

Compressive Strength and Microstructure of Hybrid Alkaline Cements

Z. Abdollahnejad, P. Torgal, J. Barroso Aguiar

Abstract—Publications on the field of alkali-activated binders, state that this new material is likely to have high potential to become an alternative to Portland cement. Classical alkali-activated cements could be made more eco-efficient if the use of sodium silicate is avoided. Besides, most alkali-activated cements suffer from severe efflorescence originated by the fact that alkaline and/or soluble silicates that are added during processing cannot be totally consumed. This paper presents experimental results on hybrid alkaline cements. Compressive strength results and efflorescence's observations show that the new mixes already analyzed are promising. SEM results show that no traditional porous ITZ was detected in these binders.

Keywords—Hybrid alkaline cements, Compressive strength, Efflorescence, SEM, ITZ.

I. INTRODUCTION

ORDINARY Portland cement (OPC) is the dominant binder of the construction industry having an annual production of almost 3 Gt [1]. The production of one tonne of OPC generates 0.55 tonnes of chemical CO₂ and requires an additional 0.39 tonnes of CO₂ in fuel emissions for baking and grinding, accounting for a total of 0.94 tonnes of CO₂. In 2000 the cement industry emitted, on average, 0.87kg of CO₂ for every 1kg of cement produced [2]. As a consequence this industry contributes about 7% of the total worldwide CO₂ emissions [3]. Global demand of OPC until 2050 will have a twofold increase reaching 6 Gt/year. The urge to reduce carbon dioxide emissions and the fact that OPC structures which have been build a few decades ago are still facing disintegration problems points out the handicaps of OPC. Portland cement based concrete can present a higher porosity that allows water and other aggressive media to enter leading to carbonation and corrosion problems. The early deterioration of reinforced concrete structures based on OPC is a current phenomenon with significant consequences both in terms of the cost for the rehabilitation of these structures, or even in terms of environmental impacts associated with these operations. Investigations [4]-[8] carried out so far in the development of alkali activated binders (also termed geopolymers) showed that much has already been investigated and also that an environmental friendly alternative to OPC is rising. According to Davidov its geopolymers generate just 0.184 tons of CO₂ per ton of binder. This numbers were not confirmed by Duxonet al. [9], [10]. These authors stated that

although the CO₂ emissions generated during the production of Na₂O are very high, still the production of geopolymers is associated to a level of carbon dioxide emissions lower than the emissions generated in the production of OPC. An independent study made by Zeobond Pty Ltd concluded that the latter had 80% lower CO₂emissions [11]. Weil et al. [12] compared Portland cement concrete and geopolymeric concrete with similar durability reporting that latter have 70% lower CO₂ emissions which confirmed the aforementioned reductions. McLellan et al. [13] reported a 44 to 64 % reduction in greenhouse gas emissions of geopolymers when compared to OPC. Habert et al. [14] confirmed that they have a lower impact on global warming than OPC but on the other side they have a higher environmental impact regarding other impact categories. Lower CO₂ emissions geopolymers are therefore needed. Besides the durability of geopolymers is still a subject of some controversy [15]. Duxon et al. [10] stated this is the most important issue on determining the success of these new materials. Other authors [16] mentioned that the fact that samples from the former Soviet Union that have been exposed to service conditions for in excess of 30 years showing little degradation means that geopolymers do therefore appear to stand the test of time. But since those materials were of the (Si+Ca) type that conclusion cannot be extended to geopolymers defined as “alkali aluminosilicate gel, with aluminum and silicon linked in a tetrahedral gel framework” [11]. On the other side Juenger et al. [1] argue that “The key unsolved question in the development and application of alkali activation technology is the issue of durability” and more recently Van Deventer et al. [17] recognized that “whether geopolymer concretes are durable remains the major obstacle to recognition in standards for structural concrete”. Efflorescence is an important drawback of two part geopolymers that so far has received very little attention. According to Skvara et al. [18], [19] the bond between the sodium ions (Na⁺) and the aluminosilicate structure is weak and that explains the leaching behavior. Kani et al. [20] showed that efflorescence can be reduced either by the addition of alumina-rich admixtures or by hydrothermal curing at temperatures of 65°C or higher. These authors found that the use of 8% of calcium aluminate cement greatly reduces the mobility of alkalis leading to minimum efflorescence (this cement has 28% of CaO). These results are very important because they constitute a step back in the development of geopolymers. The use of hydrothermal curing has serious limitations for on-site concrete placement operations. On the other hand the use of calcium based mixtures reduces the acid resistance and raises the chances for

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the occurrence of ASR. This means that this subject merits further investigations. One-part geopolymers represent a key event on geopolymer technology having been described by the first time in 2008 (Table I). These binders are also known as hybrid alkaline cements [21], [22]. In this work experimental mechanical results as well as SEM observations on these mixtures are presented. The mixtures under investigation were based on the ones described in the international patent authored by Zheng et al. [23].

II. EXPERIMENTAL WORK

A. Materials

The composition of dry mix in this study was: kaolin, fly ash, ordinary Portland cement (OPC), sodium hydroxide, calcium hydroxide ($\text{Ca}(\text{OH})_2$), water and superplasticizer. The OPC is of class I 42.5 R type with a clinker content between 95-100%, a specific weight of 3.15 g/cm^3 and a Blaine fineness of $3842 \text{ cm}^2/\text{g}$ (Table II). The superplasticizer (SP) used was SIKA 3002 HE. The SP was used to maintain a uniform consistency between the different mixes. The chemical composition of the fly ash complies with the minimum requirements indicated in EN-450-1 [24] for being used as a partial replacement of cement in concrete. Based on this standard the fly ash was categorized in class B and group N for the loss of ignition and fineness, respectively. It has a specific weight of 2.42 g/cm^3 and the chemical composition is shown in Table III. The kaolin has a BET surface area of $21 \text{ m}^2/\text{g}$ and its particle size is shown in Fig. 1. This parameter influences the dehydroxylation temperature of kaolin. The DTA/TGA curves for kaolin are presented in Fig. 2. A well defined endothermic DTA peak and sharp weight loss in the TGA curve appears between 550°C and 600°C . This loss results from the transition to the amorphous and more reactive metakaolin phase.

TABLE I
 BIBLIOGRAPHIC HISTORY OF SOME IMPORTANT ALKALI-ACTIVATED CEMENT/GEOPOLYMER RELATED EVENTS [6]

Feret	1939	Slags used for cement
Purdon	1940	Alkali-slag combinations
Glukhovskiy	1959	Theoretical basis and development of alkaline cements
Glukhovskiy	1965	First called "alkaline cements"
Davidovits	1979	"Geopolymer" term
Malinowski	1979	Ancient aqueducts characterized.
Forss	1983	F-cement (slag-alkali-superplasticizer)
Langton and Roy	1984	Ancient building materials characterized
Davidovits and Sawyer	1985	Patent of "Pyrament" cement
Krivenko	1986	DSc thesis, $\text{R}_2\text{O}-\text{RO}-\text{SiO}_2-\text{H}_2\text{O}$
Malolepsy and Petri	1986	Activation of synthetic melilite slags
Malek et al.	1986	Slag cement-low level radioactive wastes forms
Davidovits	1987	Ancient and modern concretes compared
Deja and Malolepsy	1989	Resistance to chlorides shown
Kaushal et al.	1989	Adiabatic cured nuclear wastes forms from alkaline mixtures
Roy and Langton	1989	Ancient concretes analogs
Majundar et al.	1989	C_{12}A_7 -slag activation
Talling and Brandstetr	1989	Alkali-activated slag
Wu et al.	1990	Activation of slag cement
Roy et al.	1991	Rapid setting alkali-activated cements
Roy and Silsbee	1992	Alkali-activated cements: An overview
Palomo and Glasser	1992	CBC with metakaolin
Roy and Malek	1993	Slag cement
Glukhovskiy	1994	Ancient, modern and future concretes
Krivenko	1994	Alkaline cements
Wang and Scivener	1995	Slag and alkali-activated microstructure
Shi	1996	Strength, pore structure and permeability of alkali-activated slag
Fernández-Jiménez and Puertas	1997	Kinetic studies of alkali-activated slag cements
Katz	1998	Microstructure of alkali-activated fly ash
Davidovits	1999	Chemistry of geopolymeric systems, technology
Roy	1999	Opportunities and challenges of alkali-activated cements
Palomo	1999	Alkali-activated fly ash — a cement for the future
Gong and Yang	2000	Alkali-activated red mud-slag cement
Puertas	2000	Alkali-activated fly ash/slag cement
Bakharev	2001–2002	Alkali-activated slag concrete
Palomo and Palacios	2003	Immobilization of hazardous wastes
Grutzeck	2004	Zeolite formation
Sun	2006	Sialite technology
Duxson	2007	Geopolymer technology: the current state of the art
Hajimohammadi, Provis and Deventer	2008	One-part geopolymer
Provis and Deventer	2009	Geopolymers: structure, processing, properties and industrial applications

TABLE II
CHEMICAL COMPOSITION OF THE PORTLAND CEMENT

Loss on ignition%	1.7
Cl ⁻ %	0.01
SO ₃ %	2.83
CaO Free %	1.53
CaO Reactive %	63.1
SiO ₂ %	20.9
SiO ₂ + Al ₂ O ₃ + Fe ₂ O ₃ %	92.29
MgO%	2.71
Al ₂ O ₃ %	5.03

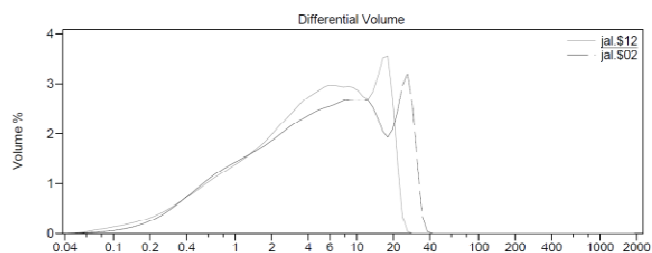


Fig. 1 Kaolin particle diameter obtained with and without a defloculation agent

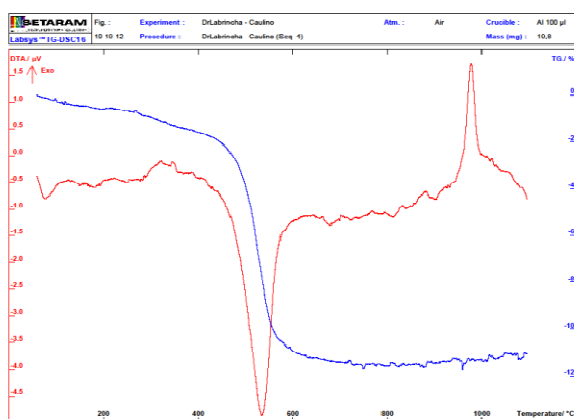


Fig. 2 DTA/TGA curves for kaolin

B. Mix Proportioning and Testing

A mixture of kaolin and sodium hydroxide was calcined in a furnace at 650°C during 140 minutes. The cooled mixture was grinded into powder. Tables IV and V show the mix proportion respectively used in phases A and B. In the mixes 7 up to 12, potassium hydroxide were used instead of sodium hydroxide. The initial phases were meant to find out the mixtures with the highest compressive strength. Phases C (Tables VI and VII) and D (Tables VIII and IX) were meant to evaluate the influence of aggregate and calcium hydroxide. Tests were performed on 50×50×50 mm³ concrete specimens according to NP EN 195-1[25]. The specimens were located in the chamber room during the curing time with relative humidity of 58%. Compressive strength for each mixture was obtained from an average of 3 cubic specimens. The specimens were tested with the pace of 0.36-0.72 N/s.mm². The selection of the speed rate depends on test duration. If test would be able to be done with the speed rate of 0.36 N/s.mm² in 30-90 seconds, the pace is acceptable. But, if with this pace exceed this duration; the pace has to be increased up to 0.72N/s.mm². Efflorescence was evaluated by means of visual observation.

TABLE III
CHEMICAL COMPOSITION AND PHYSICAL PROPERTIES OF THE FLY ASH

Cl ⁻ %	0
SO ₃ %	0.12
CaO Free%	0.1
CaO Reactive%	2.7
SiO ₂ %	40.8
SiO ₂ + Al ₂ O ₃ + Fe ₂ O ₃ %	89.9
MgO%	1.9
P ₂ O ₅ %	1.92
Total alkalis%	0.25
Retained on No. 325 sieve%	15
I.A. _{28D} %	79
I.A. _{90D} %	99

TABLE IV
MIX PROPORTIONS USED IN PHASE A

Mix	Calcined kaolin+sodium or potassium hydroxide	Fly ash	OPC	Ca(OH) ₂	W/b	Sand(g)	SP
1-A	4 %	32.5 %	30 %	33.5%	0.31	-----	-----
2-A	4 %	58.3 %	30 %	7.7 %	0.26	-----	-----
3-A	4 %	58.3 %	30 %	7.7 %	0.34	-----	-----
4-A	4 %	32.5 %	30 %	33.5 %	0.52	-----	-----
5-A	4 %	32.5 %	30 %	33.5 %	0.52	-----	-----
6-A	4 %	58.3 %	30 %	7.7 %	0.31	-----	-----
7-A	4 %	58.3 %	30 %	7.7 %	0.40	-----	-----
8-A	4 %	58.3 %	30 %	7.7 %	0.35	-----	0.8%
9-A	4 %	32.5 %	30 %	33.5 %	0.37	-----	1.3%
10-A	4 %	32.5 %	30 %	33.5 %	0.35	2000	2.5%
11-A	4 %	32.5 %	30 %	33.5 %	0.31	-----	2.4%
12-A	4 %	32.5 %	30 %	33.5 %	0.36	-----	1.5 %

TABLE V
MIX PROPORTION USED IN PHASE B

Mix	Calcined kaolin +sodium or potassium hydroxide	Fly ash	OPC	Ca(OH) ₂	W/b	Sand(gr)	SP
1-B	3.0%	33%	32.2%	33.5%	35%		2.7%
2-B	3.0%	33%	32.2%	31.6%	35%		2.3%
3-B	4%	32%	30%	33.5%	35%		1.5%
4-B	4%	32.5%	30%	33.5%	39%	2100	1.5%
5-B	3.2%	60%	30%	6.8%	35%		1.0%
6-B	4%	32.5%	30%	33.5%	34%		1.0%
7-B	4%	58.3%	30%	7.7%	30%		0.5%
8-B	4%	32.5%	30%	33.5%	35%		1%
9-B	4%	58.3%	30%	7.7%	35%		1%
10-B	4%	32.0%	30%	33.0%	30%	2200	1%
11-B	5%	32.0%	40%	23.0%	35%		1%
12-B	5%	32.0%	30%	34.5%	35%		1%

The specimens are immersed in water during 24 hours and then placed at room temperature. After 48 hours visualizations are recorded. For examination by scanning electron microscopy (SEM) samples were covered with 40nm film of Au-Pd (80-20 weight %); in a high resolution sputter coater, 208HR Cressington Company, coupled to a MTM-20 Cressington High Resolution Thickness Controller. Ultra-high Backscattering Electron images were performed with an acceleration voltage of 15kV. Chemical analyses of samples were performed with Energy Dispersive Spectroscopy (EDS) technique, using an EDAX Si(Li) detector with an acceleration voltage of 20 kV.

TABLE VI
MIX PROPORTION USED IN PHASE C

Mix	Calcined kaolin+ potassium hydroxide	Fly ash	OPC	Ca(OH) ₂	W/b	Sand(gr)	SP
1-C					34%	2114	3%
2-C	5 %	32.0%	40 %	23.0%	34%	2045	2%
3-C					29%	1937	2%
4-C					30%	1898	3%

TABLE VII
PHASE C- VOLUMETRIC RATIO

Vs/Vp	Vw/Vp	Vsp/Vp
1	0.77	0.023
0.95	0.77	0.023
0.9	0.77	0.023
0.85	0.77	0.023

TABLE VIII
MIX PROPORTION USED IN PHASE D

Mix	Calcined kaolin+ Potassium hydroxide	Fly ash	OPC	Ca(OH) ₂	W/b	Sand(gr)	SP
1-D				21.0%			2%
2-D		32.0	40	24.0 %			1%
3-D	5%	%	%	27.0 %	29%	2199	1%
4-D				19.0%			4%

III. RESULTS AND DISCUSSION

A. Mechanical Results

Fig. 3 shows the compressive strength of the mixtures tested

in Phase A. The results show that the most promising mixture (8A) as a compressive strength around 27 MPa after 28 days curing. This mixture also has the eco-efficient advantage of containing a high content of an industrial by-product. The mixture 2A shows a high compressive strength performance which is due to a low w/b ratio. The results also show that in general the curing days increase the compressive strength. This is a behavior that is not observed in two part alkali-activated cements in which the compressive strength just after one day can reach 50% to 70% of the compressive strength after 28 days curing [26]. However, while this behavior is most evident for mixture 8A, the one with the highest compressive strength at 14 days and at 28 days is not so evident for mixture 4A which as a lower fly ash content and a higher w/b. The use of a w/b=0.52 leads to compressive strength results below 12 MPa after 28 days curing which is a very modest performance unsuitable to be used in future applications. The mixture with the lowest 1 day compressive strength (6A) is of difficult explanation because it has the same composition of the mixture with the highest 28 days compressive strength with the exception of the w/b content which is lower. Mixtures based on calcined kaolin and sodium hydroxide revealed lower reactivity than the mixtures in which this last constituent was replaced by potassium hydroxide. This confirms the results obtained by other authors [27], [28] who also found that geopolymers based on several aluminosilicate minerals had a high compressive strength in KOH than in NaOH. This fact is however independent of the extent of dissolution, being that those minerals show a higher dissolution when NaOH is used. Fig. 4 shows the compressive strength of the mixtures test in Phase B. The results indicate that a higher compressive strength mixture was obtained (11B) reaching 30 MPa after 28 days curing. Environmentally speaking since this mixture has more 10% OPC and more 15% of calcium hydroxide this mixture does seems as eco-efficient as the previous mixture 8A. An interesting behavior can be observed when comparing the mixture 11B with mixture 10B. The differences between the two are the fact that mixture 10B includes less 10% of OPC but more 10% in calcium hydroxide and also has a low w/b. As a consequence its compressive strength after 28 days curing is almost 10MPa apart from mixture 11B. And probably if the w/b was the same the

compressive strength difference could be even higher. This shows the existent of very reactive constituents in OPC. Again the mixtures where sodium hydroxide was replaced by potassium hydroxide show a higher compressive strength. Fig. 5 shows the compressive strength of the mixtures test in Phase C. In this phase the mixture 11B was used as reference in order to evaluate the compressive strength variation due to aggregate content. V_s relates to the volume of sand and V_p for the volume of powder (OPC, FA, Kaolin, potassium hydroxide and $\text{Ca}(\text{OH})_2$). Increasing the sand content leads to lower compressive strength because the w/b ratio has also increased. Fig. 6 shows the compressive strength of the mixtures tested in Phase D.

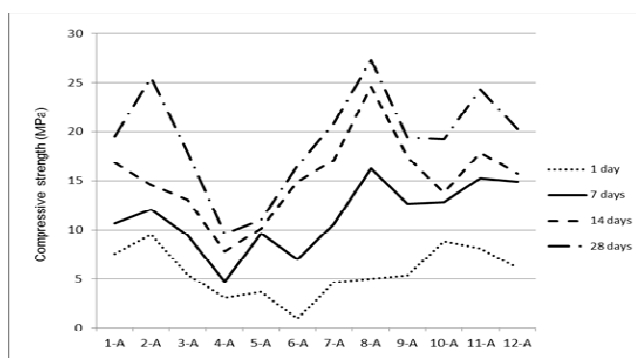


Fig. 3 Compressive strength: Phase A

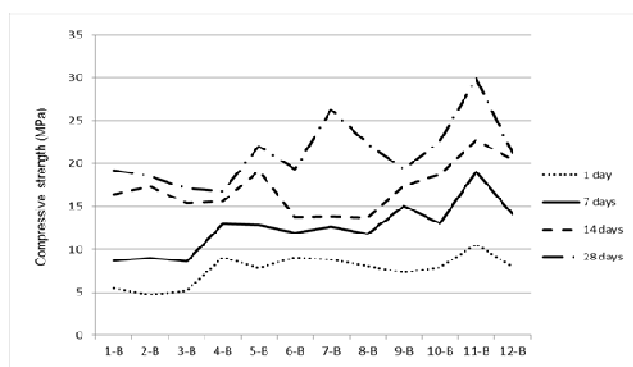


Fig. 4 Compressive strength: Phase B

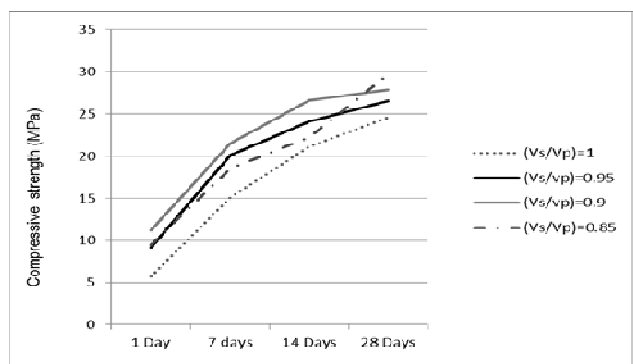


Fig. 5 Compressive strength: Phase C

In this phase the mixture 11B was used as reference in order

to evaluate the compressive strength variation due to calcium hydroxide content. The calcium hydroxide is presented as a function of the Portland cement percentage. The results show that there is not a direct linear relationship between the calcium hydroxide content and the compressive strength. The use of calcium hydroxide as much as 50% of Portland cement leads to the highest compressive strength. Increasing the $\text{Ca}(\text{OH})_2$ percentage beyond that percentage can lead to a decrease in the compressive strength. Concerning the efflorescence no relevant presence was observed. This confirmed the observations included in the international related patent.

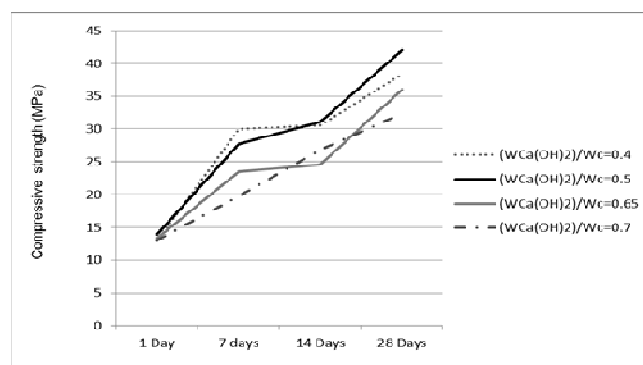


Fig. 6 Compressive strength: Phase D

B. Scanning Electron Microscopy Analysis

Figs. 7 and 8 show two SEM micrographs. In contrast with the porous typical interfacial transition zone of Portland cement mixtures, hybrid alkaline cement mortars present a very dense and uniform ITZ. The molar ratios of the analyses carried out by EDS are displayed in table 9 and 10. Typical C/S ratios in CSH of traditional OPC systems go between 1.5 and 2.0 [29], [30]. However, the areas Z2 and Z3 have a much lower C/S ratio which means it as some sodium replacing Ca^{2+} in CSH. Some authors have already demonstrated that sodium incorporation in CSH phase increased as C/S ratio decreases, and therefore they name it as Na-C-S-H [31].

The areas marked as Z2 and Z3 are identified as some form of calcium silicate with traces of some sodium and aluminum in its composition which could be associated to a (N,C)-A-S-H gel. According to Garcia-Lodeiro et al. [32] this gels usually evolve into compositions with higher calcium and lower aluminum content. Those authors also mention that this is a blank field and that almost nothing has been published concerning the interaction between aluminosilicate materials containing sodium (or potassium or sulphates) in the formation of N-A-S-H or K-A-S-H type cementitious gels.

TABLE IX
 PHASE D-WEIGHT RATIO

$\text{WCa}(\text{OH})_2/\text{Wc}$	WCa/Wc	WFA/Wc	WSP/Wc
0.45	0.12	0.79	0.01
0.5	0.12	0.79	0.01
0.65	0.12	0.79	0.01
0.7	0.12	0.79	0.01

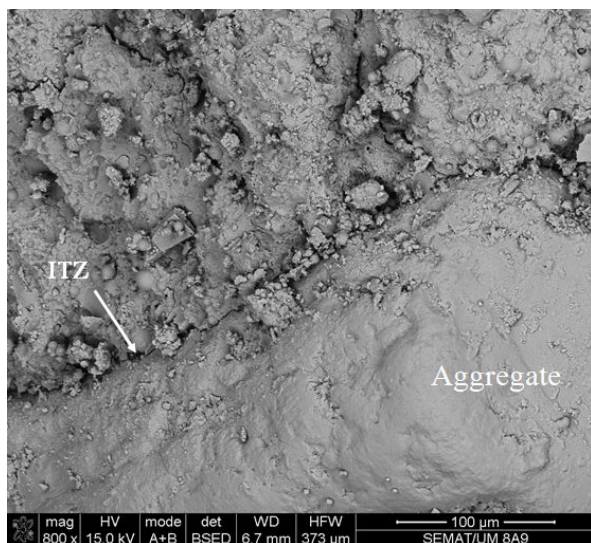


Fig. 7 SEM micrograph of interfacial transition zone

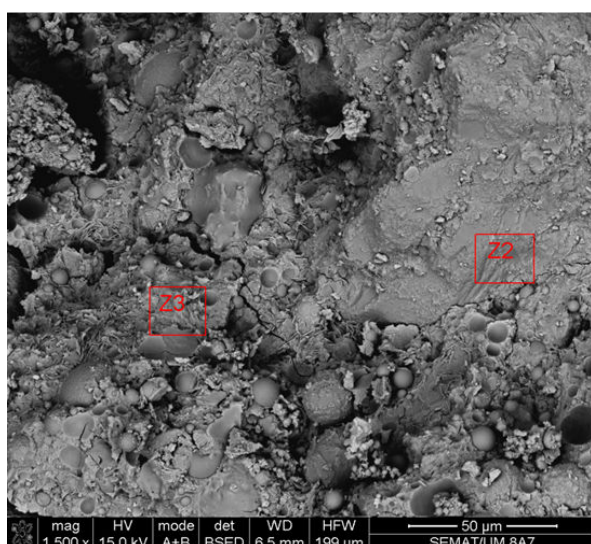


Fig. 8 SEM micrograph of hybrid alkaline cement mortar

TABLE X
EDS ATOMIC RATIO ANALYSIS

Atomic ratio	Zone	
	Z2	Z3
SiO ₂ /Al ₂ O ₃	25.6	2.89
Al ₂ O ₃ /Na ₂ O	2.15	5.44
CaO/SiO ₂	0.13	0.5
Na ₂ O/CaO	0.13	0.12
MgO/Al ₂ O ₃	-	0.15

IV. CONCLUSIONS

Concerning the preliminary investigations disclosed in this article the conclusions are as follows:

- Several hybrid alkaline cement mixtures were studied some having a high compressive strength suitable for construction purposes.
- A general trend was observed linking compressive strength evolution with curing age which is typical of

OPC chemistry.

- Mixtures based on calcined kaolin and sodium hydroxide revealed lower reactivity than the mixtures in which this last constituent was replaced by potassium hydroxide.
- The results show that there is not a direct linear relationship between the calcium hydroxide content and the compressive strength.
- All the mixtures show no signs of efflorescence
- Hybrid alkaline cement mortars present a very dense and uniform ITZ
- Further investigations on mixture composition are also needed in order to select mixtures with a high compressive strength and a high eco-efficient performance
- Analysis of durability parameters are needed
- Evaluation of LCA of hybrid alkaline cements also merits further investigations

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