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Studies on illitic calcined clays as possible inhibitors of the Alkali-Silica Reaction (ASR)

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Abstract

Illitic calcined clays acquire pozzolanic properties after thermal activation at 950 °C. Calcination causes dehydroxylation and its structure collapse forming a meta-stable alumina-silicate. In this paper an illitic calcined clay (ICC) from Olavarria, Province of Buenos Aires, Argentina, was evaluated to determine its potential as an inhibitor of the alkali-silica reaction (ASR). As a first instance, ASTM C 1260 test "Potential Alkali Reactivity of Aggregates (Mortar-Bar Method)" was applied to characterize a high reactive natural sand from Argentina. Confirmed the high reactivity of this sand, it was evaluated the potential of the ICC to control the ASR, and if so, then percentage of replacement for this objective. Following the ASTM C 1567 (Accelerated Mortar-Bar Method), mortar bars were cast using the reactive sand and a normal portland cement (OPC) replacing by different percentages (0,15, 25, 35 and 45%) of ICC by mass. The ASTM 441 test (mortar bar expansion test with Pyrex® glass at 38 °C) was applied with some selected replacement percentages of ICC (25% and 35%) to characterize the ICC as inhibitor of the ASR. At the age of 2, 14 and 28 days, the pore solution was extracted from pastes to determinate the amount of free alkalis by the atomic absorption spectrophotometer. As a complement, some mortar bar test where analyzed by petrography using SEM to identify the ASR and hydration products. The results indicate that a large proportion of ICC (35%) is needed to control the ASR reaction of high reactive sand, but the blended cement cannot be classified as ASR-inhibitor.

Keywords: illitic calcined clays; accelerated mortar bar; pyrex; free alkali in pore solution

1. INTRODUCTION

Illitic clays are one of the most abundant minerals from the earth's crust. Coming from the alteration of feldspars and micas in the rocks during the weathering process, these clays acquire pozzolanic properties when are thermally activated at ~ 950 ºC [1] due to dehydroxylation and structural collapse of illite to form an amorphous alumina silicate [2]. Blended cements with partial replacement of Portland clinker (moderate or high alkali-content) by illitic-calcined clay (ICC) may reduce the alkali silica reaction (ASR) of concrete made with reactive aggregates [3]. This is attributed to the pozzolanic reaction that consume CH to form C-S-H and C-A-S-H densifying the matrix by the pore size refinement process [3, 4]. Other calcined clays, such as metakaolin, also reduce the ASR-expansion. This is attributed to changes in the structure of C-S-H, the pH-reduction in the pore solution and the alkalis adsorption on the surface of the gel showing a decrease in the dilution gradient [3, 5].

Argentine is an extensively country with several mineralogical types of rock as aggregate sources. From different country regions, several aggregates have been characterized as potentially reactive with alkalis in concrete. To make durable concrete structures, a cement qualified as resistant to ASR is required. In this way, the development of ASR-resistant blended cements with the available pozzolan in each country region becomes as opportunity.

The aim of this paper is to evaluate an illitic calcined clay (ICC) produced in Buenos Aires Province to produce a blended cements as possible ASR reaction inhibitor. For this purpose, the potential reactivity of a natural siliceous sand, called Arena de Medanos (AM), was firstly determined using the ASTM C 1260-AMBT test "Potential Alkali Reactivity of Aggregates (Mortar-Bar Method) " [6]. Its potential reactivity is attributed to the presence of volcanic glass. Confirmed the high reactivity of AM-sand, the ASTM C 1567 test was used to determine the minimum percentage of ICC replacement that may control the ASR-reaction of the AM-sand. For the ICC- replacement percentage that inhibited the ASR reaction of AM-sand and the previous one, the ASTM C 441 test was performed using Pyrex glass as the

aggregate to characterize the blended cements as ASR inhibitor. Complementary, the free alkali content in the pore solution of pastes was determined at different ages and, selected ASTM C1567 specimens the were microstructurally characterized by SEM and EDS to determine the neo-formations resulting from ASR.

2. MATERIALS AND METHODS

An illitic clay was selected from a quarry located in Olavarria, province of Buenos Aires (Argentine). It was reduced to 5 mm-size particles and then calcined in an oven with a heating-rate of 10.5 ºC/min until reach to 950 ºC, maintaining this temperature for 90 minutes. Later, the samples were cooled into the oven. The ICC was ground in laboratory mill until the d10-parameter of the particle size distribution curve was lesser than 45 μm. The chemical composition of ICC obtained by XRF is reported in Table 1. It has an Al_2O_3 content of 13.42 %, 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 (>40%). It presents a moderate alkali-content (Na_2O_{eq} = 2.18 %), higher than common values reported by fly ash (< 2.0%), granulated blast furnace slag (< 0.5%) and metakaolin (< 1.0%).

This ICC meets the requirements to be classified as class N pozzolan (ASTM C 618): S+A+F > 70%; SO_3 < 4.0% and the loss by ignition (LOI) < 10% [7]. The XRD pattern shows slight peaks of dehydroxylate illite and the associated minerals are quartz, hematite, oligoclase and spinel.

An Ordinary Portland Cement (OPC) was used in this investigation with 0.79 % of equivalent alkali-content and its chemical composition is also reported in Table 2.1.

Table 2.1: Chemical composition of ICC and OPC.

Clay/ Cement	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	K_2O	Na_2O	Na_2Oeq	LOI
ICC	1.63	59.09	19.84	13.42	2.29	0.08	2.54	0.53	2.18	0.58
OPC	63.76	21.20	3.75	3.80	0.77	2.39	1.06	0.09	0.79	2.58

AM reactive sand used as fine aggregate was composed by quartz (23-40%), feldspars (1-2%), volcanic glass (0.5-3%), quartzite (10.5-27%), granitic rock (2.5%) chalcedony (1%) with the addition of pyroxenes and amphiboles (0.3-2.5%) and rough stone (1.5-6%) [8].

The potential reactivity of the AM sand was determined by the ASTM C 1260-AMBT test ("Potential Alkali Reactivity of Aggregates (Mortar-Bar Method)") using the OPC without addition. This method evaluates the potential reactivity of the aggregate using mortars prisms exposed to hot Na(OH) solution during 16 days. At this time, an expansion lesser than 0.10 % indicates an innocuous behavior of aggregate-cement combination; while an expansion greater than 0.20% indicates a potentially deleterious combination.

Confirmed the high reactivity of the aggregate, the ASTM C 1567 test ("Determining the Potential Alkali-Silica Reactivity of Combinations of Cementitious Materials and Aggregate (Accelerated Mortar-Bar Method)") was apply to study the performance of the blended cements and to find the minimum percentage of replacement of ICC that may to inhibit the ASR. The percentage selected were 15, 25, 35 and 45% by mass, and the mortar samples were called as 15ICC, 25ICC, 35ICC and 45ICC, respectively. As indicate ASTM C 1260 and C 1567 standards, mortar prisms (10 x 1 x 1 inches) were cast and cured during 24 hours in laboratory room (20 ºC). Thereafter, prisms were demolded and stored in water at 80 ºC for 24 hours. After 48 hours of casting, the initial length was measured and the prisms were stored in a 1N Na(OH) solution at 80 °C during 16 days. Then, a selected bar was broken and the slice section was analyzed by the petrography microscope (ASTM C 856- "Hardened concrete petrography" and Sacaning electron microscope (SEM). SEM observation, in addition to conventional studies using stereomicroscope and petrographic microscope, is useful to identify the crystalline neo-formations and the amorphous phases in mortar and hardened concrete. In this study, a SEM FEI Quanta 200 and the energy dispersive X-ray spectrometer EDAX SDD Apollo 40 (LIMF-UNLP) was used.

The pozzolanic effectiveness to inhibit the ASR was evaluated using the expansion test developed in mortar bars with Pyrex® glass (ASTM C 441). Borosilicate glass has high reactivity when is combined

with the alkalis of the cement. The blended cement, with the combination of pozzolan-PC, that inhibits the expansion is considered as resistant to ASR. Prismatic mortar bars (10 x 1 x 1 inches; w/cm = 0.485 and cement/Pyrex® glass = 1:2.25) were cast with blended cements containing the ICC-replacement percentage that inhibited the ASR reaction of AM-sand (35%) and the previous one (25%). After 24 hours cured in lime-water, the initial length of bars was measured and then stored in a container at 38 ºC according to ASTM C 227. The ASTM C 1157 standard establishes that the expansion should not exceed the limit of 0.02% at 14 days and 0.06% at 56 days to be considered the cement as ASR inhibitor.

To evaluate the free alkalis in the pore solution, cylindrical paste specimens (w/c= 0.485) were cast with OPC and blended cements (25 and 35 % ICC) and cured as the Pyrex glass prisms. At 2, 14 and 28 days, the pore liquid solution was extracted using the methodology proposed by Barneyback and Diamond [9]. The paste specimen was place into the device as shown in figure 2.1 and then compressed until reaches to ~ 550 MPa. The device had a channel and a small drain connected with a syringe to collect the extracted pore liquid after "squeezing the specimen". Once the pore liquid was obtained, the available alkalis (Na$^+$ and K$^+$) were determined using the flame emission spectrophotometer device.
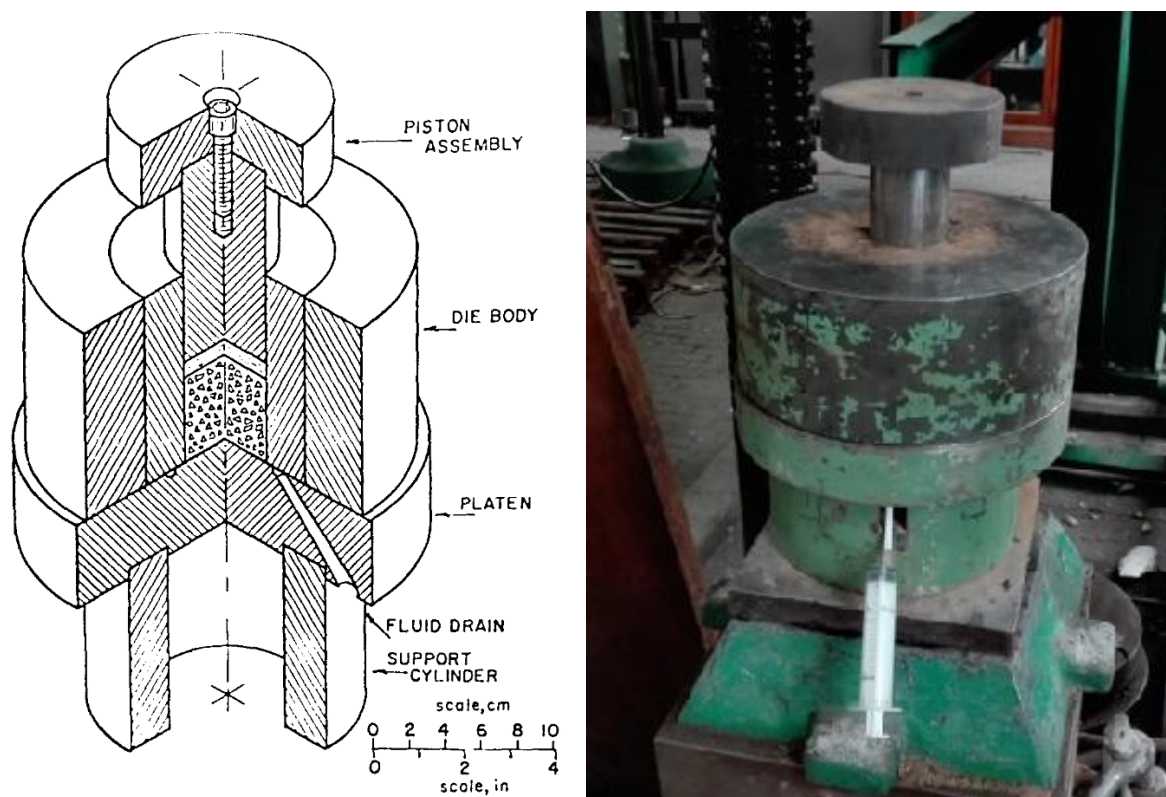

Figure 2.1: Equipment for extracting the liquid of pore solution in cement paste speciemens. a) scheme [8]; b) laboratory device.

3. RESULTS AND DISCUSSION

Expansion obtained from the mortar bars test (ASTM C 1260 and ASTM C 1567) are shown in Figure 2. The dashed line curve corresponds to the expansion of the AM-sand with the OPC used to study the sand-reactivity. It can be observed that the AM-sand classifies as a reactive aggregate, reaching at 16 days to an expansion six times (0.66 %) higher than the limit prescribed by the standard (0.10%). Figure 3.1 also shows (solid lines) the expansion measured according to ASTM C 1567 for blended cements containing 15 to 45% of ICC. It can be seen that 15ICC and 25ICC overpass the 0.10 % limit at 6 and 10 days; while, the expansion of 35ICC was 0.057% at 16 days.
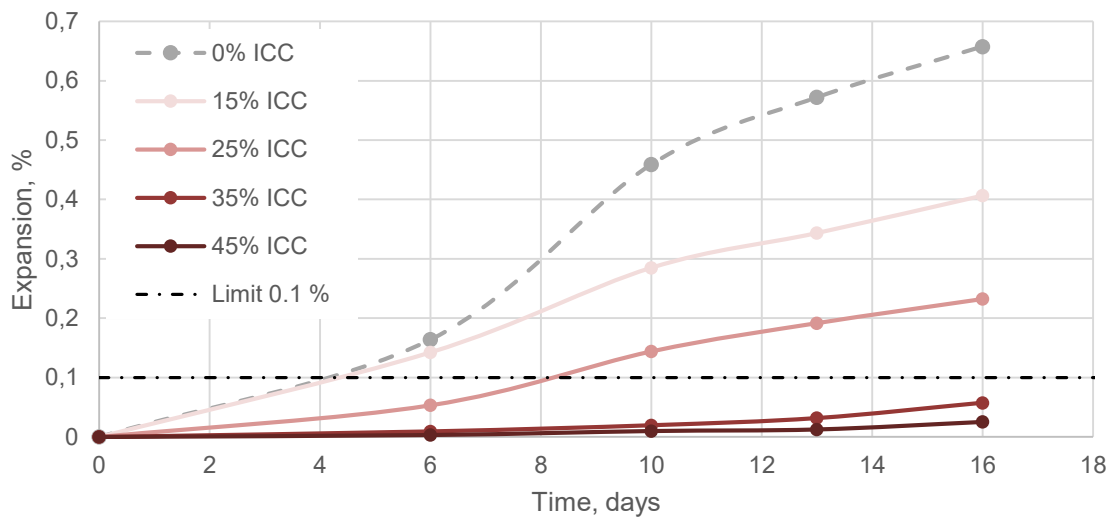
Figure 3.1: Expansion for mortar bars in the ASTM C 1260 and ASTM C 1567 test.

Figure 3.2 shows the expansion results for the 25ICC and 35ICC during de ASTM 441 (Pyrex) test at 14, 28, 56 and 90 days.
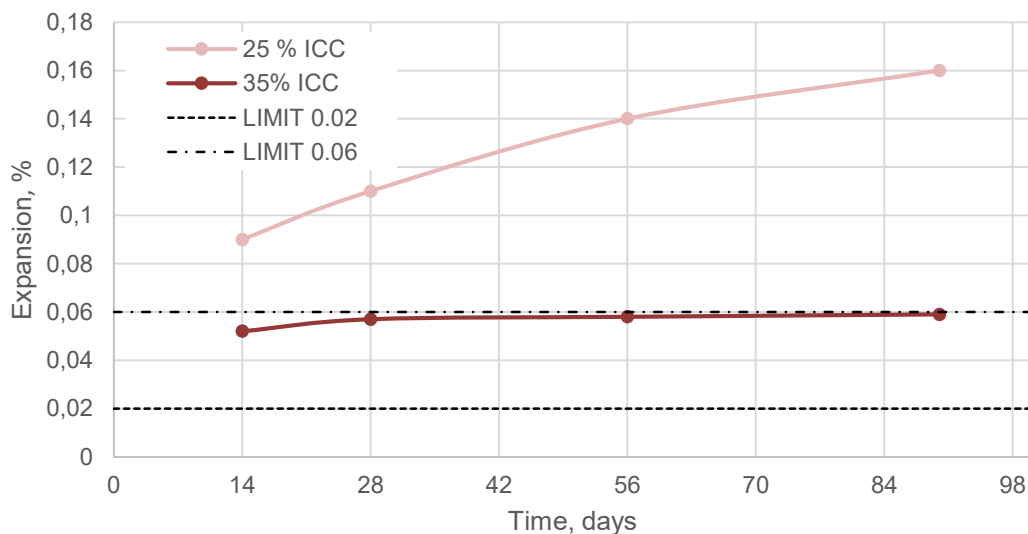

Figure 3.2: Expansion in the ASTM C 441 test.

For 25ICC, the expansion overpasses the 0.10% limit at all studied ages, and this blended cement cannot be classified as ASR resistant. This results agree with those obtained using the ASTM C 1567 test using the high reactivity AM sand. After 14 days, a slight increase of expansion was measured up to 90 days, and it is attributed to some still free products (alkalis) that could react. For Pyrex test, the expansion of 35ICC mortar overpassed the 0.02% limit 14 days, classifying this blended cement as non-inhibitor of the ASR reaction. Therefore, the second 0.06% limit at 56 days was not reached. This could indicate that the ICC has a slow reactivity and need more time that other mineral additions to improve the performance during the ASR reaction. At 90 days, the expansion caused by the ASR-reaction still low, without cross the 0.06% limit.

Table 3.1 reports the free alkalis in the pore solution for pastes made with the OPC and the replacement of 25% and 35% of ICC at different ages. For 25% ICC, the content of alkalis is greater than those obtained for the 35% replacement. These values are consistent with the expansion on mortars for these

replacement percentages. The use of 35% ICC can improve the performance against the ASR reaction. A possible explication for this behaviour it is that during the hydration of cement and ICC, the formation of N-A-S-H gel bind in its structure some free alkalis released by the OPC at early ages and those released by the dissolution of ICC at later ages.

It can be seen that the equivalent alkalis (Na$_2$O eq) almost remains constant in the pore solution for 25ICC paste. But, for 35ICC paste, there is a slight decrease in the equivalent alkalis from 2 to 14 days, and then a low increase at 28 days. This fluctuation values are low and it can say that they maintain a constant trend. More tests will be needed at later ages to understand more clearly this phenomenon.

Table 3.1: Free alkalis in pore solution extracted from pastes.

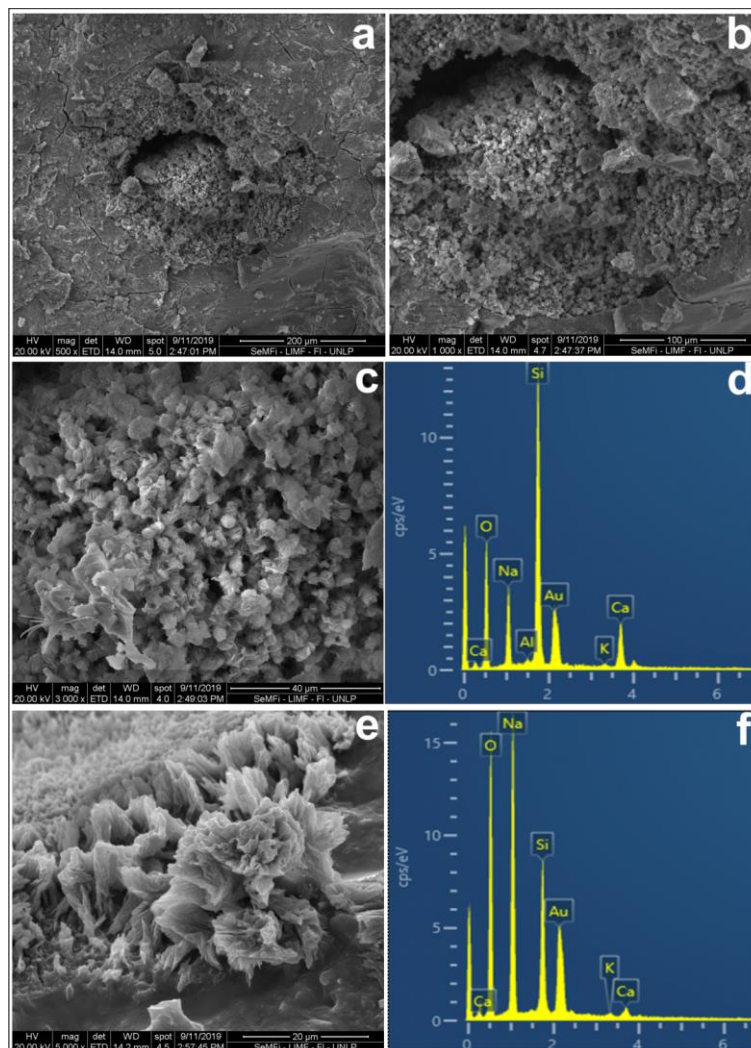| Paste	Alkalis in pore solution (ppm)								
	2 days			14 days			28 days		
	Na$_2$Oeq	K$_2$O	Na$_2$O	Na$_2$Oeq	K$_2$O	Na$_2$O	Na$_2$Oeq	K$_2$O	Na$_2$O
OPC	8779	11450	1445	9718	12375	1575	7019	8942	1136
25ICC	16975	21270	2908	17715	20890	3970	17204	20592	3655
35ICC	14429	18380	2335	13135	14018	3912	15176	17875	3415

Figure 3.3 SEM and EDS for 25ICC mortar AMBT test.

Figures 3.3 and 3.4 show images analysed with SEM and EDS for 25ICC and 35ICC AMBT mortar bars at 16 days, respectively. SEM images of 25ICC (Fig. 3.3a and 3.3b), shows a pore completely filled with neo-formation products with a morphology as rosettes (Fig. 3.3c). These compounds have a high Si-Ca-Na peaks and a low Al peak as reveals the EDS-spectrum (Fig. 3.3d). On the surface of the mortar, it can be seen some products with columnar morphology (Fig. 3.3e) and the EDS-spectrum for this zone shows high Si-Na peaks and low Ca peaks (Fig. 3.3f).

For 35ICC sample (Fig. 3.4), SEM images shows also the pores filled with neo-formation compounds (Figs. 3.4a and 3.4b) and the detail of this pore (Fig. 3.4c) shows neo-formation products with a morphology in rosettes and raw illite relicts with elongated leaf habit. The EDS spectrum for this zone (Fig. 3.4d) reveals high Si-Na-Ca peaks and low Al peak. The presence of K could be from the ICC.

SEM and EDS analyses on 25ICC shows greater amount of microcracks in comparison with the 35ICC. In addition, the ASR products (N-C-S-H) filled completely the pores for 25ICC (Fig. 3.3a) with more products at the pore edge and 120° cracks, typical pattern of the ASR. Rosette morphology products are composed by Si, Na and Ca (Fig. 3.3c and 3.3d); while that ones with columnar morphology consist of Si and Na, with lower Ca content (Fig. 3.3e and 3.3f). On the other hand, in 35ICC (Figs 3.4a and 3.4b), the pores are less filled by the reaction products and there is more free space where rosette compounds are located. Their compositions are essentially Si, Na and Ca (Fig. 3.4c and 3.4d).
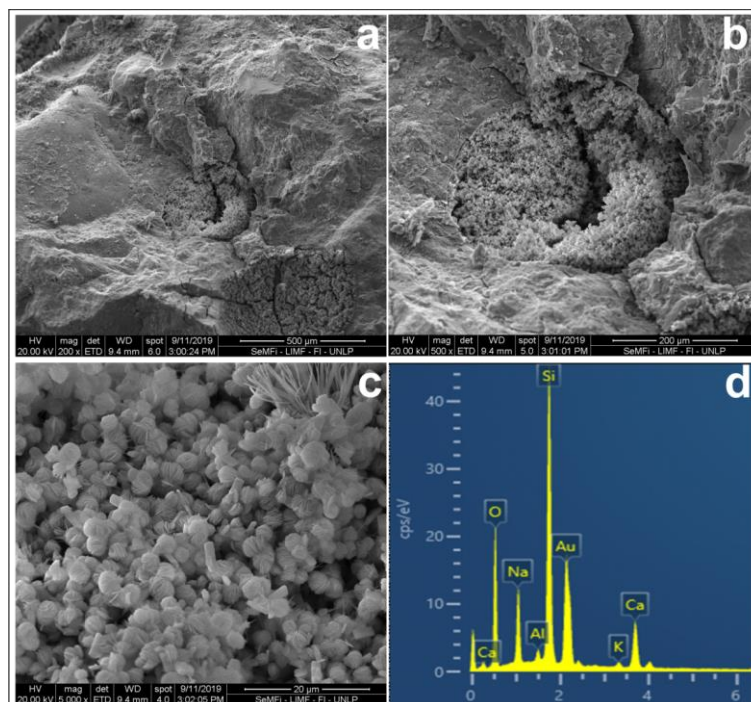

Figure 3.4: SEM and EDS for 35ICC mortar AMBT test. (Style: Caption)

4. CONCLUSIONS

In this investigation, the capacity of an illitic calcined clay combined with an OPC to inhibit the ASR reaction was studied. Based on the results, the following conclusions can be draw:

- For the ASTM C 441 test (Pyrex), the blended cement with a replacement of 35% of illitic calcined clay do not satisfy as ASR blended cement resistant, overpassing the limit of 0.02% expansion at 14 days.
- When a high reactivity sand was used to evaluate this ICC as inhibitor (study of performance) using the ASTM C 1567 test, the 35 % by mass of ICC replacement complies with the expansion limits for this test. For this combination of materials, the illitc calcined clay can controls or mitigate the ASR reaction. Long time studies on concrete specimens will be conclusive to classify this illitic calcined clay as solution to mitigate the ASR reaction.
- With respect to the evolution of free alkalis in the pore liquid solution on pastes, it could be seen that for the replacement of 25% of OPC by ICC there is a greater amount of free alkalis

equivalent than for 35%. This goes in accordance with the smaller expansions measured in the AMBT and Pyrex tests with these 2 percentages of study (less expansions on 35% than 25% OPC replacement). On the other hand, the tendency of free alkalis over time remains practically constant for both studied replacements.

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