solution when specimens were stored in a solution of 0.25 mol/L of alkalis. Spragg *et al.*⁵ have shown that specimens cured in limewater present up to 40% higher resistivity than those stored in a solution chemically similar to the pore solution.

On the other hand, specimens stored in deicing salts are prone not only to alkalis leaching but also to $\text{Ca}(\text{OH})_2$ leaching^{4,10,11,12}. The solubility of $\text{Ca}(\text{OH})_2$ increases proportionally with the increase of chloride concentration. Calcium leaching leads to increase in pore size and volume and promotes moisture redistribution, causing further leaching and facilitating diffusion of other ions into

the concrete^{10, 13}. It should be noted that in this study leaching can only occur from the uncoated ends of the specimens after the drying cycle.

Since leaching is also a function of porosity, molar concentration of ions in the liquid phase and the calcium concentration of the solid phase¹⁰, w/cm and the presence of supplementary cementitious materials have a direct influence on the leaching behavior. Alkali retention capacity of portland cement-only mixtures has been shown to be much lower than mixtures containing fly ash, slag cement or both. It has also been shown that plain mixtures even when stored in a solution containing alkalis had more than 80% of their initial alkalis leached⁹. Since diffusion is also involved in the leaching process any factor that contributes to the densification of the microstructure (w/cm and presence of SCMs) decreases the alkalis leaching¹⁴.

Degree of saturation of specimens

It is well known that the degree of saturation has a profound effect on the resistivity of concrete^{5, 6, 15-18}. All the specimens in this study were dried for the same period of time prior to their coating and immersion in different solutions. Since w/cm , paste content and SCMs can affect the concrete desorption rate^{19,20}, different mixtures may have started the exposure period at different saturation levels.

On the other hand, the fact that specimens were in solution for 28 and 90 days does not guarantee that they were fully saturated^{5,20}. Also, the degree of saturation is a function of the solution^{4,6,22,23}. For example, Farnam *et al.*²⁴ saturated samples with 15% $MgCl_2$ solution under vacuum. These specimens achieved only 40% of the saturation of the distilled water saturated samples. In another study⁴, the degree of saturation of soaked specimens increased in the following solution order $MgCl_2$, $CaCl_2$, $NaCl$ and water.

These differences are due to the fact that the absorption of aqueous solution is proportional to the square root of the surface tension and the viscosity of the solution²⁵. The estimated properties for the solutions in the current study were obtained from Spragg *et al.*²² and are presented in Table 3. The results of (surface tension/viscosity)^{0.5} in Table 3 indicate that the absorption increases in the following order $MgCl_2$, $CaCl_2$, $NaCl$ and limewater, indicating that the degree of saturation may have followed the same order.

In this study salt solution exposed samples may have reached lower saturation levels and since saturation and resistivity are inversely proportionally, it may explain why the samples in limewater did not present a much higher resistivity when compared to samples exposed to salt solution, despite the fact that ions affect the conductivity of the solution.

Chloride diffusion as a function of concrete degree of saturation

At the time of initial exposure of cylinder ends to the solutions, specimens were partially dry. So during exposure, the ingress of chlorides was due to both capillary sorption and to diffusion. Capillary sorption occurred only until sample saturation was reached near the exposed surfaces, while diffusion is always present as long as there is a solution in the pores. As the saturation of samples increased, the diffusion contribution to the total chloride ingress increased²⁶. And the portion by absorption decreased.

Several models describe the relationship between saturation and diffusion coefficient^{26,27,28,29,30,31}. While they differ, they all show a difference in the

chloride diffusion coefficient of several orders of magnitude between 15% and 100% of sample saturation^{26,27,30,32}, and increases from MgCl_2 to CaCl_2 and NaCl ³³. As a result, in the current study, the chloride content and penetration depth may have been much lower than expected, affecting the pore solution conductivity.

Chloride binding and pore clogging

As the salt solutions penetrate concrete, several physical interactions and chemical reactions may occur between the salts and the cementitious materials (such as chloride binding). Only free chloride ions contribute to a decrease in resistivity, so if chloride binding is not taken into account, the resistivity of the specimen due to the pore solution chemistry may be underestimated.

Chloride binding depends on the chloride concentration, cementitious composition, hydroxyl concentration and cation of chloride salt^{34,35}. The presence of supplementary cementitious materials significantly increases chloride binding^{35,36}, contributing to generally higher resistivities of the binary mixture specimens when compared to the plain mixtures with same w/cm and exposed to the same deicing salt. This is shown in Figure 1. Regarding the effect of different cations, Arya *et al.*³⁵ found that NaCl causes less chloride binding than CaCl_2 and MgCl_2 (but with no significant difference between CaCl_2 and MgCl_2), which could decrease resistivity on the inverse order.

In addition, the reaction products between chlorides and cementitious compounds in the paste have been reported to precipitate, forming a layer on the surface of samples, pore walls, or clogging the pores and preventing further ingress of solution, thus the sample would remain unsaturated^{4,11,13,24}. In this case, the consequence on the SR results would be an increase in resistivity, first due to decreased porosity (due to precipitation) and second due to the lower degree of saturation.

Rapid Chloride Permeability Test (ASTM C1202)

The RCPT measures the total electrical charge passed as the result of the migration of all ions, the ones from the cementitious materials, the ones from the exposure solution that penetrated the sample and the ones from the RCP cell (NaCl), so the diffusivity of each ionic species is important. Overall, RCP test is influenced by the same factors as SR (see 0).

Some other aspects of the RCP testing that may have affected the results are: 1) the electrical field applied during testing may promote further chloride binding^{34,37} and microstructure changes³⁸ and 2) the face of the sample that was exposed to solution was set to face the cell containing NaCl . If an outer layer of the reaction product between solution and cementitious materials (due to the exposure prior to RCP testing) is present, it could have hindered the ingress of ions from the cell to the specimen²⁴.

Figure 1 (c) and (d) show the effect of w/cm and the presence of supplementary cementitious materials. The effect of w/c in plain mixtures is considerable. As expected, the higher the w/c , the higher the charge passed (higher porosity, as well as higher pore connectivity)^{39,40}. Nevertheless, the effect of w/cm on the RCP results of all the binary mixtures was not significant. The effect of the w/cm may have been overshadowed by a much higher effect of the presence of supplementary materials on the pore structure.

Figure 1 (c) and (d) also show the effect of SCMs. The charge passed in mixtures containing fly ash did not differ much from the charge passed in mixtures containing slag cement. In general, when SCMs are used, a decrease in charge passed is anticipated due to the densification of the pore structure^{39,40} and the change in the pore solution chemistry, since SCMs decrease the alkalis and the OH⁻ ions in solution^{41,43}. In addition fly ashes also decrease the Ca²⁺ ions in solution⁴⁴. The decrease in ion concentration has a proportional decrease in the conductivity of the pore solution. Another factor that could have contributed to the lower charge passed in binary mixtures is that the SCMs may present lower internal degree of saturation due to the refinement and discontinuity of pores⁴⁵ and due to the testing protocol used (see 0 (0)).

In Figure 1 (c), although some of the average results may appear to be different for the various exposure conditions, when the range of maximum and minimum values are compared, in most cases there is no distinction. An exception to this, are mixtures 42PC and 50FA30, in which the limewater specimens showed a higher charge passed than the salt solution exposed specimens. In Figure 1 (d), no difference is observed for the various exposures, with exception of mixture 42PC, in which the CaCl₂ specimens presented lower charge passed. The lack of significant difference between specimens exposed to salt solutions and the ones kept in limewater is, to some extent, counterintuitive and some of the possible reasons for this are: a) leaching behavior; b) degree of saturation; c) effect of saturation on the chloride diffusion and d) effect of chloride binding and pore clogging.

When comparing Figure 1 (c) and (d), no significant changes were observed between 28 and 90 days of exposure in mixtures 50PC, 42FA30, 42SL50 and 50SL50. In mixture 42PC, a difference was only observed for samples exposed to CaCl₂ and limewater, while mixture 50FA30 showed a difference only for limewater exposed samples. Interestingly, even in the presence of chlorides, the charge passed was low in most cases.

Sorptivity (ASTM C1585)

For the sorptivity tests, samples were removed from the solutions, cut and conditioned at 50 ± 2°C and 80 ± 3% R.H. for 3 days, and subsequently stored at 23 ± 2°C, in sealed containers, for 15 days more and then the side surfaces were sealed, according to ASTM C1585. The face of the specimens that had been exposed to the solutions was placed down in contact with water for the absorption procedure.

Regarding the effect of each solution on the absorption, no trend is observed in Figure 2 (a-f), due to the interaction of factors such as pore solution chemistry (and its impact on equilibrium R.H.), microstructure, and reaction between sample and solution.

Concrete pores start drying when the R.H. of the drying environment is lower than the equilibrium R.H. of the pore solution. Nevertheless, salts (alkalis and deicing salts in solution) change the drying mechanism and lower the equilibrium R.H.^{5,6, 21,46}. Drying also depends on the pore structure, surface tension, density, viscosity of the pore solution⁴⁶.

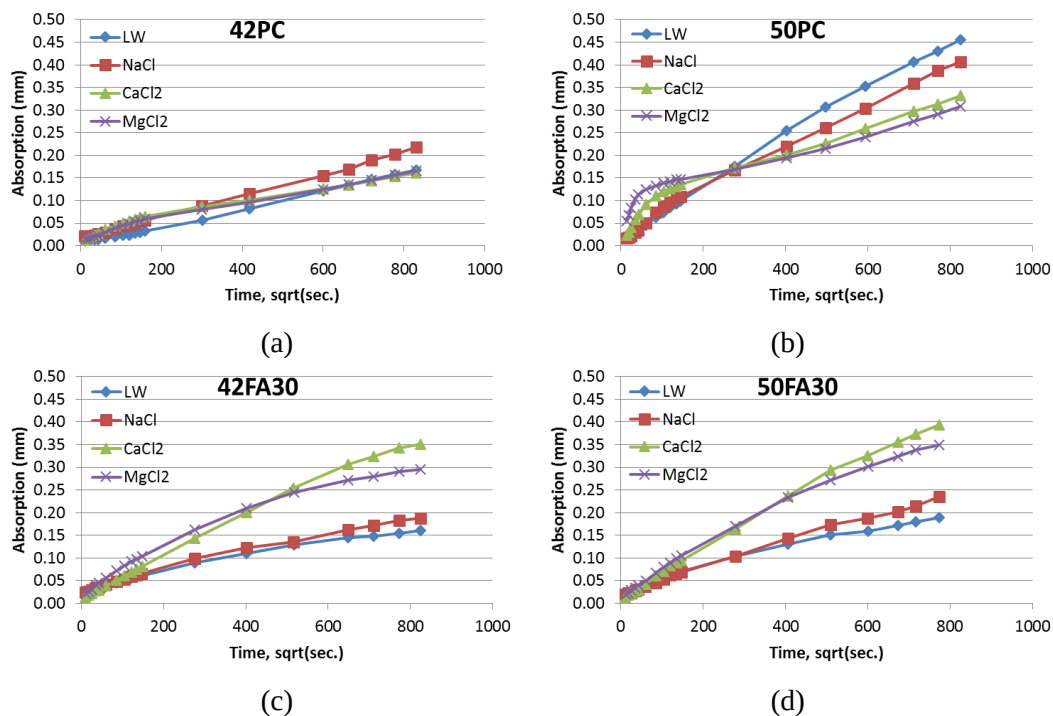
Robinson and Stokes⁴⁷ developed a simplified model to calculate the equilibrium R.H. Despite the fact that the model does not take into account the pore sizes, any possible leaching, or chloride binding, it can give a general idea of the expected equilibrium R.H. Figure 2 (g) shows the results obtained from

Robinson and Stokes model⁴⁷ for the mixtures in this study, which are comparable to the results from the literature^{21,47,48,49, 50}.

As it can be seen in Figure 2 (g), only specimens in limewater or exposed to NaCl may have dried during ASTM C1585 conditioning, since drying was carried out at lower R.H. than the equilibrium R.H. for these solutions. In reality, specimens exposed to CaCl₂ and MgCl₂ may have even absorbed moisture from the environment, instead of drying, affecting the absorption capability of the sample (see 0 for the estimation of the degree of saturation). On the other hand, the absorption is also a function of the solution to which samples have been exposed prior to the sorptivity testing⁵⁰. When the conditioning history, the microstructure and possible chemical reactions are considered, it becomes almost impossible to determine the exact mechanism that occurred.

When comparing different mixtures exposed to each salt solution, the analysis is more straightforward. For example, Figure 2 (a-f) shows that mixtures with 0.42 w/cm absorbed less water than their counterparts with 0.50 w/cm, due to their denser microstructure. Also, in most cases plain mixtures absorbed more water than the binary mixtures, with the exception of mixtures 42FA30 and 50FA30 exposed to CaCl₂ or MgCl₂, which presented higher water absorption than plain mixtures exposed to the same solutions.

After the absorption tests, specimens were split and the chloride penetration depth was measured after spraying the sample with silver nitrate solution (Figure 2 (h)). Mixtures containing slag cement presented the lowest penetration, followed by fly ash mixtures. Mixtures with higher w/cm always allowed higher penetrations. Regarding each salt solution, different solutions behaved differently depending on the mixture.



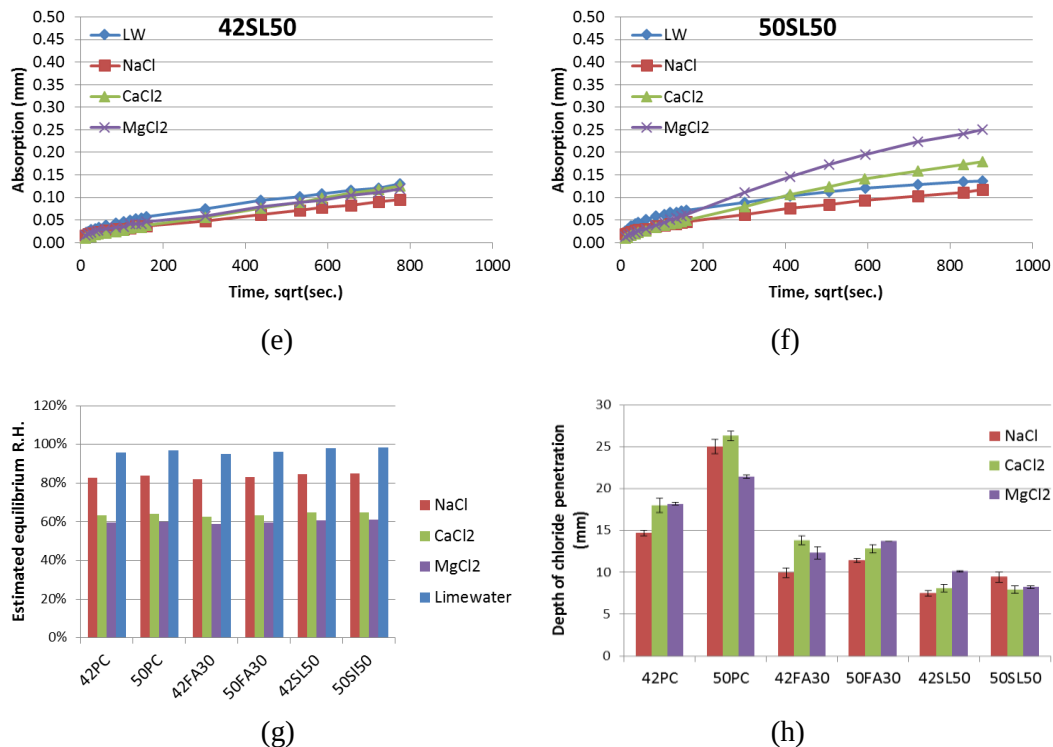


Figure 2 – Sorptivity after 90 days of exposure for (a) 42PC, (b) 50PC, (c) 42FA30, (d) 50FA30, (e) 42SL50, (f) 50SL50, (g) estimated equilibrium R.H. and (h) measured depth of chloride penetration.

Apparent Diffusion Coefficients (ASTM C1556)

Chloride diffusion coefficients are shown in Figure 3. If different mixtures are compared, mixtures with higher w/cm show higher diffusion coefficients than their counterparts with lower w/cm , plain mixtures show higher diffusion coefficients than binary mixtures and slag cement mixtures present the lowest diffusion coefficients, followed by fly ash mixtures. These results are in agreement with the literature^{4,34,36,51} and are most likely due to the pore structure of each mixture.

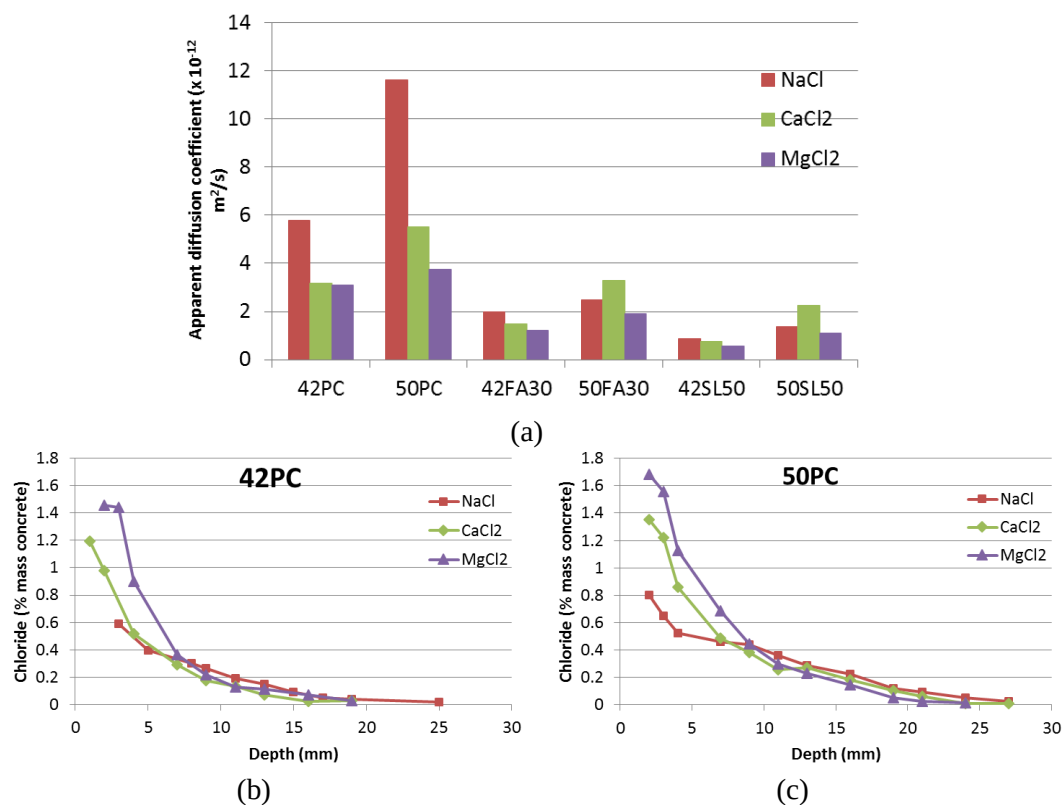
The chloride diffusion depends on the nature of the cations^{53,54,55}. In Figure 3, when comparing the apparent diffusion coefficient among the three salt solutions, the lowest diffusion coefficient is consistently the MgCl₂ exposed samples, while NaCl showed the highest diffusion coefficient in mixtures 42PC, 50PC, 42FA30 and CaCl₂ showed the highest diffusion coefficient in mixtures 50FA30 and 50SL50. No difference was observed on the NaCl and CaCl₂ diffusion coefficients in mixture 42SL50. These results seem to disagree with what is presented in the literature, where the diffusion coefficient has been reported to increase from NaCl to CaCl₂ and MgCl₂^{52,53,54}. Nevertheless, the diffusivity is indirectly proportional to the viscosity of the solution⁵⁶ and as shown in Table 3, at the concentration used in this study, MgCl₂ solution presents the highest viscosity, followed by CaCl₂ and NaCl solutions, which explains the results in Figure 3.

Other possible contributors to this disagreement may be related to the rate of absorption and resulting degree of saturation of the samples, the chloride binding and the interaction of different ionic species^{27,55,57,58}.

A model that takes into account the effect of saturation and chloride binding on the diffusion coefficient was developed by Vera *et al.*²⁷ for plain mixtures only. When this model²⁷ is applied to the plain mixtures and exposure conditions of this study, the following degrees of saturation are obtained: 67%, 55% and 55% for 42PC and 88%, 75% and 61% for mixture 50PC exposed to NaCl, CaCl₂ and MgCl₂, respectively. For both mixtures, specimens exposed to NaCl solution possibly have a higher degree of saturation than specimens exposed to CaCl₂ and MgCl₂, which is in agreement with what was expected, since the rate of absorption of NaCl is higher than the other solutions (0 (0 and Table 3). Also, NaCl shows less binding than the other salts³⁵. For 50PC, specimens in MgCl₂ may have the lowest degree of saturation, which is also in agreement with its lower rate of absorption.

It has been shown that the lower the degree of saturation, the lower the diffusion coefficient⁵⁹, which may have lowered the diffusion coefficient of the binary mixtures even further than normally anticipated due to expected denser their microstructures, affecting the absorption of the solution. In addition, the type of solution also affects the rate of absorption and the binding capacity, partially explaining why MgCl₂ exposed samples presented the lowest diffusion coefficients.

Finally, during the course of the specimens' exposure, a thin film of whitish precipitate was observed on the surface of specimens in MgCl₂ and CaCl₂ solution, but no precipitate was observed on specimens in NaCl. The formation of a dense layer of reaction products (between salts and concrete) on the surface of concrete has been reported to impede further ingress of solution and prevent specimens from fully saturating^{13,24}, which corroborates the diffusion results obtained.



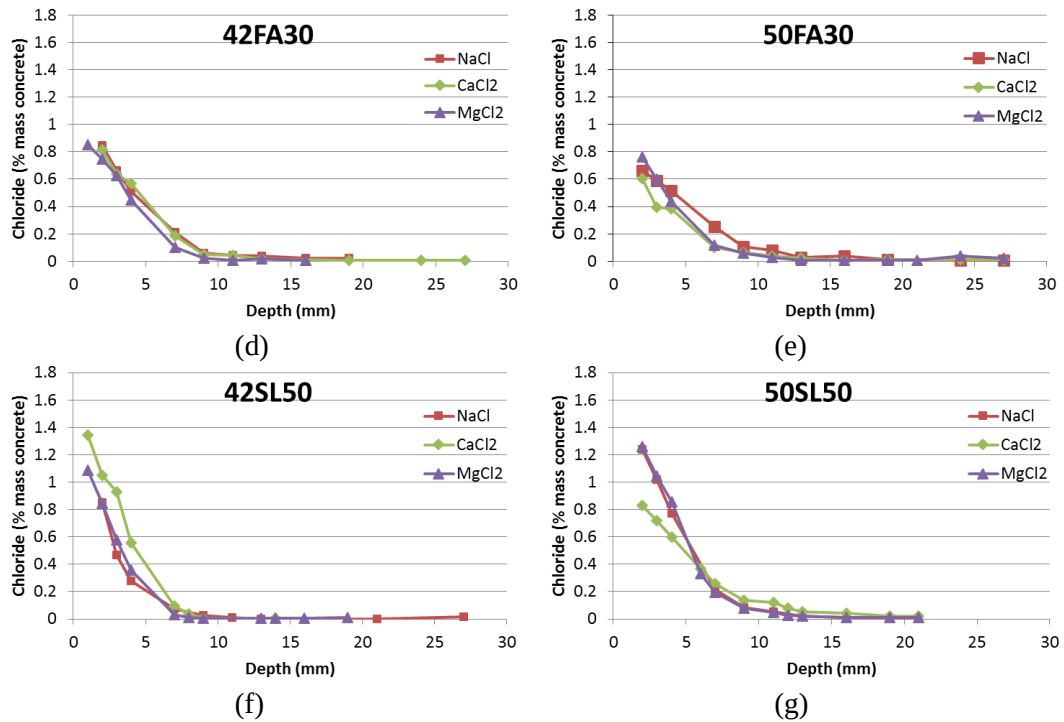
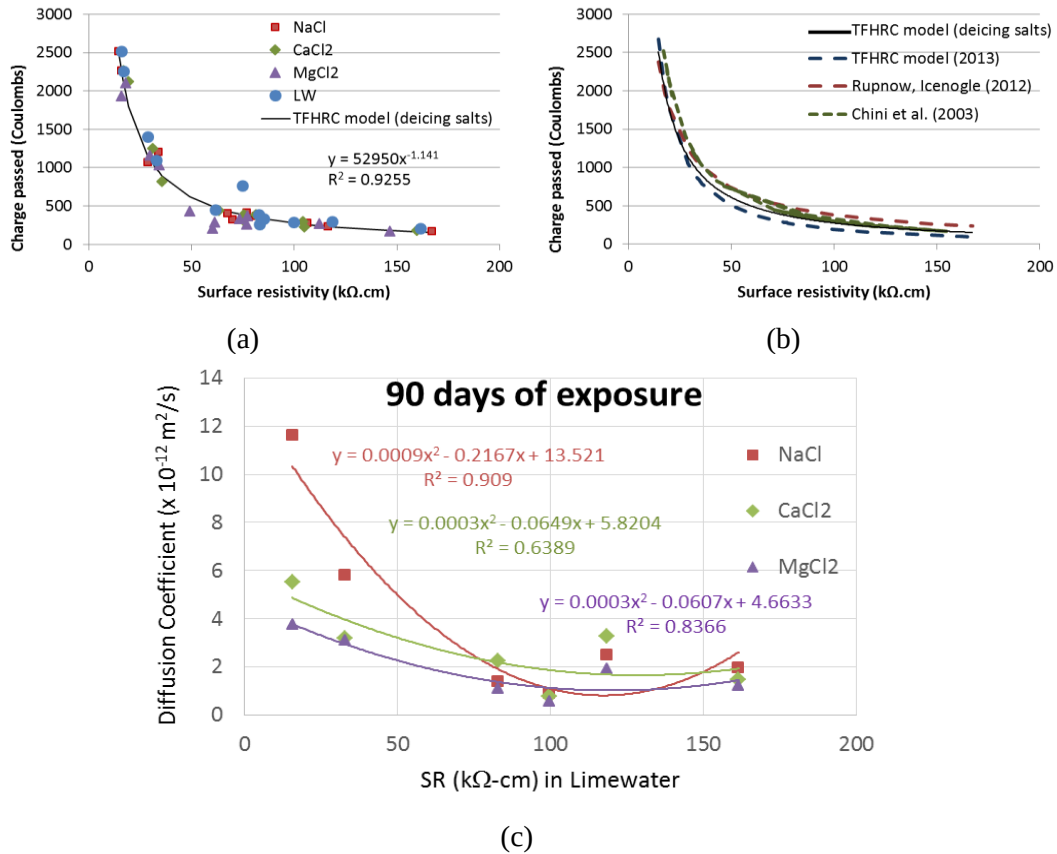
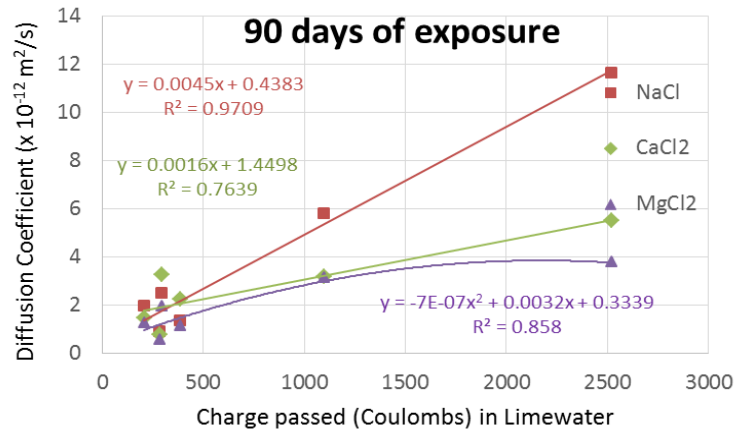


Figure 3 - Apparent Diffusion Coefficients after 90 days of exposure (a) and chloride profile (b to g).

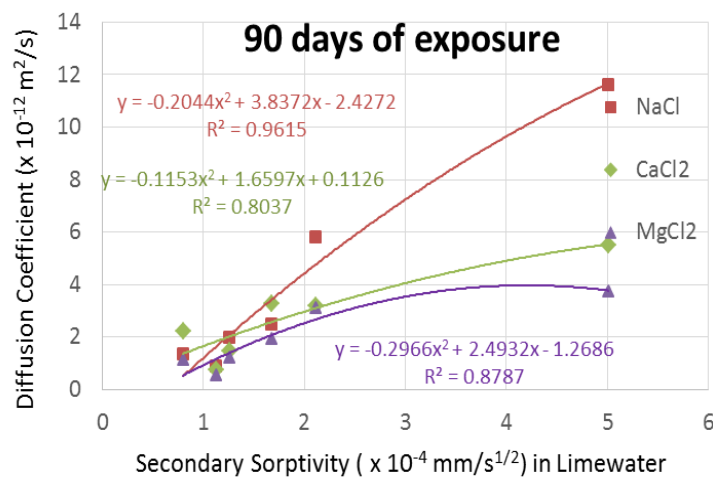
Correlations between results obtained by different methodologies

Figure 4 shows the various correlations between results obtained by different test methodologies.





(d)



(e)

Figure 4 – Correlation between test methodologies (a) SR vs RCP, (b) Different models correlating SR and RCP (c) Diffusion coefficient of specimens exposed to salts vs SR of specimens in limewater, (d) Diffusion coefficient of specimens exposed to salts vs RCP of specimens in limewater and (e) Diffusion coefficient of specimens exposed to salts vs Secondary sorptivity of specimens in limewater.

Surface resistivity and RCP testing

In Figure 4 (a) it is shown that SR and RCP correlate very well, despite the various exposure conditions, since both are measures related to electrical conductivity of the concrete and are affected by the same factors, as presented in 0 and 0., and explains why the model obtained for the best fit in this study does not differ significantly from other models in the literature^{15,60,61}, as seen in Figure 4 (b).

Apparent diffusion coefficient vs SR and Apparent diffusion coefficient vs RCP

Figure 4 (c) and (d) show that there is no unique correlation between apparent diffusion coefficient of specimens exposed to each deicing salt and the SR or RCP of specimens in limewater, so as a result, SR and RCP after soaking in limewater cannot be used as a surrogate test to estimate apparent diffusion coefficient of specimens exposed to these deicing salt solutions. When apparent

diffusion coefficient of specimens exposed to deicing salts is correlated to SR or RCP of specimens also exposed to deicing salts (not shown here), a similar behavior is found, demonstrating that apparent diffusion and conductivity tests are affected differently by each of the conditions, since apparent diffusion may be much more affected by the rate of absorption, actual diffusivity, and chloride binding differences among the solutions than SR and RCPT.

1. Apparent diffusion coefficient vs Secondary sorptivity

Figure 4 (e) also shows that there is no unique correlation between apparent diffusion coefficient of specimens exposed to each deicing salt and secondary sorptivity of specimens in limewater. Sorptivity relates to the rate of absorption and is influenced by the saturation degree and the differences in rate of absorption of the solutions (0 (b)); while apparent diffusion coefficient is not only affected by these factors, but also by chloride binding and the actual diffusivity of ions in solution.

The best correlation between apparent diffusion coefficient and any of the other test conditions was obtained on specimens exposed to NaCl, indicating that the factors that have the biggest impact on SR or RCPT or sorptivity also have a predominant effect on sorptivity when the solution used is NaCl.

CONCLUSIONS

As presented in this study, the analysis of transport properties is very complex, since different mechanisms are involved. Transport testing results have to be carefully interpreted as they depend on the exposure history and testing protocols. Without understanding the exposure conditions of the concrete and the factors that affect individual tests, relying on test results can be misleading in some cases.

In this study, the effect of deicing salts on transport properties of uncracked concrete was significantly less pronounced on mixtures containing SCMs, especially those containing slag cement. The impact of SCMs on transport properties was more pronounced than the impact of decreasing w/cm from 0.50 to 0.42.

The combined effect of absorption and diffusion had a significant impact on the transport properties and affected each test differently. Also, the rate of absorption and the apparent diffusion coefficient were found to depend on the mixture design, exposure conditions and cations of the salts (Na^+ , Ca^{2+} and Mg^{2+}) in solution.

It was observed that the correlation between test methods depends on the exposure history and seems to be specific to each solution, with the exception of the correlation between SR and RCP, since both test measures are related to the electrical conductivity of the concrete. As a consequence, when specimens have been exposed to deicing salts, none of the tests evaluated in this study can be used as a surrogate for the apparent diffusion coefficient and should not be used as an input for remaining service life models.

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