

Durability of blended cements containing illitic calcined clays

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ABSTRACT

Illitic clays have pozzolanic activity after thermal treatment at 950 °C causing dehydroxilation and structure collapse to form metastable aluminosilicate associated with large proportion of iron oxides (~7.0%) and alkalis (~5.0%Na₂O_{eq}).

In this paper, the performance against sulfate attack, chloride penetration and alkali silica reaction of different blended cements containing illitic calcined clays were studied.

Sulfate attack was studied using the ASTM C1012 expansion test in blended cements containing low and very high C3A portland cements. After one year, calcined clay completely controls the expansion of very high C3A-cement and improves the performance of low C3A-cement.

Chloride resistance of concrete mixtures was determined by natural chloride diffusion (ASTM C1556). Addition of calcined illitic clay (25%) refines the pore structure as indicate the MIP analyses improving the resistance to chloride diffusion and increasing the fraction of bound chlorides some part as chloroaluminate.

Alkali-silica reaction was studied using the ASTM C441 procedure with 25% calcined clay added to low, medium and high alkalis Portland cements. The illitic calcined clay reduces the expansion of Portland cements due to the consumption of alkali by the pozzolanic reaction as indicate the determination of available alkalis. Also, the alkalis provide from pozzolan does not impairs significantly the expansion of low alkali Portland cement.

Illitic calcined clay used as appropriate portland cement replacement improves the performance of cementitious materials due to the pozzolanic reaction that refines the porosity and consumes the calcium hydroxide and the alkalis in the system.

1. INTRODUCTION

Calcined clays are potential source for supplementary cementitious materials (SCM) to satisfy the cement demand in developing countries with low CO₂ emission. The addition of calcined clays into cement presents new challenges in concrete technology due to its large specific surface area, the small particle sizes that modifies the packing (Marchetti et al., 2018), the compatibility with chemical admixtures, and the significant increase in the total alkali-content for illitic calcined clays (Lemma, Irassar, & Rahhal, 2015). The pozzolanic reaction produces C-S-H and hydrated aluminium phases (Tironi, Trezza, Scian, & Irassar, 2014). These changes can modify the evolution of the fresh concrete when admixtures are used, the development of the pore structure of paste during hydration and, consequently the mechanical strength and durability of concrete.

Illitic clays are one of the most abundant clayed minerals of the earth's crust and they develop pozzolanic properties when that are thermally treated at 950 °C (Lemma et al., 2015) causing the dehydroxilation and the collapse of structure to form a metastable or amorphous aluminosilicate (Ramachandran, 1995).

The pozzolanic reaction of the calcined clay consumes the CH to produce C-S-H and/or C-A-S-H densifying the microstructure due the pore and grain size refinements (Li, Ideker, & Drimalas, 2015; Trümer & Ludwig, 2015). At later ages, the AFm phases are also formed, and they can improve or worsen the durability of the paste. The pozzolanic reaction is slow causing a low initial strength and a comparable strength with the portland cement at later ages. Additionally, it is necessary to prove that this new SCM do not increase the alkali silica reaction (ASR) with the aggregates containing reactive silica, contribute to the sulphate attack resistance and provide protection against corrosion of reinforcing steel in chloride environment.

For given environment and w/c ratio, the concrete durability depends on the course of pozzolanic reaction (the hydration assemblage and the microstructure evolution), the proportions of SCM and the type of cement used. For ASR, the pozzolanic reaction of the Illitic Calcined Clay (ICC) with high alkali content is enough to inhibit the reaction of the high alkali portland cement with aggregates; it has not contribution on the expansion with lower alkalis cements. The pozzolanic reaction would be able to reduce the content of OH⁻, K⁺ y Na⁺ in the pore solution (Li et al., 2015) and the amount of Ca(OH)₂ available. For sulphate attack, the pozzolanic reaction refines and segments the pore structure reducing the transport of the aggressive ions inside of the cement paste. The CH reduction limits the formation of ettringite and gypsum that are the main responsible of the expansion and degradation of the cement paste. In addition, the alumina available in SCM for the ettringite formation plays a major role in increasing the resistance of the sulphate attack in Na₂SO₄ solutions (Wild, Khatib, & O'Farrell, 1997). The diffusivity of chloride ions through concrete depends on the microstructure of the concrete cover, specially the size, tortuosity and connectivity of pores. Blended cements with calcined clays produce a concrete with a dense microstructure and hence an improvement in the physical protection of any embedded bars. Because of the capacity of chloride binding caused by aluminate hydrated phases of calcined clays to form Friedel's salt, the concentration of the free chloride ions in the pore water of concrete would be expected to decrease (Ampadu, Torii, & Kawamura, 1999).

The aim of this paper is analyse the performance of mortar and concrete with illitic calcined clay using as supplementary cementitious material against alkali silica reaction on cements with low, moderate and high content of alkalis, the sulphate attack on cements with high and low C₃A and the diffusivity of chloride ions in concrete.

2. MATERIALS AND METHODS

2.1 Materials

An illitic claystone from a quarry near to Olavarría, Province of Buenos Aires (Argentina) was studied. Crushed claystone were reduced to 5 mm-size particles and fired in an oven by heating at 10.5 °C/min up to 950 °C. This temperature was maintained during 90 min, and the sample

was slowly cooled into the oven. Finally, the ICC was ground in laboratory ball mill to obtain 90 % of the particle size lower than 45 µm.

The chemical composition of ICC determined by XRF is reported in Table 1. It has an Al₂O₃ content of 9.23 %, which is less than the amount of alumina incorporated by other additions such as the class F fly ash (20-30 %), granulated blast furnace slag (15-20 %) and metakaolin (MK) (> 40%). It presents a high alkali-content (Na₂O_{eq} = 3,8 %), higher than common values reported by the fly ash (< 2%), the granulated blast furnace slag (< 0,5%) and the MK (< 1%).

This ICC has the chemical requirements for Class N pozzolan (ASTM C 618): S+A+F > 70%; SO₃ < 4% and LOI < 10%. XRD analysis (Fig. 1) reveals low intensity peaks of dehydroxylate illite and the associated minerals are quartz and hematite. The density (ASTM C 188), retained on 75 and 45 µm sieves (ASTM D 422 and C 618), the Blaine specific surface area (ASTM C 204) and the particle size distribution (PSD) determined using the laser granulometer (Malvern Mastersizer 2000) are reported in Table 2.

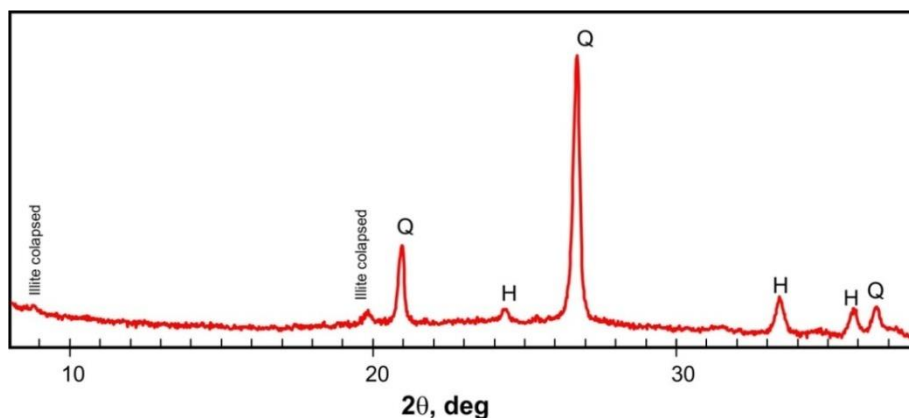


Figure 1. XRD pattern of illitic calcined clay

A Normal Portland Cement (NPC) was used for mechanical and microstructural studies. Complementary, a Low Alkali Portland Cement (LAPC) and a High Alkali Portland Cement (HAPC) were used for the ASR test; and a White Portland Cement (WPC) with high C₃A-content was used for the sulfate resistant test. Their chemical composition and their physical characteristics are reported in Table 1 and 2, respectively.

Table 1. Chemical composition and loss on ignition of calcined clay and portland cements

	Proportions, %										
	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO ₃	K ₂ O	Na ₂ O	TiO ₂	P ₂ O ₅	LOI
ICC	0.33	66.30	16.28	9.23	1.46	<0.01	5.60	0.08	0.76	0.09	0.6
NPC	60.30	20.21	3.81	4.01	0.53	3.08	1.06	0.05	-	-	2.5
LAPC	61.32	23.53	2.90	2.97	3.50	1.73	0.35	0.14	-	0.14	2.2
HAPC	63.06	20.74	3.64	1.99	3.63	2.68	1.49	0.05	-	-	2.4
WPC	>60.0	19.69	4.35	0.26	0.50	2.85	0.63	0.13	0.10	0.05	6.3

Table 2. Physical characteristics of calcined clay and portland cements

	Density, g/cm ³	Retained on sieve, %		Particle size distribution parameter, μm			Specific surface area Blaine, m ² /kg
		75 μm	45 μm	d10	d50	d90	
ICC	2.63	0.98	4.73	1.62	8.76	33.65	552
NPC	3.13	2.30	13.56	3.22	22.37	58.44	336
LAPC	3.07	3.20	13.79	3.08	23.99	81.88	276
HAPC	3.14	3.50	8.07	3.29	21.54	60.57	331
WPC	3.02	0.16	1.12	2.57	12.58	32.77	416

2.2 Characterization of blended cement and concrete mixtures

For blended cement (CPC), NPC was replaced by 25% by weight of ICC. The water demand for normal consistency (ASTM C 187) and the setting time (ASTM C 191) were determined in NPC and CPC. For the EN 196 standard mortar (cement:sand 1:3; w/c = 0.50), mortar flow was assessed according to ASTM C 230, and the compressive strength at 2, 7, 28 and 90 days was performed according EN 196-1.

Complementary, CPN and CPC pastes were prepared with w/cm of 0.5 and cured in sealed plastic bags at 20 °C during 28 days to identify the hydration compounds and the pore size distribution. At this time, paste was ground to particle size lower than 45 μm, to perform the XRD analysis on X'Pert Philips PW 3710 diffractometer (CuK α radiation at 40 kV and 20 mA) and the pore size distribution on mercury intrusion porosimeter (Pascal 140 and Pascal 440 – Thermo Scientific) from 100 to 0.04 μm on vacuum dry sample.

Natural fine siliceous sand (FM = 2.35 and density = 2.67) as fine aggregate and granite crushed stone (Max size = 16 mm and density = 2.70, UVW compacted = 1560 kg/cm³) as coarse aggregate were used in concrete mixtures. NPC and CPC concretes were proportionated with a fine/coarse aggregate ratio of 0.43; w/cm = 0.50 and unit content cement of 350 kg/m³. A polycarboxylate-based superplasticizer (BASF, Germany) with 40 % of active ingredient was used. The difference of density of the blended cement was compensated modifying the siliceous sand content. The target concrete slump (ASTM C 143) was achieved by adjusting the SP-dose (0.23-0.25 kg/m³). Compressive strength (ASTM C 39) on concrete cylinder of 100 x 200 mm and the volume of permeable pores (ASTM C 642) were determinate at 2, 7, 28 and 90 days.

2.3 Durability tests

The pozzolan effectiveness to inhibit the alkali-silica reaction (ASR) was tested using the expansion test developed in mortar bars with Pyrex® glass (ASTM C 441). One group of prismatic mortar bars (w/cm = 0.45 and cement/Pyrex® glass = 1:2.25) with LAPC, HAPC and NPC and other group with these cements containing 25 % (w/w) of ICC replacement were molded. After 24 hours, cured in lime-water it was measured initial length and the bars test were stored in a container at 38 °C according to ASTM C 227. At 14, 28, 56 and 365, the length change of the bars was measured and the expansion was calculated. According to ASTM C 411, the potential effectiveness of pozzolan is determined as the expansion reduction at 14 and 56 days. As suggest the ASTM C 311, the combination of pozzolan with a LAPC will not cause an increase of expansion due to the alkali content (5.65 % Na₂O_{eq}) in the pozzolan. For blended cements, ASTM 1157 standard establishes that the expansion should not exceed the limit of 0.02% at 14 days and 0.06% at 56 days, respectively.

For the determination of free alkalis in the paste pore solution, cylindrical specimens (diameter 55 mm and 100 mm height) of paste (w/cm = 0.45) were cast for LAPC and HAPC cements with and without 25% ICC. Cylinders were cured following the same procedure that the corresponding to Pyrex® test. At 7, 14 and 56 days, the pore solution was extracted using the methodology proposed for Barneyback and Dyamond (Barneyback Jr & Diamond, 1981) loading the paste

specimens until stress ~ 500 MPa. The content of free alkalis (Na_2O and K_2O) was determined immediately using the absorption and atomic emission spectrophotometer.

Sulfate resistance was determined using the test of the expansion of mortar bars (ASTM C 1012) with the NPC and the WPC with a high content of C_3A (11.1 %). The percentages of calcined clay replacement were 20% and 40% by weight. The flow of CPN mortar ($w/c = 0.485$ and cement-graded sand = 1:2.75) was determined and the water of blended cement was adjusted to obtain the same flow in NPC-ICC mortars. For WPC and WCP-ICC mortars, a constant w/cm (0.485) was used and the mortar flow was adjusted using superplasticizer (Viscocrete). The bars and cubes were molded according to ASTM C 157 and ASTM C 109 procedures, respectively. After 24 hours they were demolded and cured in lime water at 20 °C. After that mortar compressive strength reached to 20 MPa, test bars were immersed in Na_2SO_4 solution (0.352 mol/l) at 20 °C with a periodically pH-control through a titration with a combined solution of Na_2SO_4 (0.352 M) and H_2SO_4 (2N). This procedure was used as alternative to the periodically renovation of NaSO_4 solution. The solution is neutralized and the concentration of Na^+ and SO_4^{2-} ions is restored. As a pH indicator, few drops of phenolphthalein were used (Gonzalez, Rahhal, Irassar, & Donza, 1998). According to ASTM C 1157, blended cement is considered as high sulfate resistant (HS) when the expansion does not exceed 0.05 % at 6 months or 0.10 % at 12 months.

Chloride penetration into the concrete was determined according to ASTM C 1556-04. This test method covers the laboratory determination of the apparent chloride diffusion coefficient (D_a) for cementitious mixtures by measuring the acid soluble chloride content. Concrete cylindrical specimens (100 x 200 mm) were curing in water up to 28 days. Then, a 75 mm thick disks from the ends were cut using a diamond sawing and a second 20 mm thick disk was cut to determine the initial chloride ion content. The 75 mm thick disks were coated with epoxy resin along the perimeter but not in the ends. The saturated samples were placed in plastic containers and fully immersed in high concentrated NaCl solution (165 gr NaCl /liter). All containers were sealed with plastic lids to prevent evaporation. After 35 days, the test specimens were removed from the solution and ~ 20 g of concrete powder was extracted at eight different depths (1, 2, 4, 6, 9, 12, 15, and 18 mm) from the exposed face using a dry grinding device. The collected powder was used to determine the acid soluble chloride content (total chloride, CT) and the water-soluble chloride content (free chloride, FC) according to EN 14629 standard. The chloride binding capacity of the different binders was evaluated as the difference between the CT and CF content. The results are expressed as mass % chloride per mass of concrete. The value of the surface chloride concentration (C_s) and apparent chloride diffusion coefficient (D_a) were calculated by the best fitting of the error-function solution to Fick's second law using a to the measured total chloride ion content at different depths by means of a nonlinear regression analysis.

3. RESULTS AND DISCUSSION

3.1 Characterization of blended cement:

Water demand and setting time for the normal consistence paste are presented in Table 3. For CPN+25ICC the water demand was a little more (~ 7%) than the control paste. It can be seen that the initial and final setting time starts slightly before with the addition of the ICC.

Table 3. Characteristic of blended cement with replacement of 25% ICC by weight

	Cement Paste			Mortar				
	Water demand, %	Setting time, minutes		Mortar flow, %	Compressive strength, MPa			
		Initial	Final		2 days	7 days	28 days	90 days
NPC	27.2	205	335	132	21.6	35.8	47.9	52.7
CPC	28.2	185	330	128	17.6	30.3	40.1	48.2

For standard mortar, NCP has a flow of 132% and the CPC flow is comparable with the control mortar (Table 3) with better water retention judged by the water crown. However, the mortar flow does not modify despite observing slight increase in water demand of cement.

Figure 2 shows the compressive strength of the NPC and CPC mortars. At all ages, the compressive strength CPC mortar is lower than the corresponding to NPC, but always higher than 75% of NPC. At 2 days, the strength activity index (SAI) is 0.81 while it is 0.84 and 0.85 at 7 and 28 days. Finally, the SAI is 0.92 at the 90 days.

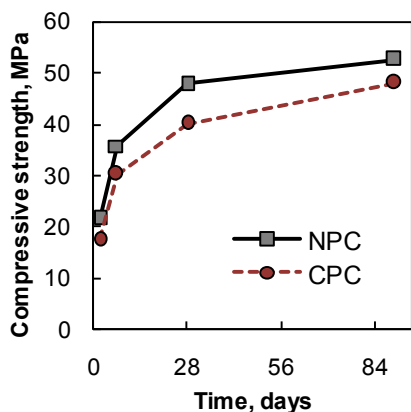


Figure 2. Compressive strength of NPC and CPC mortars.

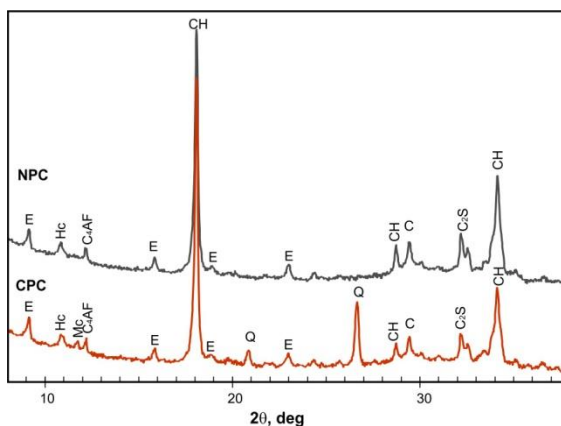


Figure 3. XRD of NPC and CPC pastes at 28 days.

3.2 Hydration and porosity

Figure 3 shows the XRD patterns for NPC and blended cement at 28 days. For NPC paste, ettringite (E) and CH are the hydrated compounds accompanied by calcite (C) and un-hydrated cement phases (C_4AF and C_2S). For blended cement, E and CH are also detected with low intensity peaks in comparison with NPC, and quartz (Q) appears as clay-associated mineral. For NPC cement, the AFm phases was hemicarboaluminate (Hc) and the insipient transformation of hemicarboaluminate to monocarboaluminate (Mc) was found in CPC. Then, it would have expected that Mc is the predominant AFm phase at later ages (Marchetti et al; 2018).

Figure 4 shows the cumulative pore volume obtained by MIP. The total porosity of blended cement (0.18%) is slightly larger than the corresponding to NPC (0.17%). However, CPC presents a large volume of capillary pores ranged from 1.0 to 0.1 μm , and large volume of very fine pores ($< 0.02 \mu m$). The pore threshold is similar for both studied pastes (0.10 and 0.08 μm for NPC and CPC, respectively). For this replacement level, the dilution effect causes a large volume of pore in the capillary pore range and the pozzolanic reaction increases the finest pores ((Wild et al., 1997; Marchetti et al., 2018)

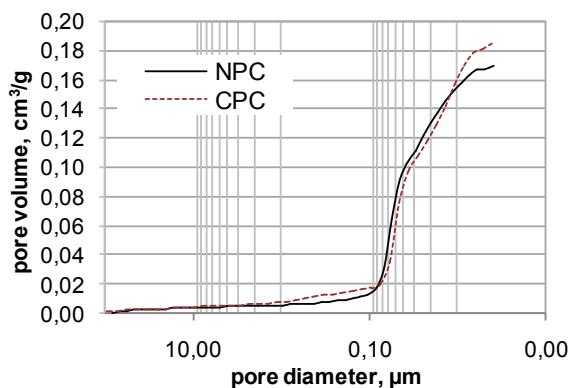


Figure 4. Cumulative pore size distribution for NPC and CPC paste at 28 days.

3.3 Concrete performance

For both concretes, the SP-dose to obtain a plastic consistency was similar and the slump was 7.5 and 7.0 cm for de NPC and CPC concrete, respectively. Compressive strength of the CPC concrete (Figure 5) is lower than the corresponding to NPC at all ages. At 2 days, the relative compressive strength was 0.71 and it increases up to 0.89 at 7 days. At 28 and 90 days, the relative compressive strength is 0.87 and 0.94. The strength gain is high from 2 and 7 days (57 and 94 for CPC and NPC, respectively). Although, both concretes present lower strength-gain between 7 and 28 days (15 and 13 % for NPC and CPC, respectively) and between 28 and 90 days (26 and 35 % for NPC and CPC, respectively).

It is observed that ICC has a good pozzolanic activity and CPC concrete develops a compressive strength similar to the NPC concrete. But the dilution effect caused by the ICC replacement reduces the available amount of NPC to react at early ages, increasing the effective w/c (0.68 for 25% replacement). The relative compressive strength, higher than 0.75, confirms the stimulation effect at early ages.

The porosity of the concrete (Figure 6) indicates that CPC has a large volume of permeable pores than the PC. The main difference occurs at seven days and it is reduced when curing time increases. At 28 days, the pore volume is 10.9 ± 0.2 % for NPC concrete and 11.7 ± 0.3 % for CPC concrete. The reduction of permeable pore volume from 28 to 90 days is slightly high in CPC concrete.

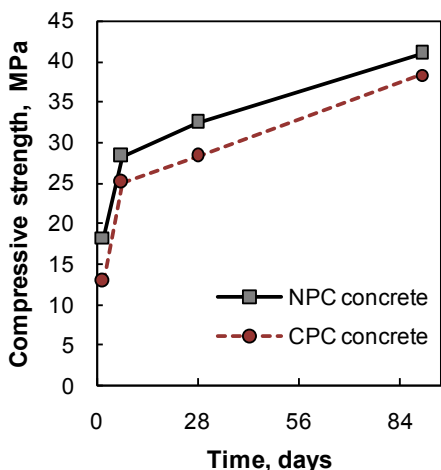


Figure 5. Concrete compressive strength

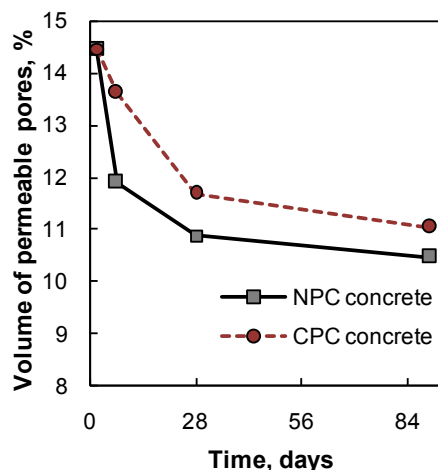


Figure 6. Volume of permeable pores in concrete

3.4 ASR Expansion

Figure 7 shows the expansion for mortar bars tested with High and Low Alkali Portland Cements without or with 25% ICC registered up to 1 year.

For the HAPC (Figure 7), the control bars have 0.221% of expansion at 14 days, which greatly exceeds the limit proposed by ASTM 1157 standards (0.020%). For the mortar HAPC+25ICC, there is a notable decrease in the expansion (0.045%), but exceeds the limit required at 14 days. At 56 days, the expansion of blended cement (0.057%) is lower than the limited proposed by ASTM 1157 standards (< 0.060%). At one year, the HAPC reaches an expansion near to 0.350%; while the HAPC+25ICC present an expansion of 0.061%. Although, the expansion limit at 14 days exceeds the limit proposed by ASTM 1157 to considered ICC as inhibitor of the ASR. When ICC is incorporated, the expansion is reduced ~ 500% and it is attributed to large part of alkalis released by HAPC are consumed by the pozzolan reactions.

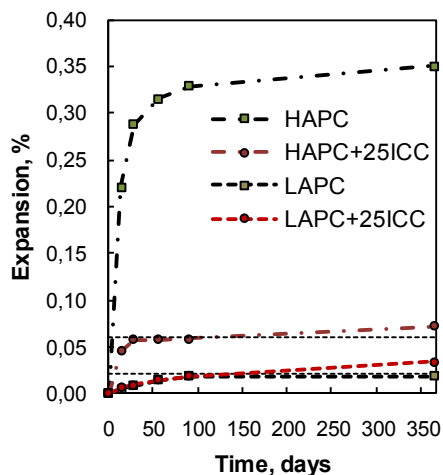


Figure 7. ASR Expansions for mortars bars for LAPC, HAPC and ICC cements

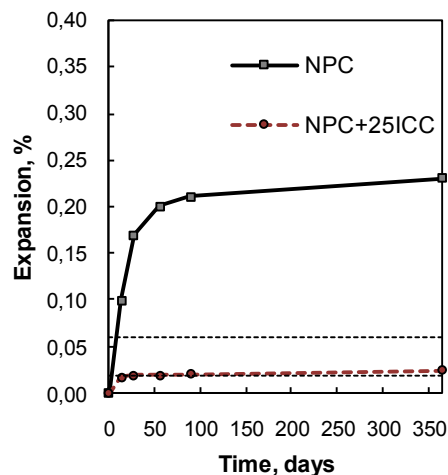


Figure 8. Expansions for mortars bars for NPC and NPC+25ICC

Figure 7 also shows the expansions up to one year for the mortar bars cast with LAPC. This mortar has very low expansion of 0.005 %, 0.014 % and 0.018 % at 14, 56 and 365 days, respectively. For the LAPC+25ICC, the expansion was 0.006 %, 0.014 % and 0.034 %, at 14, 56 and 356 days, respectively. At 14 and 56 days, the expansion values of LAPC+25%ICC are very similar to the control mortar indicating that ICC does not provide alkalis to the pore solution at early ages. At one year, the expansion of the LAPC+25ICC mortar reaches the double of the mortar control and this could be attributed to a slow liberation of the alkalis from the ICC.

For Normal Portland Cement (Figure 8), the expansions up to one year is intermediate between the reported values for LAPC and HAPC. The NPC expansion was 0.100 %, 0.200 % and 0.230 % at 14, 56 and 365 days respectively. The incorporation of 25 % ICC reduces drastically the expansion reaching to 0.001 %, 0.012 % and 0.020 % at 14, 56 and 356 days, respectively. Therefore, the blended cement qualifies as cement resistant to the ASR.

3.5 Alkalis on pore solution

Table 4 reports the concentration of the free alkalis in the pore solution of pastes cast with LAPC and HAPC with and without 25 % of ICC. The alkalis in the pore solution of the pastes reveals the role of the ICC in the release/binding alkalis during the hydration: when the free alkalis decrease with respect to portland cement indicates that the ICC reacts to form new compounds (for example, the N-A-S-H gel) and/or bind them into the hydration compounds, especially C-S-H. Then, the alkalis do not remain free to react with the amorphous silica to generate the deleterious reaction ASR that causes the expansion.

Table 4: Concentration of alkalis (Na and K) in the pore solution of HAPC and LAPC with and without replacement by ICC

Paste	Alkalis concentration, (ppm)								
	7 days			14 days			56 days		
	Na ₂ O _{eq}	K ₂ O	Na ₂ O	Na ₂ O _{eq}	K ₂ O	Na ₂ O	Na ₂ O _{eq}	K ₂ O	Na ₂ O
HAPC	41430	57885	3342	24455	32280	3215	19107	24692	2860
HAPC+25ICC	28301	39309	2436	11760	15395	1630	11920	16928	782
LAPC	8779	11450	1445	9718	12375	1575	7019	8942	1136
LAPC+25ICC	15355	20920	1590	9676	13245	980	8969	11996	1076

As expected, for HAPC the alkalis concentration (Na⁺ and K⁺) in the pore solutions is higher than that corresponding to the LAPC cement. The ICC replacement by HACP causes a reduction of the K⁺ and Na⁺ concentration in the pore solution at 7 days and then the K⁺ content decreases

very fast between 7 and 14 days and less the content of Na^+ . For the LAPC, the ICC replacement increases the content of K^+ and slightly the content of Na^+ at 7 days. At 14 days, the content of K^+ presents similar values while the Na^+ is reduced. The content of equivalent alkalis is higher up to 14 days and then its value is similar to that obtained for the LAPC, which justifies that the alkalis contained in the ICC participate in their hydration processes and they are bound after the 7 to 14 days.

3.6 Sulfate Resistance

Figures 9 and 10 shows the expansion for mortar bars made with NPC and WPC with 0, 20 and 40 % replacement by ICC in sodium sulfate solution, respectively

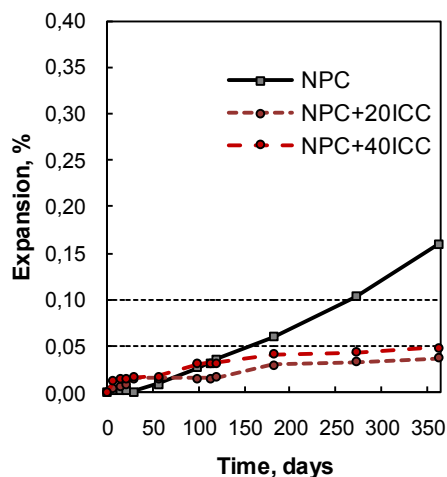


Figure 9. Expansion for NPC with 0, 20 and 40 % ICC in Na_2SO_4 solution

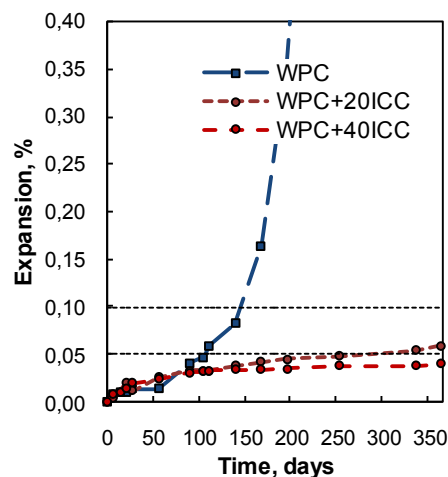


Figure 10. Expansion for WPC with 0, 20 and 40 % ICC in Na_2SO_4 solution

Figure 9 shows the expansion for NPC mortar containing 0, 20 and 40 % ICC. NPC has a poor performance against the sulfate attack, despite the low C_3A -content in this cement and the expansion at 180 and 365 days was 0.059 y 0.160 %, respectively. For both ages, the expansion is higher than the limit proposed to be considering a sulfate resistant cement and this behavior is attributed to the high C_3S content (63 %) that promote the gypsum formation causing some expansion for this test procedure with pH-control (Gonzales & Irassar.1998). On the other hand, the replacement of 20 and 40 % of ICC reduce the expansion attaining to 0.030 and 0.041 % at 180 days. Later, the expansion values remain for the 270 and 365 days. Both replacement level used shows a good performance against the sulfate attack with expansions lower than the limits proposed for 6 and 12 months.

For WPC (Figure 10), the expansion increases faster and the mortars bars exceeds the expansion limit of 0.10 % at 146 days. As expected, the ICC replacement reduces significantly the expansion and both blended cements register a lower expansion than the limit proposed at 6 and 12 months. The mortar with a replacement of 20 % of ICC exceeds the 0.05 % at 276 days. This behavior is attributed to the pozzolanic reaction that reduce the sulfate penetration and the consumption of $\text{Ca}(\text{OH})_2$ contribute to the reduction gypsum and ettringite formation in the blende cements.

3.7 Chloride profile

After 35 days of immersion in NaCl solution, the total (solid line) and free (broken line) chloride profiles for NPC and CPC concretes are shown in Figures 11 and 12, respectively. For all concretes, the total chlorides (TC) are higher than the free chlorides (FC) and their concentration decreases when the depth of the specimen increases. For CIC concrete, the concentration profile of the TC and the FC profile is very close. For CPC profile, the difference between TC and FC is slightly higher, indicating that ICC does not generate a large amount of bound chlorides. Although the ICC has an alumina content of 16.3 %, it is possible that only part of this alumina is reactive to form AFm phases that reacting with the chlorides to form Friedel's salt.

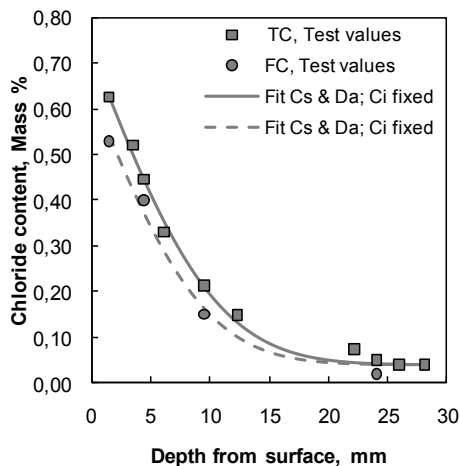


Figure 11. Chloride profile for NPC

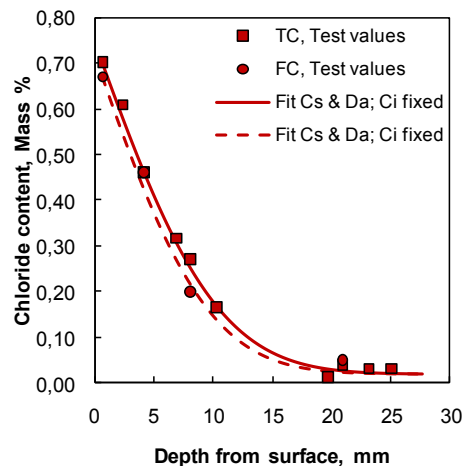


Figure 12. Chloride profile for CPC

Table 5 reports the Cs and the Da for TC and FC for both concretes. Da has similar order in both concretes, and it is slightly lower for CPC than that NPC concrete. Instead the dilution effect, CIC concrete has a compact microstructure that increases the resistance of the chloride penetration. This densification could be produced by physical or chemical effects. Firstly, the ICC addition fills the vacuums, making the pore structure more compact and tortuous. The second because the ICC was able to develop the pozzolanic reaction making secondary hydration products. Which is according to the conclusion made by Sabir (Sabir, Wild, & Bai, 2001) that the presence of pozzolans alters the structure of the pores in the concrete, which greatly improves the resistance of the water transport and the diffusion of harmful ions that conduce to deterioration of the matrix.

Table 5. Superficial concentration and chloride diffusion coefficient (Da) for total and free chloride of NPC and CPC concretes.

Concrete		Cs (mass %)	Da (m ² /seg)
NPC	Total Chloride	0.72	11.2 · 10 ⁻¹²
	Free Chloride	0.63	9.4 · 10 ⁻¹²
CPC	Total Chloride	0.75	10.9 · 10 ⁻¹²
	Free Chloride	0.72	9.4 · 10 ⁻¹²

4. CONCLUSIONS

Based on the results of this study, the following conclusions can be drawn:

Blended cement containing 25% illitic calcined clay do have significantly increase on the water demand for the paste and the setting time is slightly in advance. The compressive strength of mortar is lower than that the control mortar, but the strength activity index is 0.85 to 0.92 from 2 to 90 days. At 28 days, the hydration compound assemblage is similar and the porosity is equivalent or better than the corresponding to Portland cement.

For Alkali Silica Reaction, the addition ICC reduce significantly the expansion of high alkali content cement, but it could slightly increase the expansion for low alkali cements at early ages. The free alkalis in the pore solution decreases as the progress of the hydration indicating that the alkalis are bound or combined with the hydration products.

For sulfate attack, the addition of ICC reduces the expansion during sulfate immersion for both low and high C₃A content cements. The expansion is reduced when the replacement increase from 20 to 40% in both cements allowing the standard limits to considered the blended cements as high sulfate resistant cements

For chloride penetration, the addition of ICC did not produce significant variation in the chloride diffusion coefficient at 28 days' indication the pore structure is well developed at this time to improving the resistance against the chloride ions diffusion.

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