

Will Blended-Cement Systems with Similar Chloride Penetration Potentials Resist Similarly to Corrosion?

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ABSTRACT

The capacity of concrete to prevent chloride ions penetration represents a key durability factor for steel-reinforced structures exposed to de-icing salts and/or marine environments. Although blended-cement systems are commonly characterized with accelerated chloride penetration tests developed for Portland-cement concrete (e.g. the ASTM C1202 method), their microstructures and pore solutions are very different. This study aims to illustrate how the full potential of blended-cement systems to resist chloride ingress (and thus, chloride-induced corrosion) may not be justly disclosed by these accelerated tests using electrical current, even when tested after three months of curing. A Portland-cement-only mortar and five binary blended-cement mortars containing typical dosages of fly ash, slag, metakaolin, glass powder or rice husk ash were characterized using the ASTM C1202 chloride penetration test, bulk resistivity measurements and pore solution resistivity measurements. The results showed similar very low chloride penetration potential after three months for the investigated systems (except for the slag system which showed a low potential). The microstructure was densified with time particularly for systems with fly ash or glass powder, as shown by comparing bulk resistivity measurements after three months and one year of curing. However, measurements of the pore solution resistivity suggested a reinterpretation of the observed trends and the glass powder showed unique features for long-term resistance to chloride-induced corrosion. Finally, this work illustrates the importance of understanding the effects of supplementary cementitious materials on both the microstructure and the pore solution, while motivating further work on complementary aspects such as chloride migration coefficients, chloride binding, porosity distribution, or interfacial transition zone.

Keywords: Durability, Supplementary Cementitious Materials, Glass Powder, Chloride Ions Penetration, Bulk Resistivity, Pore Solution Conductivity.

INTRODUCTION

The durability of steel-reinforced concrete structures is mainly due to the high alkalinity of the cement paste: a pH above 11.5 forms a thin film of iron oxide around the bars and protects them against electrochemical corrosion in a phenomenon known as passivity (Neville & Brooks 2010). Carbonation and chloride ingress represent the two main aggressions responsible for the destruction of this passive film. If carbonation reduces the pH of the cement paste down to ~9 (which is clearly detrimental if reaching rebars), chloride ingress does not significantly affect the pH, but rather triggers local depassivation even at high alkalinity. Chloride ions reaching the reinforcement may react with iron to form hydrochloric acid, which destroys the passive film punctually and forms local anodic sites. Thus, chloride-induced corrosion can occur at a pH well above 11.5, and the governing parameter is the Cl^-/OH^- molar ratio: at values above 0.6, the

passivation film becomes permeable or unstable, which favors corrosion initiation (Mehta & Monteiro 2006). In addition, once corrosion is initiated, chlorides also contribute to the degradations by holding moisture into the concrete, which reduces its electrical resistivity. This resistivity (along with a possible lack of oxygen) is the remaining barrier against corrosion after depassivation (Mehta & Monteiro 2006).

The capacity to limit chloride ingress is thus a crucial durability parameter for concrete exposed to de-icing salts and/or marine environments. The ASTM C1202 standardized method represents an “Electrical Indication of Concrete’s Ability to Resist Chloride Ion Penetration”, which has been widely used and accepted among civil engineers, project owners and governmental instances. Thus, performance standards for concrete such as the Canadian standard (CSA A23.1 2009) use the charge passed as a requirement – e.g., the charge should be below

1500 Coulombs by 56 days for Class C-1 concrete (exposed to chlorides, under freeze-thaw conditions or not). An alternative much faster method is the measurement of concrete bulk resistivity, which may be correlated to ASTM C1202 (Shane et al. 1999).

Both measurements virtually measure the electrical conductivity (or resistivity) of concrete, and the results are thus function of both the pore structure characteristics and the chemistry of pore solution (Shi 2003; Stanish 2002). Changing the ionic species in the pore solution will affect the charge passed: a lower resistivity may be caused by metallic fibres or some admixtures such as calcium nitrite used as a corrosion inhibitor (ASTM C1202 2012), and a higher resistivity may be caused by the fixation of calcium ions and alkalis with the pozzolanic reaction of SCMs (Duchesne & Bérubé 1994; Ghosh & Tran 2015).

Considering that corrosion can be avoided by remaining below the chloride threshold of $Cl^-/OH^- < 0.6$, durable concrete could be obtained by (1) reducing movement of chlorides toward the steel rebars and/or (2) increasing the OH^- content of the pore solution. Interestingly, bulk resistivity will be higher for a lower connected porosity (i.e., a lower movement of ions) and for a lower ionic content (including OH^-) of the pore solution, which leads to opposite effects on the Cl^-/OH^- ratio!

By investigating binary blended-cement mortars incorporating typical dosages of Fly Ash (FA), Slag (S), Metakaolin (MK), Glass Powder (GP) and Rice Husk Ash (RHA) with an Ordinary Portland Cement mortar (OPC), this study illustrates how similar very low ASTM C1202 values may not be expected to behave similarly in terms of durability to corrosion. This is achieved by comparing the systems in terms of strength, chloride penetrability, bulk resistivity and pore solution resistivity. Notably, the results indicate that one system has unique and very promising properties.

MATERIALS AND METHODS

Cementitious Materials and Sample Preparation

The cementitious systems investigated in this study were produced using cementitious materials commercially available in Canada, as chemophysically characterized in Table 1. Mortars were prepared with tap water at a fixed water-to-binder ratio of 0.40 and a fixed sand-to-binder ratio of 2. A Portland-cement-only mortar (system OPC) was prepared along with five binary blended-cement pastes in which cement was replaced with SCMs at dosages generally considered to provide good results: the system 30FA with 30% fly ash (and 70% Portland cement), the system 50S with 50% slag, the system 12MK with 12% metakaolin, the system

20GP with 20% glass powder and the system 15RHA with 15% rice husk ash. Series of mortar cubes and cylinders were mixed and cast with a method inspired from ASTM C305 and ASTM C109, demolded at 24 hours and cured until testing in lime water at 23 °C.

Table 1. Chemical and physical properties of the raw materials including Ordinary Portland Cement (OPC), Fly Ash (FA), Slag (S), MetaKaolin (MK), Glass Powder (GP), and Rice Husk Ash (RHA), as measured by X-ray fluorescence, pycnometry and Blaine tests.

Property	OPC	FA	S	MK	GP	RHA
SiO ₂ (wt.%)	19.7	46.5	35.4	61.1	71.5	89.3
Al ₂ O ₃ (wt.%)	4.4	23.2	10.5	28.8	1.9	0.7
Fe ₂ O ₃ (wt.%)	2.7	16.5	0.4	1.2	0.3	0.6
CaO (wt.%)	61.3	4.5	42.0	3.5	10.6	2.5
MgO (wt.%)	2.9	1.0	7.9	0.5	0.8	0.1
SO ₃ (wt.%)	4.0	0.7	1.8	0.2	0.1	0.2
Na ₂ O (wt.%)	0.3	0.8	0.2	0.1	12.8	0.2
K ₂ O (wt.%)	0.9	1.9	0.3	1.7	0.6	1.4
TiO ₂ (wt.%)	0.2	1.1	0.5	0.6	0.1	0.0
LOI (wt.%)	2.7	2.7	0.3	1.8	1.0	4.1
Density (g/cm ³)	3.11	2.54	2.89	2.58	2.52	2.21
Blaine (m ² /kg)	445	382	607	1763	615	930

After more than three months of curing, mortar specimens were tested for compressive strength according to ASTM C109, for chloride penetrability according to ASTM C1202, and for bulk resistivity with a Giatec RCON2™ testing device using a frequency of 1 kHz. To obtain sufficient amounts of pore solutions, cement pastes having the same formulations were prepared and cured for one year in lime water. Pore solutions were expressed with a procedure inspired by Alonso et al. (2011), in which about 300 g of paste was crushed into pieces smaller than 5 mm from the core of cube specimens, before being pressed up to a pressure of 425 MPa with an apparatus similar to that of Barneyback and Diamond (1981). The conductivity (the inverse of the resistivity) of the expressed solution was analyzed using a Mettler Toledo instrument.

RESULTS

Different Options with Similar Strength

The six investigated systems exhibit relatively similar mechanical performances, as shown in Fig. 1. The difference of compressive strengths after three months between the blended-cement mortars and the reference OPC mortar is generally less than 10% (except for the 30FA mix which is about 15% stronger than the reference). Thus, any of these mortars could be used to meet the same structural requirements in applications without exposition to aggressive environments.

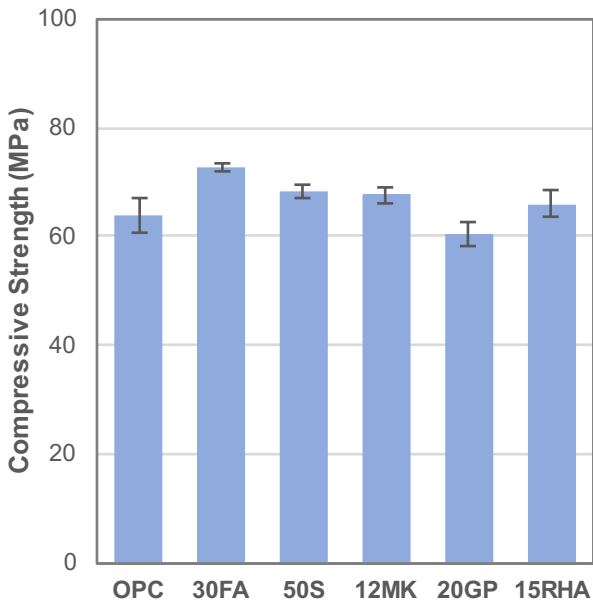


Fig. 1. Compressive strength of the investigated mortars after three months of curing.

First-Order Durability Assessment Based on Chloride Ions Penetrability

The relative performance of the investigated mortars would be much different in the case of exposure to de-icing salts and/or marine environments, as shown with the three-month ASTM C1202 results in Fig. 2.

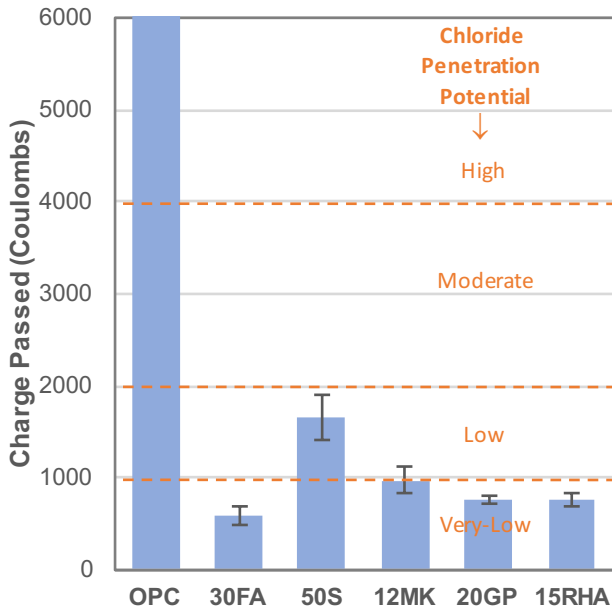


Fig. 2. Chloride penetration potential from the ASTM C1202 method after three months of curing.

Based on the charges passed categorized according to ASTM C1202, the OPC system has a high chloride ion penetration potential whereas the other systems have a very low potential (except the slag mortar with a low potential). Using these results, one could expect good durability to chloride exposure for all the blended-cement systems.

Evolution of Durability in the Long-Term, as Measured by Bulk Resistivity

Fig. 3 presents bulk resistivity results with categories for the chloride penetration potential proposed by Shane et al. (1999). After three months of curing, the results are in general agreement with the trends previously observed, i.e., the systems with SCMs have much lower chloride penetration potentials (much higher resistivity) than the OPC system. Moreover, if 30FA, 20GP and 15RHA systems show equivalent resistivity at three months, their microstructures seem to evolve differently over the long-term, with the highest resistivity for the 30FA system after one year. Based on these results, one would likely prefer 30FA, 20GP or 15RHA systems for harsher chloride exposure conditions, leaving aside 50S and 12MK systems.

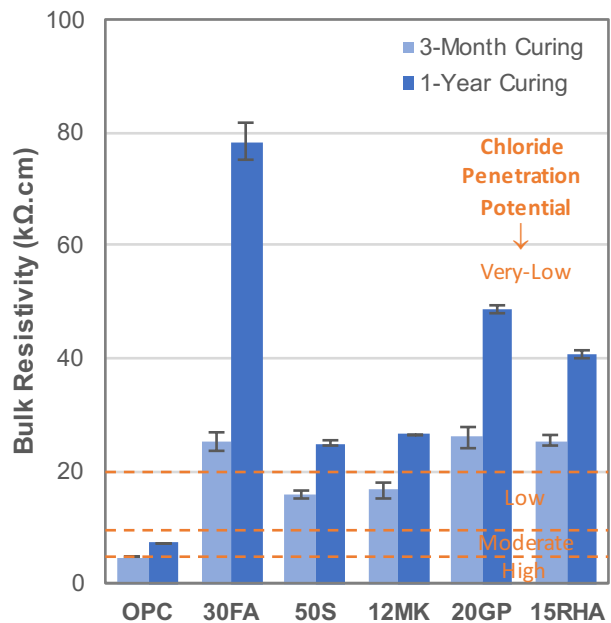


Fig. 3. Bulk resistivity measured after three months and one year of curing.

Revisited Bulk Resistivity Results Considering Pore Solution Resistivity

The pore solution was extracted from cement pastes with the same mix design as the mortars and cured for one year, enabling further appreciation of the results of Fig. 3. Fig 4 presents the pore solution resistivity relative to that of the system OPC. As expected considering previous works (e.g. Duchesne & Bérubé (1994)), the presence of 30% fly ash or 50% slag increases the resistivity of the pore solution by about 40–50%, likely by the incorporation of calcium and alkali ions in the additional hydrates from the pozzolanic reaction. This resistivity is increased even more with the incorporation of 15% rice husk ash, up to 200% that of the system OPC, which cannot be explained only by the pozzolanic reaction and requires further

investigation. Interestingly, the resistivity of the pore solution is slightly reduced with 12% metakaolin and reduced by about 30% with 20% glass powder.

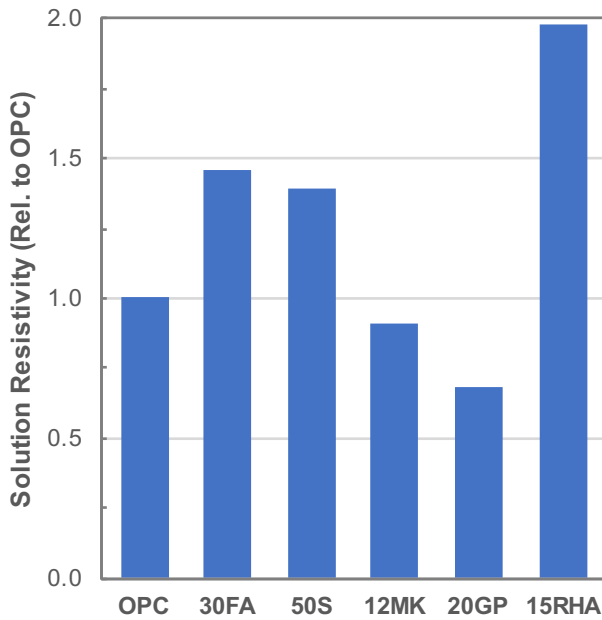


Fig. 4. Relative pore solution resistivity, as measured for solutions extracted from cement pastes after one year of curing.

Considering these large variations in the measured pore solution resistivity, the meaning of the comparisons in terms of chloride penetration potential in Fig. 2 and Fig. 3 becomes less clear. Since the bulk resistivity of mortars is intrinsically linked to the resistivity of the pore solution, an additional comparison could be made for an “equivalent” pore solution (i.e. by dividing the bulk mortar resistivity by the relative resistivity of the pore solution). Fig. 5 presents this “corrected” bulk resistivity, which could be seen as the bulk resistivity that would be measured if the porous network of all systems was emptied and filled with the pore solution of the OPC system.

Interestingly, this alternate representation changes some trends, such as a higher “corrected” bulk resistivity for the 20GP system than the 30FA system. Furthermore, the 12MK system now exhibits higher values than the 15RHA system (which does not anymore qualify in the “best-three” systems, as previously in Fig. 2 and Fig. 3).

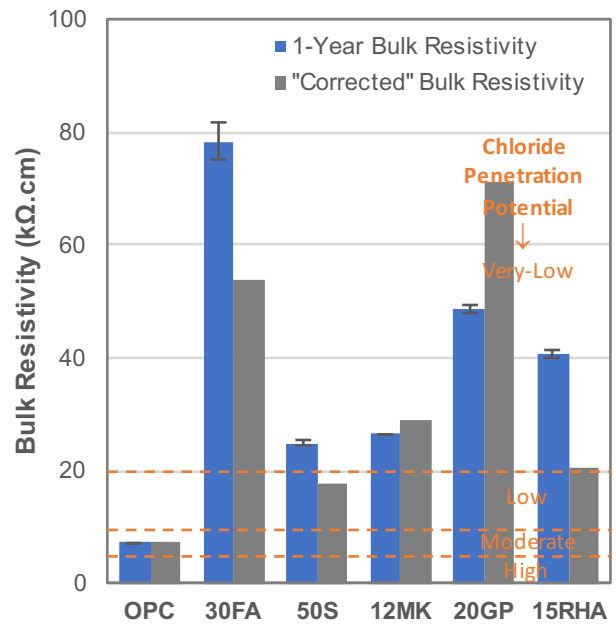


Fig. 5. Bulk resistivity and bulk resistivity “corrected” with the relative pore solution resistivity, as measured after one year of curing.

Potential Resistance to Chloride-Induced Corrosion

As described earlier, chloride-induced corrosion can occur locally when the Cl^-/OH^- ratio reaches values above 0.6 near the rebars. In addition to its very low connected porosity limiting the penetration of chlorides (i.e., a very high “corrected” bulk resistivity), the 20GP system has the unique characteristic of a higher OH^- content in its pore solution. As shown in previous work (Fily-Paré et al. 2017), the pore solution of systems with GP can have significantly higher Na^+ and OH^- contents than Portland-cement-only systems, which explains its lower pore solution resistivity. Thus, reaching the Cl^-/OH^- threshold for corrosion initiation will require more Cl^- ions than in the case of the 30FA system having a lower OH^- content (due to alkali binding in hydration products). Eventually, if the threshold is ever met, the corrosion should still progress relatively slowly due to the limited mobility of ions in the porous network (i.e., the high bulk resistivity).

Considering that concrete with 30% fly ash has been used successfully for decades in applications exposed to chlorides, this study suggests that similar systems with 20% glass powder should perform at least similarly with respect to chloride-induced corrosion (if not much better). However, validating this hypothesis would require real-time long-term corrosion testing or the measurement of other parameters than the electrical charges. Furthermore, one should consider that the trends obtained in this study do not account for all the parameters influencing chloride ingress (such as chloride binding or pore size distribution), which are currently being investigated.

CONCLUSIONS

The results presented in this study showed that the consideration of the pore solution resistivity in the interpretation of electrically accelerated chloride penetrability tests enables disclosing a more precise potential of blended-cement systems to resist chloride ingress (and chloride-induced corrosion). More specifically, the investigation of blended-cement systems at a water-to-binder ratio of 0.40 including typical dosages of different SCMs (0% SCM, 30% fly ash, 50% slag, 12% metakaolin, 20% glass powder or 15% rice husk ash) provided the following findings:

- The blended-cement systems showed similar very low chloride penetration potential after three months of curing compared to a high potential for the Portland-cement-only system (except for the slag system which showed a low potential);
- Bulk resistivity measurements confirmed the trends while showing further refinement of the microstructure after one year of curing;
- Pore solution characterization showed very different resistivity for the investigated systems ranging from ~66% to ~200% that of the Portland-cement-only system, which was employed to determine a “corrected” bulk resistivity and to question the previously presented trends;
- The glass powder exhibited a unique combination of a very high “corrected” bulk resistivity with a higher OH⁻ content in the pore solution, both contributing to delayed initiation of chloride-induced corrosion.

Finally, by considering the one-year pore solution properties in the investigation of the chloride-induced corrosion potential of blended-cement systems, a system with 20% glass powder stood out as a unique SCM (even if it shared with several other systems a very low chloride penetration potential after three months of curing). To corroborate these findings, further investigations of the same systems will include chloride migration tests (steady state and non-steady state), analyses of the pore size distributions, chloride binding capacity, and more.

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