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Long Term Permeability and Acid Resistance of Self-Compacting Concretes with Micro and Nano Mineral Additions

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ABSTRACT

Self-Compacting Concrete (SCC) can incorporate different types of Supplementary cementitious materials (SCM), as filler and other active mineral additions, to increase the amount of paste without increasing the amount of cement. SCM modify the SCC hardened microstructure due to the filler effect, the seeding effect as nucleation points for hydration products and the pozzolanic effect in the case of reactive SCM, as mineral additions (MA). The pore network is also modified which produce changes in the permeability of SCC. It is generally considered that the increase of fine particles improves SCC durability due to the larger compactness of the hardened material. However, MA also modifies the hydration process and consequently the hardened microstructure that could, in some cases, reduce the chemical resistance. Accordingly, the durability of SCC can also be modified by the use of MA due to the combination of permeability and chemical resistance, which mainly depends on the paste phase of the composite. When subjected to chemical attacks, SCC with MA would also modify the microstructure and the permeability properties in the long term. In order to evaluate the effect of different mineral additions, as limestone filler, microsilica, nanosilica and metakaolin, on SCC long term performance and assess their impact on its durability, an experimental study was carried out. Air and water permeability was measured on 5 years old samples SCC with different MA. It was seen that SCC air permeability was similar independently of the MA type and amount used. The samples were then subjected to acetic and sulfuric acid attacks. It was observed that the chemical resistance against acids depended on both permeability, the type of acid and the MA. The particle size and reactivity of the MA also contributed to the chemical resistance and therefore, to SCC durability.

Keywords: Self-compacting Concrete; Mineral additions; Durability; Permeability; acid attack.

1.0 INTRODUCTION

Self-compacting Concrete (SCC) hardened properties have been reported to be similar to those of conventional concretes with moderate strength. SCC usually incorporates Supplementary cementitious materials (SCM) as fillers to increase paste volume. In some cases, different types of SCM, reactive and non-reactive mineral additions (MA), are combined to improve SCC early age and hardened properties (Poppe and De Schutter, 2005; Siddique and Klaus, 2009; Barluenga *et al*., 2015 a, 2015 b).

MA modifies SCC hardened microstructure due to the seeding effect of the small size particles, the micro filler effect and their pozzolanic activity, in the case of reactive MA (Scrivener and Kirkpatrick, 2008). MA also modify the porous network of the hardened material, producing changes in total porosity, interconnectivity and average pore size and, consequently, altering SCC permeability (Barluenga *et al*., 2015 b).

It is generally considered that the extra amount of fine particles to the composite material improves SCC durability due to the increase on compactness and the reduction on permeability. However, SCM also affects cement hydration and the microstructure formation at early age which can also affect the chemical resistance of the material, mainly related to the paste phase of the composite. Therefore, the long term performance assessment of SCC requires the simultaneous study of both the physical and chemical aspects involved in the effect of external attacks on SCC microstructure and properties. Besides, the effect of chemical agents on concrete comprises both the chemical reactions and the microstructural changes which also affects the pore network and permeability, jeopardizing the overall durability. (Borosnyoi, 2016).

The aim of this study was the assessment of the effect of different SCM with various types and particle sizes on SCC durability. An experimental program was designed to analyze air and water permeability and chemical resistance against acetic and sulfuric acids on SCC samples stored in the laboratory for 5 years.

2.0 EXPERIMENTAL PROGRAM

2.1 Materials and SCC Compositions

Table 1 summarises the SCC basic compositions used in this study and the fresh properties. The modifications of the basic compositions are also described.

Table 1. Self-compacting concrete compositions (kg/m^3) and fresh properties.

	HRefg	HCA	HCAm	HCAn	HCAmk
Cement I 42,5 R	700	350	350	350	350
Limestone Filler	-	350	315	332	332
Water (*)	198.75	204	204	142	204
HRWRA.	10.50	5.25	5.25	5.25	-
Micro-Silica	-	-	35	-	-
Nano-Silica	-	-	-	79.5	-
Metakaolin	-	-	-	-	17.50
Gravel (4-20[mm]	790	790	790	790	790
Sand (0-4 [mm])	691	691	691	691	691
w/c (**)	0.36	0,71	0.71	0.71	0,71
w/fines (cem. + add.) (**)	0.36	0,36	0.36	0.36	0,36
djf(***)[mm]	875	815	750	795	865
CbE(***) %	37%	29%	36%	79%	43%

(*) Liquid water added.
(**) The amount of water included in the components (sand humidity 6.25%, HRWRA and nanosilica) was also considered.
(***)UNE 83362:2007- Self-compacting concrete. Characterization of the flowability through rebars. Slump-flow test with J-ring (djf: slump flow diameter, CbE: blocking coefficient).

HCA50 and HCA75 contain 50 and 75% of limestone filler regarding HCA, respectively, which was replaced by cement.
HCA-f has the same composition as HCA, with different amount of superplasticizer.
HCAMS50 and HCAMS25 contain 5 and 2.5% of microsilica respectively.
HCANS25 and HCAMC25 contain 2.5 % of nanosilica and metakaolin, respectively.

A reference SCC mix, only with cement (no SCM), was designed (HRefg). Then, 50 % of cement was replaced by limestone filler (P1-Betocarb, supplied by Omya Clariana S.L.), (HCA). Finally, limestone filler was partially replaced by three types of active mineral additions:

- Microsilica (m) Meyco MS610, supplied by BASF, with a real density of 2.3 kg/m^3 and an apparent density of 0.23 kg/m^3 and more than 90 % of silica content.
- Nanosilica in a water suspension (n), Meyco 685 MS supplied by BASF, with a density of 1.134±0.003 kg/m3 a 20ºC and a solid content (100ºC) of 22±1.5%.
- Metakaolin (mk), Optipozz®, manufactured by Burgess Pigment Company and supplied by Omya Clariana S.L.

Accordingly, the total weight of powder (cement, filler and additions) remained constant for all the mixes at 700 kg/m^3. Water to powder ratio also remained constant at 0.36. The superplasticizer 1.5% regarding cement weight except for the mixes HCA-f, where 0.5, 1 % and 1.5% of superplasticizer jointly with 1.6 % of a viscosity admixture, Rheomatrix 175 supplied by BASF, was used.

The physical and mechanical properties of the mixes were characterized at 28 days and several samples were stored in the laboratory for 5 years (22±2ºC and 60±10 HR) and tested afterwards.

2.2 Experimental methods

The mixes were characterized at 28 days and the physical and mechanical testing procedures have been reported in another publication (Barluenga, 2015). In this section only the experimental methods used to characterize the air and water permeability and the acid resistance of the 5 years old samples are described.

Air and water permeability of SCC mixes was measured on 150 x 300 mm cylindrical specimens using a commercial permeability device (PorosiscopeTM) based on the Figg method (Figg and Leeming, 1989). The device measures air permeability as the time required for a negative pressure in a chamber to drop from -55 to -50 kPa. Water permeability was measured with the same device as the time required in the same chamber for 0.01 ml of water to diffuse through the material sample surface (NDT James Instrument).

Chemical resistance against acetic and sulfuric acid was evaluated on 100 mm x 50 mm x 30 mm samples. Two samples of each mix were introduced in an acetic acid solution of 5% g/g of water mass with an initial pH of 7 and in a sulfuric acid solution 5.21% g/g of water mass with an initial pH of 2. Sample mass, pH of the solution, apparent density, open porosity accessible to water and P- and S- waves ultrasonic pulse velocities (UPV) measured with 250 kHz shear transducers were recorded at 1, 3, 7, 28, 56, 90 and 180 days (Girardi and Di Maggio, 2011). The acid solutions were renewed at 28, 56 and 90 days.

3.0 EXPERIMENTAL RESULTS AND ANALYSIS

The experimental results of the study are reported and analyzed in two sections. First, the main physical and mechanical properties at 28 days are summarized, although a more extensive description can be found elsewhere (Barluenga *et al*., 2015 b). Then, the experimental results of permeability and chemical attack resistance of 5 years old samples against acetic and sulfuric acid are presented.

3.1 Physical and mechanical characterization of hardened SCC (28 days)

The experimental results obtained with mercury intrusion porosimetry on SCC paste samples prepared according to the proportion of the binder phase of SCC are presented in Table 2. It was observed that the replacement of 50 % of cement by limestone filler increased total porosity and average pore diameter of the pastes. On the other hand, the replacement of limestone filler by microsilica did not modify paste porosity. On the contrary, the pastes with nanosilica and metakaolin showed lower porosity and an average pore diameter similar to the reference mix only with cement (pHRefg). The smaller particle size in these two cases can explain this change, as they increased addition reactivity, acted as microfiller and produced a seeding effect (Barluenga *et al*., 2015 b).

Table 2. Mercury intrusion porosimetry results of SCC paste samples

	Porosity [%]	Average pore diameter 4V/A [μm]
pHRefg	7.60	0.3635
pHCA	8.92	0.5839
pHCAm	8.83	0.5894
pHCAn	5.02	0.4166
pHCAmk	6.48	0.3677

Table 3 summarizes the apparent density (Dapp), open porosity accessible to water (P.open), compressive strength and compressive UPV and ultrasonic compressive modulus (E) of the SCC mixes at 28 days.

Table 3. Physical and mechanical properties of hardened samples at 28 days

Mix	HRefg	HCA	HCAm	HCAn	HCAmk
Dapp [g/cm³]	2.38	2.31	2.33	2.31	2.25
Popen [%]	0.53	2.35	2.15	2.44	1.57
Resist. Cs [MPa]	47.10	25.50	31.15	25.50	30.50
UPV [m/s]	4701.50	4660.70	4757.50	4369.00	4566.00
ES[GPa]	48.72	44.57	52.33	44.44	43.28

It was observed that the replacement of 50% of cement by limestone filler or the other mineral additions reduced apparent density and open porosity. Regarding the mechanical properties, the replacement of 50 % of cement by filler halved compressive strength, while the use of active mineral additions mitigated this reduction. The ultrasonic compressive modulus remained almost constant between 45 and 50 GPa, showing that the use of these SCM did not affect SCC mechanical stiffness.

3.2 Air and water permeability (5 years old samples)

Table 4 presents the average time of six measurents recorded in the air and water permeability tests, where the larger time, the lower the permeability. Reference SCC mix (HRefg), only with cement, showed the lower permeability values both for air and water. The SCC mixes with reactive mineral additions with smaller particle size (with nanosilica and metakaolin) showed lower permeability than the mixes with filler and with microsilica. Regarding water permeability, no differences were observed among the mixes with SCM. In a previous study, it was observed that these differences on permeability values can be measured on un-cracked specimens. If the specimens were subjected to early age cracking, permeability was reported to be similar for all the mixes, included the reference SCC only with cement (Barluenga *et al*., 2017).

Table 4. Air and Water Permeability of 5 years old samples

Composition	Air perm. (s)	Water perm. (s)
HRefg	293	193
HCA	90	46
HCAm	75	41
HCAn	106	24
HCAmk	210	36

3.3 Acid attack resistance (5 years old samples)

The chemical resistance of the SCC mixes was assessed for two types of acids: acetic, a weak acid, and sulfuric, a strong acid. To evaluate the effect on the samples, three parameters were selected: mass loss of the samples, open porosity accessible to water and the compressibility modulus (K) calculated using the UPV of compression waves (p-waves) and shear waves (s-waves) (Barluenga *et al*, 2015b).

Acetic acid resistance

The mass loss of the SCC samples subjected for 180 days to acetic acid attack are plotted in Fig. 1. A pattern can be observed for all the mixes. In a first stage, the mass loss increased slowly at a very low rate. There were some samples that even slightly increased their weight, probably due to the formation of reaction products inside the samples. In a second stage, that began at 28 days in all cases but metakaolin that began at 56 days, the mass loss increased at a faster rate.

The SCC reference mix suffered the lowest mass loss (8%), being half of the loss of the mixes with SCM (16%). Among the SCC mixes with SCM, the mix only with filler suffered lower than the mixes with active mineral additions (HCAMS, HCANS and HCANS).

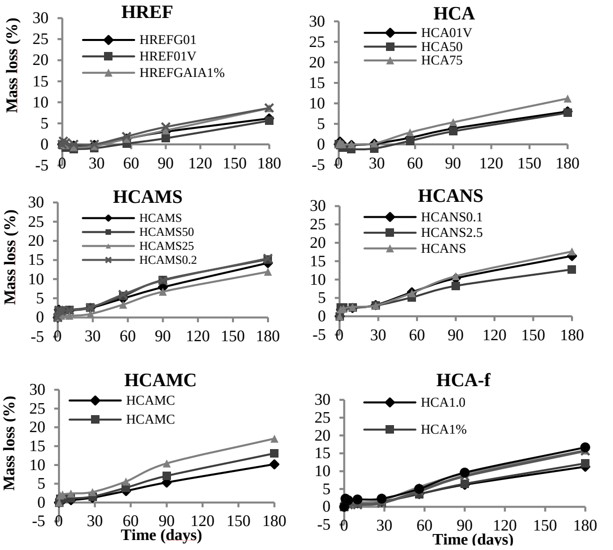

Fig. 1. Mass loss of SCC samples (%) under acetic acid attack for 180 days.

It was also observed that the amount of active mineral addition did not affect the mass loss. Accordingly, it can be said that the use of SCM influenced the chemical resistance of SCC when a weak acid is used. Regarding the amount of superplasticizer, it was observed that the lower the amount of admixture, the larger the mass loss. The inclusion of a viscosity agent also increased mass loss.

Figure 2 plots open porosity accessible to water of the SCC samples subjected for 180 days to acetic acid attack. The same two-stage pattern observed for mass loss can be identified in the evolution of this parameter. The initial stage was characterized by a moderated and quite irregular increase of porosity while the second stage that began at 90 days showed a faster linear increase. No substantial differences were observed between the mixes and the largest values reached 19-21 %

The evolution in time of the compressibility modulus (K) of the SCC samples subjected to acetic acid attack can be observed in Figure 3. As it happened with the former parameters, two stages were identified. The first stage was characterized by an irregular behavior, with an initial slight increase, then a drop in some cases but a later recovery in those cases. This period lasted 56 days. Afterwards, a pronounced linear drop occurred.

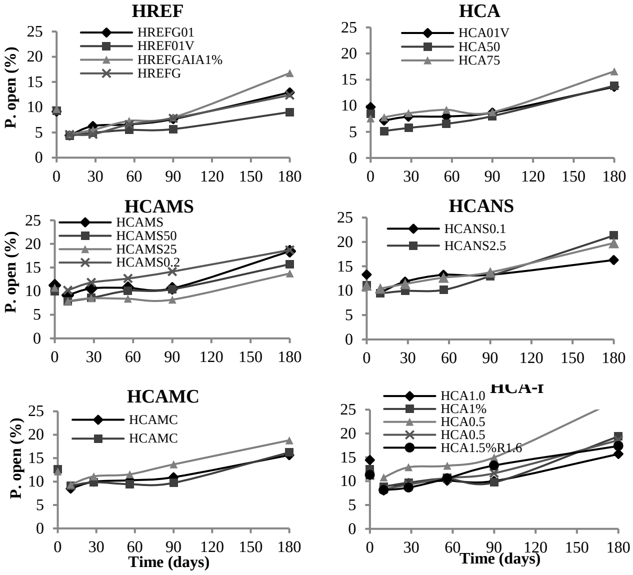

Fig. 2. Open porosity variation (%) of SCC samples under acetic acid attack for 180 days.

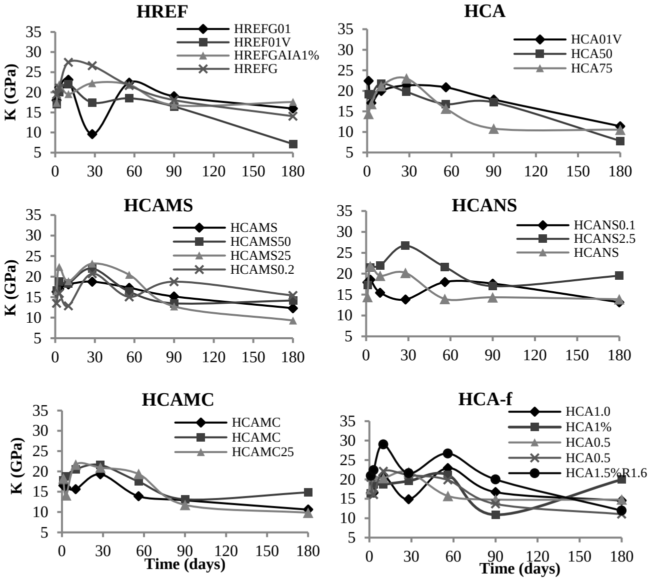

Fig. 3. US Modulus K (GPa) variation of SCC samples under acetic acid attack for 180 days.

The lowest K value at the end of the test (7 GPa) was recorded for the mix with 50 % replacement of cement by limestone filler (HCA) and the largest value (19.5 GPa) corresponded to the mixture with the highest amount of nanosilica (HCAns). The mixes with limestone filler and changes in the superplasticizer's amount (HCA-f) showed more pronounced waves on the graph in the first stage and larger K values at the end of the test (12-19GPa) when compared to HCA (1,5% of superplasticizer).

Sulfuric acid resistance

The mass loss of the SCC samples subjected for 180 days to sulfuric acid attack are plotted in Fig. 4. The same two-stage pattern was observed. The first stage of low rate increase lasted for 28 days in most cases but the mixes with nanosilica and metakaolin that reached 56 days. The second stage is again characterized by a more prominent linear increase.

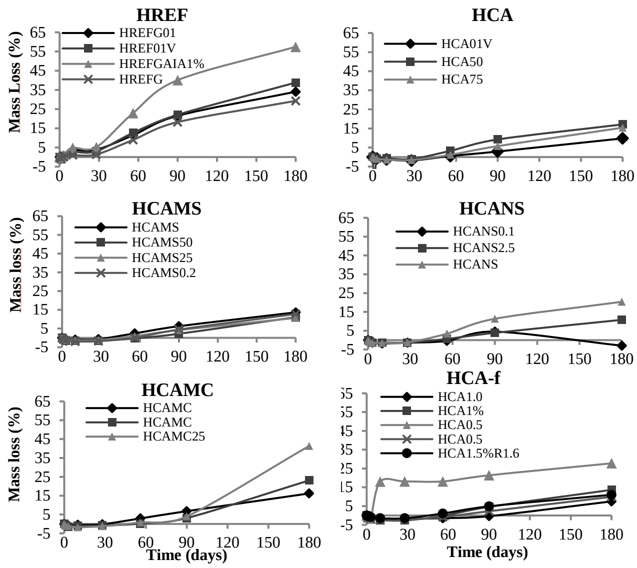

Fig. 4. Mass loss of SCC samples (%) under sulfuric acid attack for 180 days

Unlike the samples subjected to acetic acid attack, the SCC mixes only with cement were the ones with larger mass loss, being the highest during the test and reaching values of 55 %, while the mixes with SCM barely reached 20 %. In this case, no effects of the amount of superplasticizer were observed. Regarding the amount of active mineral addition, an effect on samples with nanosilica and metakaolin was observed.

Figure 5 plots open porosity accessible to water of the SCC samples subjected for 180 days to sulfuric acid attack. Again, two stages were identified. The first stage was characterized by an increase of porosity until 28 days and a decrease until 56 days. In the second stage, a significant linear increase occurred, reaching values between 15 and 20 %. SCC mixes with active mineral additions showed larger porosity than mixes with cement and with filler (HRefg and HCA). It was observed that the amount of superplasticizer also increased open porosity.

The evolution in time of the compressibility modulus (K) of the SCC samples subjected to sulfuric acid attack for 180 days is displayed in Fig. 6. There were also two stages: an initial irregular phase that lasted 90 days and a steady decrease later. SCC mixture only with filler (HCA) showed the highest value in the first stage, while SCC with microsilica (HCAms) had the largest at the end of the test. The amount of active mineral addition did affect K, with values in the case of HCAms between 9 and 21 GPa. The lowest value at the end of the test (6 GPa) was recorded for SCC mix with metakaolin.

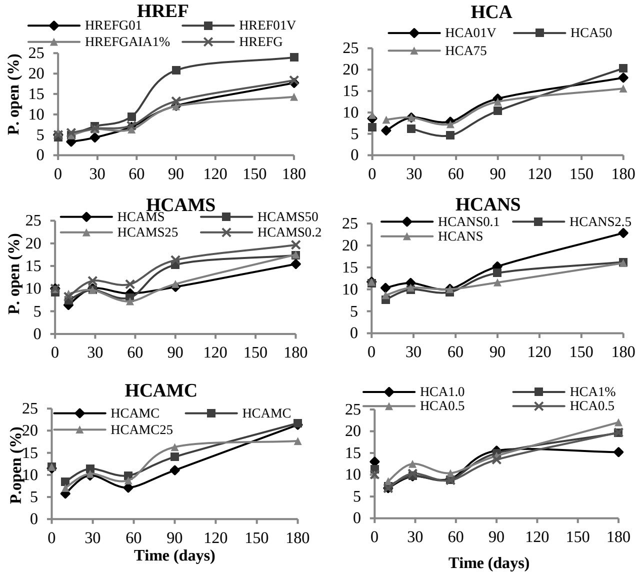

Fig. 5. Open porosity variation (%) of SCC samples under sulfuric acid attack for 180 days

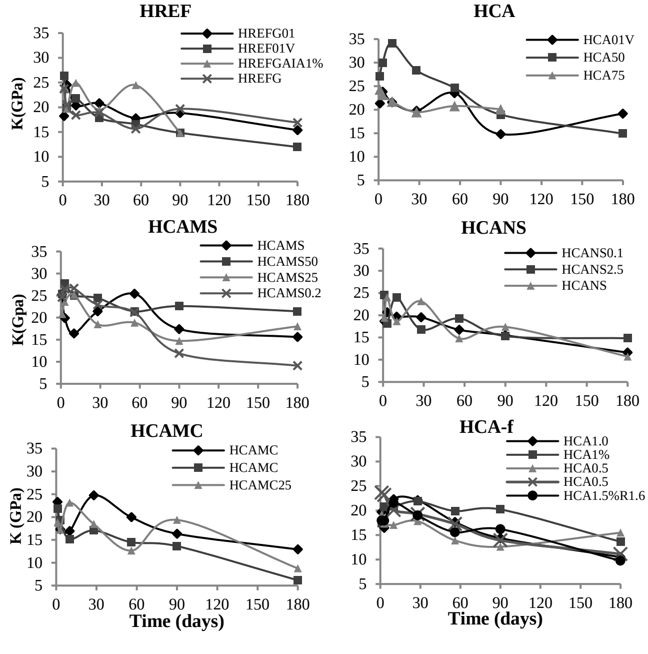

Fig. 6. US Modulus K (GPa) variation of SCC samples under sulfuric acid attack for 180 days

4.0 DISCUSSION OF RESULTS

The use of SCM produced different effects depending on the type and particle size of the compound. The replacement of 50 % of cement by limestone filler reduced the acid resistance of SCC, as expected considering it exceeded 15 % of total powder content (Celik, 2015; Ghrici, 2007). On the other hand, the replacement of filler by active mineral additions moderated this reduction, mainly due to their effect on pore network. Total porosity reduction reached up to 77.6 % for nanosilica while the average pore diameter decreased 58.79% in the case of SCC with metakaolin. However, the change on porosity did not produce a similar reduction of permeability. Limestone filler increased SCC both air and water permeability while mineral additions with smaller particle size only reduced air permeability. Water permeability was very similar for all SCC mixes with SCM. It seemed to be a relation between total porosity and air permeability, as it has been previously described (Barluenga *et al*., 2015 b). Water permeability did not show any relation with average pore diameter, contrary to what it was expected. As liquid water transport is related to capillary pores, possibly the pore size distribution could be a better comparison parameter, although the results obtained with mercury intrusion porosimetry has been questioned as an adequate technique to measure it on cement based materials (Diamond, 2000).

Regarding the acid resistance of the SCC mixes, it was observed a two-stage pattern of damage that could be followed by the three parameters selected: mass loss, open porosity accessible to water and K modulus. Mass loss varied in the first stage depending on the formation of reaction products, but showed a clear increase during the test. The same occurred with open porosity. Both are parameters related to microstructure; although mass loss depends on solid phase while open porosity depends on pore network and connectivity.

The acid resistance of the SCC mixes depended on the compositions and the type of acid, because the damage produced is a combination of easiness to access inside the sample and the chemical reactivity of the pastes.

In the event of acetic acid attack, the reference SCC mix only with cement, that showed the lower permeability for both air and water, also suffered the lowest level of damage. Considering that acetic is a weak acid and the solution pH was high, it can be said that the attack was conditioned by the transport properties of the material rather than its chemical resistance.

On the contrary, when SCC samples were subjected to sulfuric acid attack, the reference SCC mix showed the highest damage level of all. The variations on the evaluation parameters in the first stage can be related to the formation of ettrigite, which is a product of the reaction of sulfate and cement paste and crystallizes inside the pores densifying the material. In the second stage, the extensive formation of ettringite plus the new formation of thaumasite (Schmidt, 2008; Ghrici, 2007) governed the microstructure changes and the subsequent reduction of K modulus. The volumetric changes due to the formation of these two phases produce micro-cracking inside the paste phase that facilitates the acid attack. On the other hand, thaumasite formation consumes CSH and degrades aluminate phases into more soluble compounds (Schmidt, 2009). Accordingly, the SCC mixes with limestone filler showed the best sulfate resistance, which was unexpected because other authors have reported a negative effect for limestone filler contents above 20 % (Bassouni, 2007). Among the active mineral additions, metakaolin suffered larger damage due to its aluminates phases.

5.0 CONCLUSIONS

In this study, the effect of limestone filler, microsilica, nanosilica and metakaolin as SCM on SCC durability was evaluated. Air and water permeability of 5 years old samples and their chemical resistance against acetic and sulfuric attacks for 180 days was reported. The properties of a reference SCC mixture only with cement were compared to those of SCC mixes replacing cement by the SCM. The main findings of the study were:

- SCC with mixes with limestone filler and microsilica showed larger total porosity and average pore diameter than the reference mixture only with cement.
- SCM with smaller particle size, as nanosilica and metakaolin, improved physical and mechanical properties and reduced air permeability of SCC, with values similar to the reference SCC.
- The damage suffered by all the SCC samples under acid attacks followed a two-stage pattern: a first stage characterized by a slow degradation rate that lasted 30-60 days and a second stage with a pronounced damage increase following a linear tendency.
- The reference SCC mix only with cement suffered a lower damage level when subjected to acetic acid attack because it was the lowest permeable mix. The transport properties of the material governed chemical resistance against a weak acid attack.
- When the samples were subjected to sulfuric acid attack, the reference SCC mix showed the largest damage of all because it had larger amounts of hydrated cement phases which are more susceptible to react with sulfates. In this case, the chemical reactivity of the paste with the aggressive agent governed chemical resistance under a strong acid attack.

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