Self-healing of self-compacting concretes made with blast furnace slag cements activated by crystalline admixture

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Abstract: Test samples were examined using a specific crystalline admixture, AR glass fibre and three types of cements with percentages of blast furnace slag (BFS) of 55%, 35% and 0%. Test specimens were loaded under compression until 90% of their failure load, in order to generate a network of micro-cracks. These samples were subsequently immersed in lime water to trigger the self-healing mechanism, followed by various tests at 28, 56 and 84 days. As BFS content ratio was increased to 55%, there was a noticeable increase in mechanical recovery and permeation reduction properties, indicating good self-healing.

Keywords: concrete structures; self-healing; materials technology; blast furnace slag; BFS; mechanical properties; permeation properties; cement; crystalline admixture; Cat-X; construction material; cracks.

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1 Introduction

1.1 Concrete technology

Concrete is a material with a long history of being used as a building material; its importance continually requires more research to solve the almost unavoidable issue of cracking in reinforced concrete. Research has focused on a scientific approach to the casual observations of self-healing cracks in concrete (Yoon, 2012; Gilford et al., 2014; Lee and Ryou, 2014; Ma et al., 2014; Yildirim et al., 2014). Repairing cracks in mechanically loaded reinforced concrete elements has been a long-time goal. The conventional repair methods either physically block water off by applying a waterproofing material with crack-bridging abilities or by injecting low viscosity resins into the cracks. By contrast, self-healing concretes (SHC) can waterproof the entire

concrete structure – as well as cracks – by applying a crystalline waterproofing admixture (Mori et al., 1996).

Dry (1994) was the first one to propose the intentional introduction of self-healing properties in concrete. This researcher began working on a self-sealing concrete that could be improved with the addition of hollow polypropylene fibres filled with methyl methacrylate adhesive as the healing agent. Crack propagation would then make the fibres break down and release the adhesive, thus healing the crack. Subsequent research about self-healing properties in cementitious materials suggested a focus on autonomous healing approaches with capsule and vascular-based self-healing (which react through contact with a second component present in the cementitious matrix or with a second component provided by additional capsules) (Tittelboom and Belie, 2013). However, autogenic healing proved to be a far more practical approach because it is based on improving the natural healing mechanism of the concrete and uses generic material components that could otherwise also be present even when not specifically designed for self-healing (Rooij et al., 2013).

1.2 Self-healing

The self-healing phenomenon, which is largely attributed to the dissolution and redeposition of hydrates, should be differentiated from improved autogenous healing, which is due to the continuing hydration of unhydrated material with CaCO₃ nucleation and subsequent crystal growth. There are two major differences:

- a the self-healing effect is observed in a system closed to CO₂, where carbonation of the dissolved Ca(OH)₂ is not possible
- b the condition under which the self-healing effect becomes significant occurs after extensive micro-cracking, usually caused by drying and/or mechanical loading during the service life of a concrete structure.

Both are water exposure dependent, while continued hydration may continue under stagnant conditions (Hearn, 1998). Also, several researchers have recently observed the formation of cementitious products such as ettringite (Aft), monosulfate (AFm) and CaCO₃ in the cracks and Ca(OH)₂ crystals in the air voids of cracked concrete. It was hypothesised that these hydration products had been leached and recrystallised in water that had flowed through the cracks (Ahn and Kishi, 2009).

Self-compacting concrete (SCC) is one of the latest achievements in concrete technology. However, in comparison to conventional concretes, SCCs shows much higher levels of thermal and autogenous shrinkage; these high strength SCCs are far more likely to crack at an early age than normal strength concretes. Theses cracks have a dangerous effect of accelerating the ingress of aggressive agents, such as chlorides or carbon dioxide (Toutanji et al., 2007; Medeiros and Helene, 2008; Medeiros et al., 2009a, 2012; Maes et al., 2014).

Investigations into the self-healing properties of SCCs subjected to mechanical loading led to the development of further hydration processes for unhydrated cementitious particles when exposed to water (Şahmaran et al., 2008). In subsequent investigations about the self-healing capabilities of cementitious composites incorporating different supplementary cementitious materials (SCM), a more evident self-healing product was observed from mixtures incorporating blast furnace slag (BFS)

(Qian et al., 2009; Şahmaran et al., 2013). Moreover, the large surface area of BFS provides more nucleating sites, as well as OH^- ions and alkalis for the pore fluid when BFS is hydrated (Li and Zhao, 2003). The hydration products from Portland-slag cements are the same as the ones from Portland cement, except that smaller quantities of calcium hydroxide (Ca(OH)₂) are found at higher slag contents. The lower Ca(OH)₂ content and the finer pore structure of BFS concrete could therefore contribute to its greater chemical resistance (Belie et al., 1996). Furthermore, cements with additions (BFS or pozzolan, for example) generally produce a denser cementitious matrix, hindering the entry of aggressive substances into the concrete (Gesoğlu and Özbay, 2007; Hoppe Filho et al., 2013; Medeiros-Junior et al., 2015; Balestra et al., 2016; Medeiros-Junior and Lima, 2016).

Moreover, chemical and mineral additives can significantly affect the formation of re-hydration products. Ahn and Kishi (2010) found that high alumina silicate materials and other chemical additives significantly affected the chemical stability and the rate of crack self-healing. There was no loss of re-crystallisation products, which were primarily composed by fibrous phases from the crystalline admixture (Cat-X) and calcite. This indicates that these fibrous phases play an important role in crack bridging (Ahn and Kishi, 2010). While most healing agents are chemically-based, the possible application of bacteria spores as self-healing agents has also been considered (Wiktor and Jonkers, 2011).

1.3 Crystalline admixture

Cat-X is a synthetic cementitious material classified as a hydrophilic waterproofing and as a permeability-reducing admixture for hydrostatic (PRAH) conditions (ACI Committee 212.3R, 2010). Thus, ACI Committee 212.3R (2010) classifies the product as an admixture for reducing permeability in hydrostatic conditions. According to Sisomphon et al. (2013), Cat-X is a synthetic cementitious material, composed by very fine treated silica and other active chemicals. Some chemical components react with calcium hydroxide to form crystalline products which disconnect pores and also fill cracks in the cementitious composites. The crystalline products can only occur when sufficient moisture is present (Sisomphon et al., 2012). Cat-X has many physical and chemical properties that are surprisingly similar to those of clay minerals. Described as re-activated cement it is considered as spherical shell-like crystals due to the large number of polar groups. For stereometric reasons these crystals have a positive charge in the outside and a negative charge towards their centre. This Cat-X structure makes the high cations exchange capacity versatile and easily achieved. Cat-X has been extensively studied for the suppression and control of alkali-aggregate reactions (AAR) in concrete through the alkali discharge resulting from its chelating function (Kuramoto et al., 1992, 1996, 2000). This water stopping technique was used to improve the impermeability property of the concrete and to decrease the migration of radionuclides (137 Cesium) during the treatment, storage and disposal of low level radioactive waste in Japan. It was also used for waterproofing the bridges and tunnels of the Japan Railways Shinkansen bullet train lines (Maki and Ohnuma, 1992).

The effect of water exposure conditions plays an important role in self-healing efficiency and in the type of healing products formed. The exposure conditions of wet/dry cycles shows that, in an optimal mechanical recovery, a mixture of calcium carbonate (CaCO₃), calcium silicate hydrate (C-S-H) and Aft is considered as major internal crack

healing products. Continuous water exposure leads to the formation of $CaCO_3$ on the crack mouth, which is preferable in terms of water tightness, however, this formation decreases the recovery speed of mechanical properties (Sisomphon et al., 2013).

Therefore, multiple cracking with relatively small crack widths (in comparison to ordinary cracked concrete) generally results in increasing the resistance of this material to the ingress of fluids and gases (Sivaraja and Kandasamy, 2009; Mechtcherine and Lieboldt, 2011). The proposed self-healing mechanisms have the added advantage that a second healing action may occur and will be easily implemented into concrete structures that are not easily accessible for maintenance and repair, such as underground structures, bridges and dams. Although the initial costs will be higher, the maintenance costs can be reduced, and the service life of the structures may be extended as damage is immediately repaired (Tittelboom et al., 2011).

Thus, the aim of this paper is to test the self-healing capabilities of concrete specimens with three different types of Brazilian Portland cements. Those cements have different BFS contents and are widely used in Brazil. Several laboratory tests were applied to investigate the mechanical recovery and decreased permeability of the samples. So, this article aims to contribute for developing a SCC with self-healing capabilities that enables the design of more durable concrete structures subjected to water exposure.

2 Experimental program

In this program, the experiments performed on hardened concrete were grouped into tests to determine the mechanical properties and into tests to determinate permeation properties. Concrete specimens for self-healing tests were loaded up to 90% of their compressive strength at 28 days of age (t'_1) . Mechanical properties (compressive strength and ultrasonic pulse velocity – UPV) was determined at 28 days old – after 28 and 56 days of lime water curing after pre-loading, respectively – those tests were executed again. Three specimens were used for each age. Permeation properties were also determined at intervals (t_1, t_2) by using water sorptivity and rapid chloride permeability (RCPT) tests.

2.1 Material properties

Three types of Brazilian commercial cements with distinct percentages of BFS (BFS) ranging from 0% until 55% were used: CPIIIRS cement (slag content about 55%) (NBR 5735, 1991; NBR 5737, 1992) is equivalent to ASTM Type IS (MS) blast-furnace slag cement. CPIIE cement (slag content about 35%) (NBR 11578, 1997) is equivalent to ASTM Type I (SM) slag-modified Portland cement. CPV cement (slag content = 0%) (NBR 5733, 1991) is equivalent to ASTM type III high early-strength Portland cement. A specific Cat-X (Cat-X) was used in this study at a rate of 2.5% by weight of cement content. Cat-X is a powder that is mixed together with cement and that have the same fineness of cement. The chemical composition and physical properties of the three cements and of Cat-X are presented in Table 1.

A mixture of aggregates was performed in order to provide a graduated particle size distribution and, therefore, a denser and less permeable concrete microstructure. Regarding the fine aggregates, natural quartz sand (70%) and crushed stone artificial sand (30%) with a maximum aggregate size of 4.8 mm were used. Both of the fine aggregates had water absorption of 0.2%, powder content respectively of 1.3 and 11.7%, and specific gravity of 2.64 and 2.68, respectively. Regarding the coarse aggregates, sources of crushed stone with a maximum aggregate size of 9.5 mm (30%) and 25.0 mm (70%) were used. Both coarse aggregates had powder content of 0.8%, water absorption of 0.7% and 0.5%, and specific gravity of 2.66 and 2.69, respectively.

A polycarboxylic superplasticizer (SP) with specific gravity of 1.20, pH of 4.0 and solid content of 40%, together with a polycarboxylate ether superplasticizer (PCE) with specific gravity of 1.05, pH of 4.5 and solid content of 30%, was used in all concrete mixtures. These two superplasticizers are commonly used together in constructions in Brazil, therefore, this paper tries to simulate real conditions. Both SP and PCE reduce surface tension between concrete components and improve the dispersion of cement particles. They also provide an improvement in cohesion and workability of the concrete, thus reducing water demand.

Properties	CPIIIRS	CPIIE	CPV	Cat-X
CaO (%)	56.84	56.19	63.33	30.9
SiO ₂ (%)	24.01	21.05	19.48	20.3
Al ₂ O ₃ (%)	7.85	5.41	5.14	1.7
Fe_2O_3 (%)	2.35	2.33	2.99	4.3
MgO (%)	2.48	5.41	5.14	19.4
SO ₃ (%)	1.7	2.85	2.95	1.0
K ₂ O (%)	0.5	0.72	0.67	0.15
Na ₂ O (%)	0.1	0.09	0.09	5.0
Loss on ignition (%)	2.72	4.73	3.41	-
Insoluble residue (%)	0.81	1.2	0.49	-
Specific gravity (g/cm ³)	2.98	3.03	3.14	2.03
Blaine fineness (cm ² /g)	4615	4450	4855	-

 Table 1
 Chemical composition and physical properties of cements and Cat-X

A viscosity modifying admixture (VMA) with specific gravity of 1.08, pH of 7.7 and solid content of 30% was added to avoid any segregation or bleeding in the mixtures. Ductile alkali-resistant (AR) type glass fibres were added to enhance the cementitious matrix in all SCC mixtures. Glass fibres also help to restrict the opening of the crack during loading, therefore facilitating self-healing.

2.2 SCC mix design, preparation and casting

Six SCC mixtures were prepared with proportions summarised in Table 2 for all three types of cements, with and without the addition of the Cat-X. Total cement content and water/cement ratio (w/c) of 0.5 (by mass) were kept constant. Cat-X was not considered as a binder.

Ingredients	Quantities	Note
Cement	392.0 kg	CPIIIRS/CPIIE/CPV
Water	196.0 kg	w/c ratio = 0.5
Crystalline admixture	9.8 kg	2.5% of cement content
Quartz sand	573.3 kg	70% of fine aggregate
Crushed stone sand	245.7 kg	30% of fine aggregate
Crushed stone 9.5 mm	651.0 kg	70% of coarse aggregate
Crushed stone 25 mm	279.0 kg	30% of coarse aggregate
SP superplasticizer	2.35 kg	0.6% of cement content
PCE superplasticizer	3.92 kg	1.0% of cement content
Viscosity modifier	1.96 kg	0.5% of cement content
AR glass fibre	0.90 kg	Alkali-resistant 12 mm

Table 2SCC mix design (kg/m³)

After mixing, slump flow, J-ring and L-box tests were executed on the fresh concrete in order to determine slump flow diameter and natural air content (Table 3). Visual inspection of fresh concrete did not detect any segregation or bleeding in any of the mixtures during the tests. Slump flow diameters of all mixtures were in the range of 680–780 mm, and J-ring and L-box tests confirmed the filling and passing abilities of the SCCs. According to Table 3, mixtures with Cat-X had slightly reduced workability. Electrosteric dispersion and stabilisation employing optimal concentrations of PCE and VMA, along with appropriate mixing procedures, contributed to producing a satisfactory SCC mix with fibres that displayed high deformability, high flow rate, and high self-consolidation in the fresh state and strain-hardening performance in the hardened state (Kong et al., 2003).

Code	Cement used	Slump flow diameters (mm)	Natural air content (%)
Mix 1	CPIIIRS	760	0.8
Mix 2	CPIIIRS + Cat-X	700	0.7
Mix 3	CPIIE	780	0.7
Mix 4	CPIIE + Cat-X	730	0.7
Mix 5	CPV	720	0.7
Mix 6	CPV + Cat-X	680	0.8

 Table 3
 Definition of mixtures and SCC fresh properties

From each concrete mixture, $\emptyset 100 \times 200$ mm cylinder test specimens were prepared for the mechanical and permeation tests, according to recommendations from test standards (NBR 12655, 2006; ASTM C1585, 2004; ASTM C1202, 2012). All specimens were cast in a single layer without any compaction. At 24 hours, specimens were removed from the moulds and stored in lime-saturated water at $23 \pm 2^{\circ}$ C for 28 days.

2.3 Compressive strength

The application of mechanical stress leads to cracking, which in turn adversely affects transport properties. Some studies show that stress induced cracking leads to a surge in fluid flow and there exists a threshold value for both the applied stress and for the resultant crack width associated with fluid permeability in concrete (Hoseinia et al., 2009). Crack intensity increases with increasing loads and it is at the maximum near failure. It was determined that load-induced micro-cracks result in an increase of permeability and in loss of compressive strength when pre-loads exceed approximately 70% of the ultimate strength (Shi, 2004). Şahmaran et al. (2008) found that when test specimens were pre-loaded to 90% of their ultimate strength and then subjected to 30 additional days of water curing, a reduction in compressive strength loss indicated substantial healing.

Thus, in this paper, after 28 days of moist curing, the compressive strength of each mixture was determined according to (NBR 5739, 1992), and the remaining specimens were pre-loaded to 90% of their corresponding compressive strength during a period of 2 minutes. It is noteworthy that the size of the micro-cracks was less than 0.11 mm, thus the micro-cracks were not visible for the naked eye in the surface of the concrete specimens. Immediately after pre-loading the compressive strength test was performed in some specimens (t_1). Some other pre-loaded specimens were then further stored in lime saturated water at 23 ± 2°C for additional 28 days and 56 days, when this test was performed again (t_2 , t_3).

2.4 Sorptivity test

The sorptivity test method is used to determine the absorption rate of water in concrete by measuring the increase in the mass of a pre-dried specimen as a function of time when only one surface of the specimen is exposed to water. The procedure suggested by ASTM C1585 (2004) was followed. Cylindrical specimens were sawed into 50 mm thick slices, and the middle slices from each specimen were used. The specimens were previously dried in oven at $50 \pm 5^{\circ}$ C during three days. Only one surface of the specimen was allowed to be in contact with water at a depth of 3 to 5 mm. The sides of the specimen were sealed with a silicone coating to assure one-directional flow through the specimen. The test was applied at ages t_1 and t_2 , so after preloading.

2.5 Rapid chloride permeability test

The rapid chloride permeability test (RCPT) is a measurement of the concrete's resistivity, which is an indirect measurement of chloride penetrability (Medeiros et al., 2009b; ASTM C1202, 2012). In this test a 50 mm thick, 100 mm diameter, water saturated concrete test specimen was subjected to a 60 V DC voltage during 6 h, according to the ASTM C1202 (2012) standard. One end of the specimen was in contact with a 0.3 M NaOH solution, while the other end was in contact with a 3.0% NaCl solution. The charge passing through the concrete sample was monitored during the test. The test was applied after preloading at age's t_1 and t_2 .

3 Results

3.1 Compressive strength and ultrasound pulse velocity

Figure 1 presents the compressive strength of concrete specimens at t'_1 (28 days of age, before preloading), t_1 (28 days, immediately after preloading), t_2 (56 days, after preloading and 28 additional days in lime saturated water) and t_3 (84 days, after preloading and 56 additional days in lime saturated water). Table 4 shows the ultrasound pulse velocity after preloading.

Figure 1 Compressive strength results - cracking and healing effect of cracks, (a) mix 1 (b) mix 2 (c) mix 3 (d) mix 4 (e) mix 5 (f) mix 6 (see online version for colours)



Code	t_1	t_2	t_3
Mix 1	4,413	4,646	4,580
Mix 2	4,514	4,540	4,560
Mix 3	4,247	4,843	4,714
Mix 4	4,566	4,665	4,799
Mix 5	4,679	4,494	4,549
Mix 6	4,,565	4,492	4,545

Table 4Ultrasound pulse velocity results (m/s)

3.2 Sorptivity test

Results of the water ingress rate through fissured specimens (F) at age t_1 and through fissured concrete specimens at 28 days and cicatrised (FC) (i.e., self-healed by immersion in lime water) at age t_2 are shown in Figure 2. Table 5 presents the water absorption rates for all concrete mixtures.

According to results, self-healing can reduce the water absorption of cracked specimens.





Code	(F) specimens at t_1 WA	(FC) specimens at t_2 WA	Reduction (%)
Mix 1	0.0041	0.0025	39.0
Mix 2	0.0033	0.0023	30.3
Mix 3	0.0057	0.0036	36.8
Mix 4	0.0044	0.0038	13.6
Mix 5	0.0057	0.0036	36.8
Mix 6	0.0044	0.0038	13.6

Table 5Water absorption rates (WA, in mm/s1/2) of fissured (F) and 'fissured and cicatrised'
(FC) specimens

3.3 Rapid chloride permeability test

Figure 3 presents the total charge passed during the 6 hour period. This amount, determined in Coulombs, is related to the concrete's ability of resisting chloride ion penetration through the fissured (F) specimens at t_1 days and through the fissured and cicatrised (FC) specimens at t_2 days.

According to Figure 3, samples with lower contents of BFS have a higher permeability to chloride. This means that using SCM such as BFS may have a significant effect on the permeability of the concrete as measured by the RCPT. While the active component in the cement (Portland clinker) is a hydraulic binder, BFS (a residue from the steel industry) also has latent hydraulic properties. According to other studies (Kong et al., 2003) this means that the hydration reaction with water must be activated by substances such as Ca(OH)₂, e.g., from clinker hydration. However, it is known that currently used SCMs such as BFS react more slowly when compared with cement. Also, Figure 3 shows that the self-healing effect contributed for reducing the load passing by the specimens.





4 Discussion

4.1 Compressive strength – effects of Cat-X

Under the 90% preloading conditions (t_1) , and as BFS content ratio was increased to 55%, there was a noticeable increase in the mechanical recovery and permeation reduction properties due to the Cat-X addition, particularly regarding compressive strength. Cat-X enhanced the compressive strength of the unhealed fissured specimens at t_1 by 12.6% on CPIIIRS [Figure 1(a) to Figure 1(b)], by 6.0% on CPIIE [Figure 1(c) to Figure 1(d)] and by 2.0% on CPV [Figure 1(e) to Figure 1(f)]. Therefore, it appears that unhealed fissured specimens with addition of BFS and Cat-X are less affected by mechanical loads. Because these fissured specimens were tested immediately after the release of the preloading (t_1) , they had no time to undergo any crack healing.

When the effect of self-healing is considered (i.e., t_2 and t_3), Cat-X also enhanced the compressive strength of FC specimens, but at a lower intensity by 5.6% on CPIIRS, 5.5% on CPIIE and 3.6% on CPV at t_2 , and 4.3% on CPIIRS, 5.5% on CPIIE and 2.0% on CPV at t_3 . According to Table 4, the effect of Cat-X was less clear in the UPV. This is probably related with the following hypothesis discussed by Shi (2004): concrete permeability depends on the pore structure, while some other properties of the concrete (electrical conductivity, resistivity, and, for this case, ultrasonic pulse) are determined by both pore structure and by the chemistry of the pore solution. Thus, according to Table 4, UPV should not be used individually as an indication of concrete performance but, in conjunction with other tests (compressive strength and sorptivity tests, for example). Although Cat-X affects other properties of the concrete, no tendency for UPV results was found. However, UPV can be used as a quality control indicator when concretes have the same components and mixing proportions. Further studies are required to confirm this trend.

4.2 Compressive strength – effects of self-healing

According to Figure 1, compressive strength is reduced at 28 days (t'_1 and t_1) after preloading. However, resistance increases after the period in lime saturated water (t_2 and t_3), indicating a self-healing effect for all samples. The results of the compressive strength recovery can be attributed to the self-healing of pre-existing micro-cracks due to the hydration of the anhydrous particles of the cement and, particularly, by the activating effect of the Cat-X on the surfaces of these cracks. This is determined as a percentage gain of mechanical properties. Figure 4 shows the percentage reduction in compressive strength immediately after applying the pre-loading (t'_1 and t_1) and also the percentage recovery due to self-healing in lime saturated water at time intervals t_1 to t_3 .

According to Figure 4, as BFS incorporation level increased up to 55%, the compressive strength recovery was more visible (CPIIIRS > CPIIE > CPV). This is explained by the fact that, in SCC mixtures with BFS, the unhydrated BFS material available for further hydration was also greater. Therefore, it appears that BFS significantly influences the self-healing of the mechanically preloaded specimens. Even after 56 days, moist curing is critical to long-term self-healing. The C-S-H gels formed through the activation of BFS reactions developed a good bond within the micro-cracks.



Figure 4 Reduction and recovery (%) of compressive strength (see online version for colours)

Results of this paper were similar to results found in other studies (Sahmaran et al., 2008; Sisomphon et al., 2013). For example, Sahmaran et al. (2008) also studied the self-healing of mechanically-loaded self-consolidating concretes. The same type, curing period and size of specimens were used in this study. However, Sahmaran et al. (2008) used fly ash instead of BFS and the Cat-X was not used. The investigated properties were the same studied in this article: compressive strength; sorptivity test; and rapid chloride permeability. Sahmaran et al. (2008) found an initial difference of 27% in compressive strength of cracked concrete compared to concrete without micro-cracks. This difference decreases to 7% after 30 days of self-healing. According to Figures 1 and 4, internal cracking due to mechanical loading initially reduced the compressive strength (depending on the type of cement); a recovery of compressive strength was also observed between 4%~30% due to self-healing effects. Therefore, it can be said that this experiment was successfully reproduced.

4.3 Sorptivity test

Water absorption rate reduced because of Cat-X's effect, at t_1 it was 24.2%, 29.5% and 29.5% on CPIIIRS, CPIIE, and CPV, respectively. Thus, Cat-X improved the water absorption of the unhealed fissured specimens.

According to Table 5, self-healing reduced water absorption between 13.6% and 39.0%. Considering only the compressive strength results, samples with higher concentrations of BFS had better results in absorption, indicating the beneficial effect of this addition. Thus, the healing time in lime-saturated water is essential to improve the water absorption of cracked concrete. According to Sahmaran et al. (2008), ongoing chemical reactions between the Cat-X and cement by-products could be driven by those saturation conditions resulting in reduced volumes of permeable voids.

According to results of water absorption (samples with Cat-X), as BFS amount increases to 55% (as shown in Figure 2), a significant decrease of the accumulated quantity of water absorbed with the square root of time is observed. Specimens healed without Cat-X show a higher recovery percentage (Table 5). This means that Cat-X had

no good effect on the absorption of the healed specimens, although the water absorption rate was reduced due to Cat-X's effect on fissured (F) concrete.

4.4 RCPT

Cat-X's effect on RCPT is between 2.4% and 8.4% (see Figure 3). The effect of self-healing is expressive, as shown in Figure 5.





Figure 5 shows a greater reduction in chloride permeability for the sample with CPV (Mix 5 and Mix 6). Although this result apparently induces that cements without BFS had better performances, it must be taken into consideration that this cement also provided higher values of charge passing through concrete samples during the test, as shown in Figure 3. This may explain the reason why a greater reduction was found for cement without BFS.

According to Figures 4 to 5 and Table 5, the effects of self-healing are more visible on the permeation properties when compared with the mechanical properties. As shown in other studies (Tittelboom et al., 2012), the recovery of compressive strength and permeation properties can be related with the progressive filling of cracks by the newly formed C-S-H gels due to their self-healing effects. Therefore, according to all tests performed in this study, such as the recovery of mechanical properties and watertightness, interesting self-healing values were obtained in all of the used specimens. The following mechanisms must be considered for a robust autogenic self-healing concrete:

- a mechanism for continuous hydration using cement composed by large amounts of BFS
- b a mechanism of chemical healing with a dosage of Cat-X to cause a cementitious recrystallisation effect in the concrete cracks
- c a mechanism of crack restriction with the addition of ductile type AR glass fibres in order to enhance the cementitious matrix.

4.5 Practical relevance of the study

In Brazil, it is common to use cement with different percentages of BFS. The study of self-healing in SCC is challenging and the research performed in this paper contributes to the subject.

In order to systematically design a self-healing technology improving the crack self-healing with alternative binders such as BFS, a Cat-X is recommended. Predicting the physical, chemical, and microbiological phenomena is important for developing techniques that can assure long-term durability for concrete structures when subjected to continuous water exposure.

This study contributes to the development of this technology and the results showed significant progress, encouraging the use of self-healing concrete. This fact also contributes to the sustainability of concrete technology.

5 Conclusions

This study investigated the self-healing behaviour of SCCs incorporating SCMs. Preloading the concrete caused a loss in its ultimate compressive strength. Internal cracking, due to mechanical loading, initially reduced the compressive strength from 3%~19% when pre-loaded until up to 90% of ultimate compressive strength. However, a recovery of compressive strength was also observed between 4%~30% due to self-healing effects.

More evident self-healing was observed from BFS mixes and from mixes containing a Cat-X. This happened because the high volume of BFS, a hydraulic latent material, had a significant amount of unhydrated particles available in its microstructures, thus contributing to the self-healing effect of the pre-existing cracks activated by the Cat-X. Also, Cat-X modified slag cement and slag-modified concretes benefited from prolonged lime water curing, showing more significant reductions in water absorption rates than control mixes. Plus, the Cat-X was effective in improving the mechanical and permeation properties of the SCC stressed by mechanical loads.

References

- ACI Committee 212.3R (2010) Report on Chemical Admixtures for Concrete, pp.1–61, American Concrete Institute.
- Ahn, T. and Kishi, T. (2009) 'The effect of geo-materials on the autogenic healing behavior of cracked concrete', *Proc., Concrete Repair, Rehabilitation and retrofitting II*, pp.235–240, London.
- Ahn, T. and Kishi, T. (2010) 'Crack self-healing behavior of cementitious composites incorporating various minerals admixtures', *Journal of Advanced Concrete Technology*, Vol. 8, pp.171–186 [online] http://www.j-act.org/headers/171.pdf (accessed 5 February 2016).
- ASTM C1202 (2012) Standard Test Method for Electrical Indication of Concrete's Ability to Resist Chloride Ion Penetration, American Society for Testing and Materials, West Conshohocken, PA.
- ASTM C1585 (2004) Standard Test Method for Measurement of Rate of Absorption of Water by Hydraulic-Cement Concretes, American Society for Testing and Materials, West Conshohocken, PA.

- Balestra, C.E.T., Lima, M.G., Silva, A.S. and Medeiros-Junior, R.A. (2016) 'Corrosion degree effect on nominal and effective strengths of naturally corroded reinforcement', *Journal of Materials in Civil Engineering*, Vol. 28, No. 10, p.04016103/1-9, DOI: 10.1061/(ASCE)MT. 1943-5533.0001599.
- Belie, N.D., Verselder, H.J., Blaere, B.D., Nieuwenburg, D.V. and Verschoore, R. (1996) 'Influence of the cement type on the resistance of concrete to feed acids', *Cement and Concrete Research*, Vol. 26, No. 11, pp.1717–1725, DOI: 10.1016/S0008-8846(96)00155-X.
- Dry, C. (1994) 'Matrix cracking repair and filling using active and passive modes for smart timed release of chemicals from fibers into cement matrices', *Smart Materials and Structures*, Vol. 3, No. 2, pp.118–123, DOI: 10.1088/0964-1726/3/2/006.
- Gesoğlu, M. and Özbay, E. (2007) 'Effects of mineral admixtures on fresh and hardened properties of self-compacting concretes: binary, ternary and quaternary systems', *Materials and Structures*, Vol. 40, No. 9, pp.923–937, DOI: 10.1617/s11527-007-9242-0.
- Gilford III, J., Hassan, M., Rupnow, T., Barbato, M., Okeil, A. and Asadi, S. (2014) 'Dicyclopentadiene and sodium silicate microencapsulation for self-healing of concrete', *Journal of Materials in Civil Engineering*, Vol. 26, No. 5, pp.886–896, DOI: 10.1061/ (ASCE)MT.1943-5533.0000892.
- Hearn, N. (1998) 'Self-sealing, autogenous healing and continued hydration: what is the difference?', *Materials and Structures*, Vol. 31, pp.563–567, DOI: 10.1007/BF02481539.
- Hoppe Filho, J., Medeiros, M.H.F., Pereira, E., Helene, P. and Isaia, G.C. (2013) 'High-volume fly ash concrete with and without hydrated lime: chloride diffusion coefficient from accelerated test', *Journal of Materials in Civil Engineering*, Vol. 25, No. 3, pp.411–418, DOI: 10.1061/ (ASCE)MT.1943-5533.0000596.
- Hoseinia, M., Bindiganavilea, V. and Banthia, N. (2009) 'The effect of mechanical stress on permeability of concrete: a review', *Cement and Concrete Composites*, Vol. 31, No. 4, pp.213–220, DOI: 10.1016/j.cemconcomp.2009.02.003.
- Kong, H-J., Bike, S.G. and Li, V.C. (2003) 'Development of a self-consolidating engineered cementitious composite employing electrosteric dispersion/stabilization', *Cement and Concrete Composites*, Vol. 25, No. 3, pp.301–309, DOI: 10.1016/S0958-9465(02)00057-4.
- Kuramoto, Y., Matsuda, Y., Nakamura, Y. and Irie, M. (2000) 'Verification of suppression of AAR by a metal carrying complex compound', *Proc.*, 11th International Conference of Alkali-Aggregate Reaction in Concrete, pp.1–9, Québec, Canada.
- Kuramoto, Y., Nakamura, Y. and Matsuda, Y. (1996) 'Effects of alkali substitution on suppression of AAR', Proc. 10th International Conference of Alkali-Aggregate Reaction in Concrete, pp.876–883, Melbourne, Australia.
- Kuramoto, Y., Nakamura, Y. and Shimamura, M. (1992) 'Control of AAR by catalysed alkali discharge', Proc., 9th International Conference of Alkali-Aggregate Reaction in Concrete, pp.564–569, London, UK.
- Lee, Y-S. and Ryou, J-S. (2014) 'Self healing behavior for crack closing of expansive agent via granulation/film coating method', *Construction and Building Materials*, Vol. 71, pp.188–193, DOI: 10.1016/j.conbuildmat.2014.08.045.
- Li, G. and Zhao, X. (2003) 'Properties of concrete incorporating fly ash and ground granulated blast-furnace slag', *Cement and Concrete Composites*, Vol. 25, No. 3, pp.293–299, DOI: 10.1016/S0958-9465(02)00058-6.
- Ma, H., Qian, S. and Zhang, Z. (2014) 'Effect of self-healing on water permeability and mechanical property of medium-early-strength engineered cementitious composites', *Construction and Building Materials*, Vol. 68, pp.92–101, DOI: 10.1016/j.conbuildmat.2014.05.065.
- Maes, M., Tittelboom, K.V. and Belie, N.D. (2014) 'The efficiency of self-healing cementitious materials by means of encapsulated polyurethane in chloride containing environments', *Construction and Building Materials*, Vol. 71, pp.528–537, DOI: 10.1016/j.conbuildmat. 2014.08.053.

- Maki, Y. and Ohnuma, H. (1992) 'Application of concrete to the treatment and disposal of radioactive waste in Japan', *Nuclear Engineering and Design*, Vol. 138, No. 2, pp.179–188, DOI: 10.1016/0029-5493(92)90294-6.
- Mechtcherine, V. and Lieboldt, M. (2011) 'Permeation of water and gases through cracked textile reinforced concrete', *Cement and Concrete Composites*, Vol. 33, No. 7, pp.725–734, DOI: 10.1016/j.cemconcomp.2011.04.001.
- Medeiros, M.H.F. and Helene, P. (2008) 'Efficacy of surface hydrophobic agents in reducing water and chloride ion penetration in concrete', *Materials and Structures*, Vol. 41, No. 1, pp.59–71, DOI: 10.1617/s11527-006-9218-5.
- Medeiros, M.H.F., Castro-Borges, P., Aleixo, D.M., Quarcioni, V.A., Marcondes, C.G.N. and Helene, P. (2012) 'Reducing water and chloride penetration through silicate treatments for concrete as a mean to control corrosion kinetics', *International Journal of Electrochemical Science*, Vol. 7, pp.9682–9696 [online] http://electrochemsci.org/papers/vol7/71009682.pdf (accessed 5 February 2016).
- Medeiros, M.H.F., Gobbi, A., Réus, G.C. and Helene, P. (2013) 'Reinforced concrete in marine environment: effect of wetting and drying cycles, height and positioning in relation to the sea shore', *Construction and Building Materials*, Vol. 44, pp.452–457, DOI: 10.1016/ j.conbuildmat.2013.02.078.
- Medeiros, M.H.F., Helene, P. and Selmo, S. (2009a) 'Influence of EVA and acrylate polymers on some mechanical properties of cementitious repair mortars', *Construction and Building Materials*, Vol. 23, No. 7, pp.2527–2533, DOI: 10.1016/j.conbuildmat.2009.02.021.
- Medeiros, M.H.F., Hoppe Filho, J. and Helene, P. (2009b) 'Influence of the slice position on chloride migration tests for concrete in marine conditions', *Marine Structures*, Vol. 22, No. 2, pp.128–141, DOI: 10.1016/j.marstruc.2008.09.003.
- Medeiros-Junior, R.A. and Lima, M.G. (2016) 'Electrical resistivity of unsaturated concrete using different types of cement', *Construction and Building Materials*, Vol. 107, pp.11–16, DOI: 10.1016/j.conbuildmat.2015.12.168.
- Medeiros-Junior, R.A., Lima, M.G., Brito, P.C. and Medeiros, M.H.F. (2015) 'Chloride penetration into concrete in an offshore platform – analysis of exposure conditions', *Ocean Engineering*, Vol. 103, pp.78–87, DOI: 10.1016/j.oceaneng.2015.04.079.
- Mori, S., Kuramoto, Y., Takagi, E.M., Horie, M. and Tanimoto, S. (1996) 'Repair of road bridge RC floor slab with advanced cracks from the floor underside', *Proc.*, 51st Annual Meeting of the Civil Engineering Society of Japan, pp.344–345, Tokyo.
- NBR 11578 (1997) Cimento Portland composto (Portland Composite Cement Specification), Brazilian Association of Technical Standards – ABNT, Rio de Janeiro, Brazil.
- NBR 12655 (2006) Concreto de cimento Portland Preparo, controle e recebimento procedimento (Portland Cement Concrete – Preparation, Control and Receiving – Procedure), Brazilian Association of Technical Standards – ABNT, Rio de Janeiro, Brazil.
- NBR 5733 (1991) Cimento Portland de alta resistência inicial [High Early Strength Portland Cement – Specification], Brazilian Association of Technical Standards – ABNT, Rio de Janeiro, Brazil.
- NBR 5735 (1991) Cimento Portland de alto-forno (Blast Fumace Slag Portland Cement Specification), Brazilian Association of Technical Standards ABNT, Rio de Janeiro, Brazil.
- NBR 5737 (1992) Cimento Portland resistentes a sulfatos (Portland Cement Sulfate-Resistant), Brazilian Association of Technical Standards – ABNT, Rio de Janeiro, Brazil.
- NBR 5739 (1992) Concreto Ensaio de compressão de corpos de prova cilíndricos (Concrete Compression Tests of Cylindrical Specimens), Brazilian Association of Technical Standards – ABNT, Rio de Janeiro, Brazil.
- Qian, S. ,Zhou, J., de Rooij, M.R., Schlangen, E., Ye, G. and Breugel, K.V. (2009) 'Self-healing behavior of strain hardening cementitious composites incorporating local waste materials', *Cement and Concrete Composites*, Vol. 31, pp.613–621, doi: 10.1016/ j.cemconcomp.2009.03.003.

- Rooij, M., Tittelboom, K.V., Belie, N.D. and Schlangen, E. (2013) Self-Healing Phenomena in Cement-Based Materials, Vol. 11, pp.1–266, RILEM State-of-the-Art Reports, Springer, Heidelberg, Netherlands.
- Şahmaran, M., Keskin, S.B., Ozerkan, G. and Yaman, I.O. (2008) 'Self-healing of mechanically-loaded self-consolidating concretes with high volumes of fly-ash', *Cement and Concrete Composites*, Vol. 30, No. 10, pp.872–879, DOI: 10.1016/j.cemconcomp. 2008.07.001.
- Şahmaran, M., Yildirim, G. and Erdem, T.K. (2013) 'Self-healing capability of cementitious composites incorporating different supplementary cementitious materials', *Cement and Concrete Composites*, Vol. 35, No. 1, pp.89–101, DOI: 10.1016/j.cemconcomp.2012.08.013.
- Shi, C. (2004) 'Effect of mixing proportions of concrete on its electrical conductivity and rapid chloride permeability test results', *Cement and Concrete Research*, Vol. 34, No. 3, pp.537–545, DOI: 10.1016/j.cemconres.2003.09.007.
- Sisomphon, K., Copuroglu, O. and Koenders, E.A.B. (2012) 'Self-healing of surface cracks in mortars with expansive additive and crystalline additive', *Cement and Concrete Composites*, Vol. 34, No. 4, pp.566–574, DOI: 10.1016/j.cemconcomp.2012.01.005.
- Sisomphon, K., Copuroglu, O. and Koenders, E.A.B. (2013) 'Effect of exposure conditions on self healing behavior of strain hardening cementitious composites incorporating various cementitious materials', *Construction and Building Materials*, Vol. 42, pp.217–224, DOI: 10.1016/j.conbuildmat.2013.01.012.
- Sivaraja, M. and Kandasamy, S. (2009) 'Characterisation of natural fibres as concrete composites for structural applications', *International Journal of Materials and Product Technology*, Vol. 36, Nos. 1/2/3/4, pp.385–395, DOI: 10.1504/IJMPT.2009.027844.
- Tittelboom, K.V. and Belie, N.D. (2013) 'Self-healing in cementitious materials a review', *Materials*, Vol. 6, No. 6, pp.2182–2217, DOI: 10.3390/ma6062182.
- Tittelboom, K.V., Belie, N.D., Loo, D.V. and Jacobs, P. (2011) 'Self-healing efficiency of cementitious materials containing tubular capsules filled with healing agent', *Cement and Concrete Composites*, Vol. 33, No. 4, pp.497–505, DOI: 10.1016/j.cemconcomp.2011.01.004.
- Tittelboom, K.V., Gruyaert, E., Rahier, H. and Belie, N.D. (2012) 'Influence of mix composition on the extent of autogenous crack healing by continued hydration or calcium carbonate formation', *Construction and Building Materials*, Vol. 37, pp.349–359, DOI: 10.1016/ j.conbuildmat.2012.07.026.
- Toutanji, H.A., Zhao, L. and Isaacs, G.J. (2007) 'Durability studies on concrete columns confined with advanced fibre composites', *International Journal of Materials and Product Technology*, Vol. 28, Nos. 1/2, pp.8–28, DOI: 10.1504/IJMPT.2007.011507.
- Wiktor, V. and Jonkers, H.M. (2011) 'Quantification of crack-healing in novel bacteria-based self-healing concrete', *Cement and Concrete Composites*, Vol. 33, No. 7, pp.763–770, DOI: 10.1016/j.cemconcomp.2011.03.012.
- Yildirim, G., Sahmaran, M. and Ahmed, H. (2014) 'Influence of hydrated lime addition on the self-healing capability of high-volume fly ash incorporated cementitious composites', *Journal of Materials in Civil Engineering*, Vol. 27, No. 6, pp.1–11, DOI: 10.1061/(ASCE) MT.1943-5533.0001145.
- Yoon, I-S. (2012) 'Effect of various mixing properties of concrete on chloride penetration through cracks', *International Journal of Materials and Product Technology*, Vol. 44, Nos. 3/4, pp.174–186, DOI: 10.1504/IJMPT.2012.050188.