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VALORIZATION OF SECONDARY RAW MATERIALS THROUGH ALKALI ACTIVATION: STUDY OF BINDERS BASED ON SULFATE-BEARING CLAY AND PIETRA SERENA SLUDGE

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INTRODUCTION

Alkaline activation is a chemical process through which an aluminosilicate precursor (with amorphous or vitreous structures) reacts with an alkaline solution to give rise to materials with good binding and cementing properties. Nowadays, Alkali Activated Materials (AAMs) have emerged as alternative to traditional construction materials, such as mortars or Ordinary Portland Cement (OPC), with the aim to become primary components in the development of environmentally sustainable building products, above all considering the growing interest of the scientific community for the themes of sustainability and CO_2 footprint reduction. Since the recent global interest in maximizing the re-use and recycling of waste to minimize the environmental impacts associated with their treatment and disposal, use of high-volume wastes in the production of blended or novel cements (including AAMs) is well known as a key pathway by which these wastes can be reused. Studies and efforts are needed in order to increase the volume of these residues and to introduce new types of resources and industrial by-products in the production chain. Valorization of a wide variety of mining, metallurgical, societal and agricultural wastes can be achieved through the use of these materials as precursors or activators for alkali-activated binders. Considering that transportation of material at all stages leading up to the production of the binder is of key importance, the cost and emissions metrics (especially for waste products) can be highly affected by the distance and mode of transport (O'Brien *et al.*, 2009; Weil *et al.*, 2009).

The present work is aimed at evaluating italian feedstock in alkali activation. In particular, two italian raw materials were selected: a sulfate-bearing clay and a sludge of an ornamental sandstone rock, called Pietra Serena. For the sulfate-bearing kaolin, the occurrence of alunite, $KAl_3(SO_4)_2(OH)_6$, which is present in kaolin deposits deriving from trachyte, rhyolite, and similar potassium-rich volcanic rocks, normally hinders its use in the ceramic industry due to the release of SO_3 at high temperature. However, alunite can be considered a valuable source of potassium and aluminum in alkali activation. In a previous study (Gasparini *et al.*, 2015), the possibility of using this kaolinitic clay containing alunite to prepare AAMs was assessed by activating the clay at temperature below desulfation (< 700°C, Kristóf *et al.*, 2010), opening the way for utilizing sulfate-bearing kaolin as raw material. However, the presence of thenardite, Na_2SO_4, deriving from the dissolution of alunite, was observed in the final products.

The matter associated to the Pietra Serena sandstone sludge, common to all stone processing, is its suitable disposal which needs precise requirements; although the coarser fractions of quarrying wastes can be reused in construction industries (Akbulut *et al.*, 2007, Felekoglu, 2007), the finest fraction often contains high content of water, and could represents a problem of uneconomical energy-consuming drying process (Yang *et al.*, 2013). To this purpose, the reuse, rather than disposal, would be the ideal solution.

Aim of this work is the valorization of "secondary raw materials" for designing cements and binders, through alkaline activation process. In particular, the use of kaolinitic clay containing sulfate in the alkali activation process was evaluated. In fact, sulfate can act as promoter of zeolite crystallization, as proposed by Criado *et al.* (2010), or can be hosted by the metakaolin-based AAM gel. In addition, the reactivity of Pietra Serena sewage sludge and its behavior in the alkali activation process when mixed to the sulfate-bearing clay were investigated. The resulting cements could be associated to those called *hybrid alkaline cements*, in which binders of two different compositions form C-(A)-S-H and N-A-S-H. The former, well known, is characteristic of Portland cement hydration, whereas the second is characteristic of the alkaline activation of aluminosilicate, such as fly ash or metakaolin. As in Portland cement manufacture, in which a small amount of gypsum is added to the clinker to control the initial hydration reactions and prevent flash setting, in the studied system, alunite, a sulfate-bearing mineral, is present. At the high pH of the slurry, this mineral dissolves to release SO_4^{2-} and Al^{3+}, which, in turn, react with $Ca(OH)_2$ to form sulfo-aluminate compounds, which could improve the mechanical properties of the resulting binder (Katsioti *et al.*, 2009).

Compositional and microstructural characterizations of the synthesized samples were performed to explain the different mechanisms involved in the alkaline process. The local structure and properties of the products were investigated in order to strengthen the basis upon which alternative materials can be developed.

The versatility of the alkali activation process, which allows employing different materials as precursors, has led to assess the synergic use of more than one type of raw materials. Such study will allow to start building the bases of designing materials that may achieve a balance of commercial and technical goals, and increase resource efficiency.

STARTING MATERIALS

Sulfate-bearing clay, labelled L02-K, derives from Piloni di Torniella quarry, located in Tuscany (Central Italy) and it was provided by Eurit S.r.l. company (Italy). This clay is found in kaolinitic deposits belonging to the Roccastrada district. Alunite is present in these deposits and its formation was related to the alteration of plagioclase and K-feldspars due to an high S concentration in the fluid during hydrothermal process of these riolites (Viti *et al.*, 2007). L02-K is composed by 47.6 wt.% of kaolinite, 13.0 wt.% of alunite, 26.0 wt.% of quartz, and 19.0 wt.% of feldspars (see Table 1 for chemical composition).

In order to investigate the effect of sulfate deriving from alunite in AAMs, binders prepared by using L02-K were compared to binders prepared by using mixtures an high-grade kaolin, labelled Sl-K, and alunite (from a vein of Piloni di Torniella mine) as starting materials. Sl-K kaolin derives from the Seilitz kaolin deposits (Germany) and was supplied by Sibelco Italia S.p.A. company. The latter is composed by 73 wt.% of kaolinite and 27 wt.% of quartz (see Table 1 for chemical composition).

Table 1 - Chemical composition of precursors used for the preparation of AAMs.

Major oxides (wt.%)	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	Na_2O	K_2O	TiO_2	Others	SO_3	L.o.I
L02-K	59.02	22.85	0.11	1.26	0.12	0.82	3.30	0.28	0.26	6.07*	12.98
Sl-K	67.0	31.5	0.12	0.32	0.23	-	0.35	0.24	0.24	-	10.02
sPS	43.50	8.28	2.44	19.53	4.19	1.46	4.19	0.42		0.18	18.0

*SO_3 for L02-K clay was calculated separately by Combustion Infrared Detection Method.

The L02-K clay was submitted to thermal treatment at 550°C for 3 hours to obtain the reactive metakaolin, and dehydroxilated alunite, (see also Gasparini *et al.*, 2015). In this study, Sl-K was heated at 550°C (hereafter labelled Sl-MK_550) for 3 hours, in order to be comparable to L02-MK. Therefore, at this temperature Sl-K kaolinite was not fully transformed into metakaolinite as in the L02-K clay; thus, some experiment were conducted heating Sl-K kaolin at 800°C (hereafter labelled Sl-MK_800) for 2 hours. More information about Sl-K characterization are reported in Gasparini *et al.* (2013) and Clausi *et al.* (2016).

Pietra Serena sludge, labelled sPS, was provided by Pietra Serena Group S.r.l. company (Firenzuola, Italy). Pietra Serena sandstone comes from a quarry in the Firenzuola district (Florence, Italy) and it can be classified as a feldspathic litharenite. Chemical composition of sPS was determined by XRF after drying at 100ºC for 24 hours in an oven and the data are reported as L.o.I., determined by mass loss up to 1000°C, is also reported in Table 1. The mineralogical composition, provided by Pietra Serena Group S.r.l. company on the basis of UNI-EN 12407:2007 “Natural Stone Test Methods- Petrographic Examination”, indicated a dominant silicoclastic component, constituted by quartz, feldspars (K-feldspar and plagioclase), phyllosilicates (biotite, chlorite and muscovite), accessories minerals, and a carbonatic component (clasts and cement). In this study, the sludge was thermally treated at 800°C for 2 hours (hereafter labelled sPS_800) in order to obtain the decomposition of carbonates. More information about Pietra Serena sludge are reported in Clausi *et al.* (2016).

A sodium silicate solution supplied by Ingessil S.r.l. company (Na_2O = 14.37 wt.%, SiO_2 = 29.54 wt.%, H_2O = 56.09 wt.%) as well as NaOH pellets (purity ≥ 98%) and silica fume powder (average particle size = 0.2-0.3 µm) supplied by Sigma Aldrich company were used in the preparation of the AAMs.

EXPERIMENTAL

For the preparation of the AAMs, two different systems were considered. The first system was calcium free, Na_2O-Al_2O_3-SiO_2-H_2O and a sodium silicate solution was used as activator. Binders prepared by using L02-MK were compared to those prepared by using mixtures of Sl-MK and alunite as starting materials. Three sets of AAMs based on different metakaolin precursor and annealing temperature were prepared as reported in Table 2 (mix 1, 2, 3). Synthesis parameters were defined on the basis of the potential reactive SiO_2 and Al_2O_3 from available metakaolinite and alunite after each thermal treatment. The initial SiO_2/Al_2O_3 molar ratios of the precursors was modified by adding waterglass and eventually by adding silica fume in order to achieve two SiO_2/Al_2O_3 molar ratio (3.6 and 4.6) for each set, in separated experiments. Metakaolin based AAMs, with these silica content are characterized by good mechanical strength, good development of aluminosilicate gels (Duxson *et al.*, 2005; Fletcher *et al.*, 2005; Komnitsas & Zaharaki, 2007). The $Al_2O_3/(Na_2O+K_2O)$ molar ratio was maintained around 1. Pastes were prepared by mechanically mixing the precursor powder (thermally treated) with sodium silicate for 5 minutes, then poured into cylindrical molds, having size 2 cm in diameter and 4 cm in height, and cured at 50°C for 20 hours in sealed vessels to ensure 99% relative humidity (R.H.).

In the second system, Na_2O-CaO-Al_2O_3-SiO_2-H_2O, the reactivity of the sPS when mixed to sulfate-bearing clay, together with the effect of sulfate was investigated. Sodium hydroxide was selected as activating solution. L02-K clay and sPS were thermally treated and then mixed in different weight proportions (see Table 2, mix 4, 5, 6, 7). Three different sodium hydroxide solutions were prepared with different molarities (8M, 6M and 4M) by dissolving NaOH pellets in deionizer water. The slurries were mixed for 3 minutes by using a mechanical mixer before being poured in 1×1×6 cm^3 prismatic steel molds and compacted by mechanical vibrations for 60s to remove the entrained air. Specimens were cured at 85°C for 20 hours in sealed vessels to ensure 100% R.H. conditions. At the end of the curing, specimens were unmolded and stored at room temperature until the end of curing time. Some experiments were also conducted curing the sample directly at 25°C in a room with 99% R.H. condition.

Table 2 - Scheme of synthesis of AAMs

Mix	L02-K annealing temperature (°C)	Sl-K annealing temperature (°C)	Alunite annealing temperature (°C)	sPS annealing temperature (°C)	Precursors Proportion for 100g	Activating solution
1	550°C	-	-	-	87.7/12.3*	Na_2SiO_3
2		550°C	550°C	-	90/10	Na_2SiO_3
3		800°C	550°C	-	80/20	Na_2SiO_3
4	550°C	-	-	-	100/0	NaOH
5	550°C	-	-	800°C	90/10	NaOH
6	550°C	-	-	800°C	80/20	NaOH
7	550°C	-	-	800°C	50/50	NaOH

*this proportion is related to the mineralogical composition of the original clay

Liquid/solid ratio for each formulation was chosen in order to guarantee the minimum workability of the slurry and to allow its pouring in the molds.

Raw materials and alkali activated samples were analyzed by X-ray Fluorescence (XRF), X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy in attenuated total reflectance (FTIR-ATR), Thermogravimetric analysis and Differential thermal analysis (TG-DTA), Field Emission Scanning Electron

Microscopy (FESEM), leaching tests according to UNI EN 1245 standard. Sulfate ion in the liquid phase was analyzed by ion chromatography.

ALKALI ACTIVATION OF SULFATE-BEARING CLAY

The feasibility to produce AAMs from low-T activated sulfate-bearing clay was assessed. The results were focused on the investigation of the effects of SO_4^{2-} on the nature and chemical composition of the resulting products. Some studies were conducted on the effect of the sulfate in alkali activation system (*e.g.*, Lee & van Deventer, 2003; Criado *et al.*, 2010; Desbats-Le Chequer & Frizon, 2011; Komnitsas & Zaharaki, 2007). Actually, sulfate was studied in fly ash systems, as possible alkali activation catalyst in zeolites formation or retarding agent in the condensation reaction of the silicon and aluminum species (Criado *et al.*, 2010). The products of alkali activation of the AAMs based on L02-MK and Sl-MK (with and without alunite addition) included mainly an amorphous N-A-S-H gel and no new crystalline phases apart for thenardite were detected by the XRPD analyses. The latter was soluble in water and disappeared after leaching tests.

Morphological analyses outline that, regardless the soluble silica content, an amorphous gel was formed from all mixtures. Leaching tests and chemical analyses performed on leached solution as well as on the resulting leached materials demonstrated that not all sulfate was combined with sodium to form thenardite but some amount was still present in the samples. Backscattered electron images on powder pellets of the samples were analyzed before and after water leaching as shown in Fig. 1.

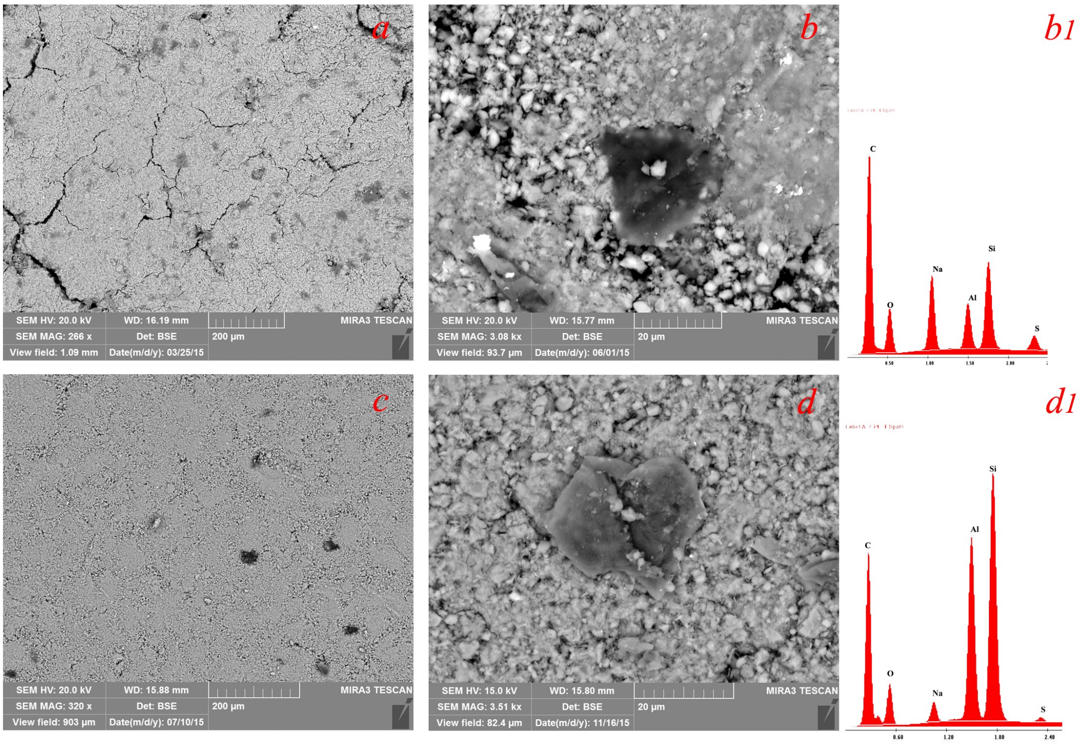

Fig. 1 - FESEM micrographs of AAMs binders with Sl-MK_500 and alunite (90:10 weight proportion, with SiO_2/Al_2O_3 ratio of 4.6): a, b) matrix and particular of the matrix before water leaching; c, d) matrix and particular of the matrix after water leaching. Scale bar and magnification are showed in each image; b1, d1) EDS analysis of the dark particles, respectively.

The microstructures appeared composed by a light matrix and several darker grains scattered in the matrix. Both samples resulted composed by Si, Al, and Na corresponding to the aluminosilicate N-A-S-H gel composition, with an amount of S which seemed to be concentrated after water leaching in these dark particles as confirmed by EDS analysis (Fig. 1, d1). Sulfur-rich particles containing Si and Al, likely amorphous or nano-sized zeolites phases, might be the responsible structures able to take the sulfate in the gel. However, since lower leachability were found in the samples with higher silica content and lower capability to form zeolitic phases, the uptake of sulfate ions by the gel itself cannot be excluded.

Infrared spectra of sulfate-bearing AAMs after water leaching are dominated by the vibration of Si-O-T bonds related to the formation of amorphous N-A-S-H gel and by the S-O bonds of the sulfate anion, which however did not seem to form new compounds. The ability to retain sulfate by the gel or by nano-zeolite-like structures eventually formed makes these binders a promising materials in the exploitation of their matrix as ion encapsulation/immobilization matrix. Optimization of the synthesis parameters, like for example adding calcium oxide or varying the soluble silica content in order to change the stability between amorphous-crystalline, could provide a way to improve the sulfate retention and achieve its complete immobilization. The possibility to vary the synthesis parameters based on the mix formulation makes these materials highly versatile and promising as waste encapsulating materials.

ALKALI ACTIVATION OF MIXTURE OF SULFATE-BEARING CLAY AND SANDSTONE SLUDGE

The features of a S- and Ca- bearing aluminosilicate multi-component system in the presence of NaOH solution as alkaline activator, along with the reaction products were explored. In particular, the effects of *i*) addition of Pietra Serena sandstone sludge (10%, 20%, or 50% weight proportion) to sulfate-bearing clay, *ii*) molarity of the activating solution (4, 6, or 8M NaOH solution), and *iii*) curing temperature (85°C or 25°C) were evaluated. The presence of CaO produced after dehydroxylation of sPS can modify the mechanical properties of the binder and the type and composition of the reaction products, leading to the development of hybrid alkaline cements (García-Lodeiro *et al.*, 2013). Moreover, CaO can react with sulfate to form calcium sulfo-aluminate hydrate phases, similar to those observed in the OPC system as ettringite (AFt compound) or monosulfate (AFm compound). Hence, the CaO presence in the reacting system could offer further paths to increase the sulfate uptake and storage in the solid products.

The first part of the work dealt with the effect of the addition of sPS_800 in different proportions to L02-MK. Mixtures were activated with 8M NaOH and compared to pastes prepared by using L02-MK and NaOH 8M. When L02-MK was activated without sPS_800 mechanical strength was below 5 MPa. Whereas, when 10 wt.% of sPS_800 was added to L02-MK the average value of compressive strength was 12.0(1) MPa. This value was 3 times higher than that achieved in the sample without sPS_800. This was because when sPS was heated at 800°C calcium from the original dolomite and calcite was present mainly in the form of highly reactive oxide CaO that with hydration behaved as in cements enhancing the mechanical performance of the final material. However, a further increase of the sPS_800 content in the mix did not correspond to an increase of the mechanical strength. In fact, samples made with 20 wt.% and 50 wt.% of sPS_800 showed similar compressive strength values (10.6(9) MPa and 10.3(2) Mpa, respectively). The phase composition was investigated by XRPD analyses and the results revealed that all the binders showed a more or less marked halo between 20-35° 2θ, which is typical of the amorphous gel precipitation. Soluble sodium sulfate (thenardite, visible also as efflorescence on the hand sample) and gibbsite formed in the sample prepared using only L02-MK and NaOH. Whereas, crystalline phases as CAN-type zeolites, in particular a sulfate-bearing end member, formed in all samples regardless the sPS_800 content. When 50 wt.% of sPS_800 was added to the mix, beside CAN-type zeolites, calcium sulfo-aluminate products as U-Phase and poorly crystalline C-S-H phases formed.

At 8M of NaOH, when L02-MK was activated without sPS_800, all sulfate deriving from alunite dissolution was soluble as measured by leaching tests and ICP-OES. Then, adding sPS_800 to L02-MK the sulfate retention increased. This was due to the formation of sulfoaluminate compounds and zeolites which could hold the sulfate in their structures. Differences in microstructure were related to the sPS_800 content. Two types of morphologically distinguishable gels were recognizable (Fig. 2), one more granular with concatenated spherical particles interconnected to create small clusters of aluminosilicate gel (left side of the micrograph), and another in which the arrangement in parallel planes was revealed (morphological feature related to metakaolin). The left side seemed to have more alumina, and less sulfate content with respect to the right side. The EDS analyses showed no important differences in composition between the oxides molar ratio, and the sulfate results distributed in the whole matrix. Effects of the CaO content, deriving from sPS_800, in the mixtures lead to the formation of hydrated calcium silicate of C-(A)-S-H gel type together with N-A-S-H gel.

Varying the molarities (at 4, 6 and 8M) and fixing L02-MK and sPS_800 proportion (at 80 : 20 in weight), it was observed that samples activated with 4M NaOH solution showed the lowest value of compressive strength, with 4.5(2) MPa. When the alkalinity of the NaOH solution rose up to 6M, the mechanical strength values was two times higher, whereas the samples activated at 8M NaOH solution showed an average value of compressive strength of 10.6(9) MPa.

Results obtained for samples prepared fixing L02-MK and sPS_800 proportion (to 50:50 in weight), at different molarities, and curing at 25°C and 85°C, showed different results. After curing at 25°C for 20 hours, samples did not develop strength. Whereas, a positive trend related to the increase of molarity of activating solution was observed for the samples cured at 85°C. The mechanical strength increased linearly with increasing the molarity of the activating solution with an average rate of 1.5, from 4.0(3) MPa to 10.3(2) MPa. XRPD analyses of all samples showed characteristic bands of amorphous gel as for the other binders.

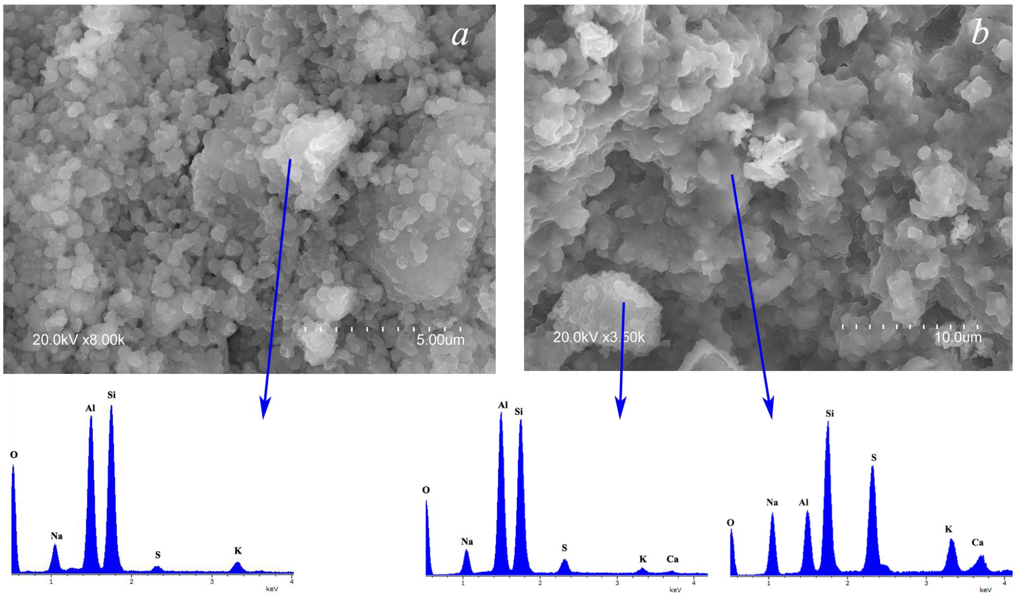

Fig. 2 - FESEM micrographs of AAMs binders with L02-MK and sPS_800 mixed in different proportion, activated with NaOH solution 8M: a = L02-MK 100 wt.%; b = L02-MK 90 wt.% and sPS_800 10 wt.%. Scale bar and magnification are showed in each image; EDS spectra are reported at the bottom of the figures.

After curing at 25°C, A-zeolite and traces of X-zeolites were found in the sample at 4M and 8M, whereas no new crystalline phases were detected for the sample at 6M. After curing at 85°C, as in the previous case, U-Phase was formed at 6M and 8M and ettringite was formed at 4 M, confirming their stability at different molarities. CAN-type zeolite appears only in the sample at 8M. Overall, the FT-IR spectra of these samples confirmed the formation of alkaline aluminosilicate gel, as the main T-O stretching band was shifted toward lower frequencies with respect to the same peak in metakaolin. Also microstructural analyses by SEM-EDS confirm that the gel was formed and showed a morphology that can be related to the amount of calcium. The finding confirmed that in this type of multi-component mixtures and at these alkaline conditions the main reaction product was a mixed (N, C)-A-S-H gel.

From the results obtained here, it was seen that addition of sPS_800 to L02-MK could have a positive effects in the AAMs binders when the concentration of NaOH was 8M. The L02-MK activated with sodium hydroxide did not show good properties since it was characterized by low values of strength, efflorescences, crystals of gibbsite and finally showed a granular N-A-S-H gel structure. When alkaline activation of L02-MK was carried out in the presence of lime, the formation of an amorphous aluminosilicate with a tridimensional network and cementitious properties was the resulting main reaction product. Mechanical strength values considerably increased as well the absence of efflorescences and the increase of sulfate retention. Effects of sPS_800 in the mixtures lead to a formation of hydrated calcium silicate of C-A-S-H gel type together with N-A-S-H gel.

Literature studies have shown that the co-precipitation of these two gels in hybrid cements is possible (Alonso & Palomo, 2001; Yip *et al.*, 2005; Palomo *et al.*, 2007). Although recent research has revealed that, the two products do not develop singly as two separate gels, but they interact undergoing structural and compositional changes in the process (García-Lodeiro *et al.*, 2011). Leaching tests have demonstrated that with a little amount of calcium in these systems it is possible to reduce sensibly the sulfate solubility (over 50%). These effects could be ascribed to the formation of some crystalline products, which are able to fix sulfate in their structures, as CAN-type zeolites, or sulfoaluminate compounds as ettringite or U-Phase. The latter similarly to those forming in cement system. Experiments made maintaining fixed the calcium content in the system and varying the alkalinity of the solution have shown affect sensibly the mechanical properties of these binders. In this system, a reduction of the alkalinity of NaOH solution produces a decreasing of the mechanical properties but promotes the formation of AFt (as ettringite) and AFm (as U-phase, a sodium-substituted AFm) which are calcium sulfoaluminate compounds commonly found in concrete (Damidot & Glasser, 1993).

Finally, when more calcium was added to the mix varying molarities and curing conditions, the results demonstrated that the development of mechanical strength is related to curing temperature. Even if calcium could act as retardant agent in the setting at room temperature, pastes cured at 25°C after one day does not develops strength. Higher temperature, 85°C, accelerated setting and strength development. However, it was seen that the samples activated at 8M and cured at 25°C showed a values of sulfate retention of 50% perfectly comparable to those showed for the sample activated at 8M with 10 wt.% of sPS_800 and at 6M with 50 wt.% of sPS_800 both cured at 85°C. This fact suggest that even regardless the formation of crystalline compounds able to retain sulfate in their structure as for example, zeolites or sulfoaluminate compound, it cannot be excluded that the sulfate could be hold by the gel itself. The decarbonation process of the sewage sludge could be useful in order to valorize this waste material. In binary matrices with metakaolin sPS_800 acted as a pozzolanic cement in which the calcium oxide (CaO) was hydrated and reacts with the silica present in the material a mixture of (N, C)-A-S-H / C-A-S-H gels, similar to those produced in so-called mixed alkali cements or hybrid cements.

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