Spectroscopic and microscopic study of alkali activated mortars based on Tunisian phosphate washing waste

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ABSTRACT

The calcination of phosphate washing waste has a significant effect on the microstructure and mechanical properties of the phosphate washing waste-based alkali activated mortars. This study aims to investigate the reaction products of the phosphate washing waste activated with sodium hydroxide (SH) and sodium silicate (SS) with mass ratio of the two solutions SH/SS = 1.

Different techniques were used to characterize the obtained mortars including: Compressive strength, X-ray diffraction XRD, Solid state magic angle spinning nuclear magnetic resonance (MAS-NMR) of 3 nuclei (²⁷Al, ²⁹Si and ³¹P), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) and Electron microscope scanning and energy dispersive spectroscopy (SEM-EDS). The obtained results reveal that the alkali activation of phosphate washing waste generate 2 types of reactions and 2 types of products (N-A-S-H)/(C,N)-A-S-H as 3D network and C-S-H/C-(A)-S-H as 2D gel. The Al and reactive Ca have a strong effect on the final mechanical properties.

1. Introduction

Phosphate rock contains a high concentration of phosphate mineral to be mined commercially [1]. At the international level, the production of this ore attains 147 million tons in 2017 and it will increase to achieve 168 million ton in 2021 [2]. The extraction of P₂O₅ ore generates unwanted gangue minerals as waste. Two types of waste can be determined, the waste rock after mining and the phosphatic tailing after mineral processing [1,3,4]. The phosphate tailing also named phosphate washing waste or phosphate sludge is generated with a large quantity: 1 ton of ore generate about 1 ton of tailing waste [5–9]. This waste is deposited in a large tailing pound and cause a serious environmental problem like, covering vast areas, elution of phosphate, fluorine and metal in the sediments, water and marine organisms [10,11]. For a sustainable management, the recycle, valorization and reuse of this waste will be one of the greatest challenges. Therefore, the phosphate washing waste has been an issue in the last decade. The phosphate washing waste was used in a wide range of field to reduce its environmental problem. In the field of building materials, the phosphate waste was used as a geopolymeric binder and alkali activated materials [12–15] or in the cemented backfill domain [16–18]. This mining waste

was investigated also in the field of ceramic, in the development of bricks [19,20] or membranes [21,22] and in heavy metal recovering [23–25].

Turning now to other environmental problem which is the production of cement. The production of this material reached 4.1 billion tons in 2017 [2]. The emission of 1 ton of CO₂ per 1 ton of OPC is the worst-case scenario. This production contribute with approximately 5–7% of global anthropogenic CO₂ emissions [26,27]. As a solution, researcher found a new material during the last decades which are the alkali activated materials (AAM). Those materials can be divided in 2 categories based on the method of synthesis. First category corresponds to the material which is based on the activation of aluminosilicates precursors by an alkali solution sodium/potassium hydroxide with or without sodium/potassium silicates [28–30]. The second category named one part alkali activated materials “just add water” which is a formulation based on the activation of the precursors with solid alkaline activators [31–33]. It has previously been studied that the precursors can be divided into three categories [34–36] according to the calcium content of the binder. Low-calcium precursors like fly ash class F or metakaolin [28–30] in which the main binding is the 3 dimensional amorphous aluminosilicate named “geopolymer”. High calcium based

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on blast furnace slag or also fly ash class C [37–39] and this category has calcium silicate hydrate C–S–H as the main binding. Other class designated as intermediate or hybrid materials characterized by the presence of the 2 types of gel “geopolymer” and C–S–H [40–42].

The aim of this study is to explore the relation between the reactivity and the microstructure of the alkali activated materials based on calcined phosphate washing waste, examined using various experimental techniques (XRD, MAS-NMR, FTIR-ATR and SEM-EDS) in order to study the complexes reactions of the binder.

2. Materials and methods

2.1. Materials

The phosphate washing waste (PWW) was provided by Gafsa Phosphate Company (CPG) from (Lavrie (IV)) Metlaoui (Tunisia). The waste was characterized by the high amount of Silicon 42 wt%, Calcium 26.5 wt%, Phosphorus 10 wt% and Alumina 9.77 wt%. The powder was investigated with different technics discussed in a previous work [43]. The mineralogical study shows that the phosphate washing waste present the calcite, heulandite, palygorskite and carbonate fluorapatite as major phases and display also the presence of gypsum and quartz. The powder was calcined for 2 h with heating rate 10 °C/min from room to the target temperature 600 °C, 700 °C and 800 °C to be studied for alkali activation. The choice of these temperatures was based on the DSC-TG analysis which present the interval of the decarbonation phenomena in this range of these temperatures.

The alkali activated mortars based on phosphate washing waste were prepared by the use of sodium hydroxide NaOH (10 M) and sodium silicate solution Na_2SiO_3 with chemical composition $\text{Na}_2\text{O} (\text{SiO}_2)_x \cdot y (\text{H}_2\text{O})$ with $3.19 < x < 3.53$ and $50\% < y < 60\%$ from the Portuguese Industry MER-KANDA. The mass ratio of the 2-alkali solution is of the order of 1. The aggregate used for the preparation of these alkali activated mortars was a sand with particle size distributed with maximum and minimum grain diameters of approximately 8 mm and 0.2 mm, respectively and just 2% of the particles are with a size superior to 4 mm. A detailed preparation procedure of this alkali activated mortars was described in a previous work [13]. As a result, the Alkali Activation of phosphate washing waste calcined at 800 °C ($\text{AAP}_{800^\circ\text{C}}$) presents a problem of the quick setting. Therefore, only the $\text{AAP}_{600^\circ\text{C}}$ and $\text{AAP}_{700^\circ\text{C}}$ will be studied in this work.

2.2. Analytical techniques

The XRD analysis was conduct for uncalcined and calcined powders and also for the samples at 7 and 28 days. For the MAS-NMR and FTIR (ATR) characterization, the mortars were crushed by hand and sieved to eliminate the aggregate. The SEM-EDS characterization was conduct at 28 days without any special preparation of the samples.

The identification of the phases present in the samples was performed by powder X-ray diffraction XRD Bruker D₈ Discover using Cu K α radiation $k = 1.54060 \text{ \AA}$ at 40 kV and 40 mA in the range from 5° to 60° with a step width of 0.02° at a speed of 0.02°s⁻¹ and a front-loading preparation method of the samples. Phase identification was done using X'Pert Highscore software.

The solid-state magic angle spinning nuclear magnetic resonance of the samples were carried out using high resolution UXMNR, Bruker Analytische Messtechnik GmbH AMX300 spectrometer. Parameters for

each experiment are outlined in Table 1. All data were processed using MestreNova.

An attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) spectra were performed from 400 to 4000 cm⁻¹ wavenumbers using the Fourier Infrared model PerkinElmer spectrum BX spectrometer and the spectra were collected from 4 scans at resolution 2 cm⁻¹ and no special preparation of the samples were needed. The data were processed using Origin Pro software.

The microstructure analysis of the samples was executed using a scanning electron microscope SEM 200 operating at 15 kV An X-ray energy dispersive (EDX) detector was used to determine chemical compositions of different zones for the samples cured for 28 days.

3. Results

3.1. Compressive strength

Compressive strength is the most important property of building materials. Fig. 1 shows the compressive strength of the two mortars at 7 and 28 days which indicate that the two samples react differently. The compressive strength of the $\text{AAP}_{600^\circ\text{C}}$ and $\text{AAP}_{700^\circ\text{C}}$ show a significant difference at 7 days of curing it is about $3.6 \text{ MPa} \pm 0.09$ and $5.99 \pm 0.02 \text{ MPa}$ for $\text{AAP}_{600^\circ\text{C}}$ and $\text{AAP}_{700^\circ\text{C}}$ respectively. At 28 days the two mortars present different results, the compressive strength of $\text{AAP}_{600^\circ\text{C}}$ increase slightly and become $4.9 \pm 0.14 \text{ MPa}$ which is equal to 36%, while the $\text{AAP}_{700^\circ\text{C}}$ exhibits a compressive strength that increase to achieve 10.7 ± 0.12 and it is about 81%. This difference is mainly due to the precursors before and after alkali activation.

3.2. X-ray diffraction

The X-ray diffractograms of the untreated PWW and calcined at 600, 700 °C and the AAP cured for 7 and 28 days are presented in Fig. 2 (A, B and C). The PWW and its mineralogy before and after calcination were intensively discussed in a previous work [43]. As presented in Fig. 2A, the uncalcined PWW is characterized by the presence of the heulandite, palygorskite, calcite, carbonate fluorapatite, gypsum and quartz. After

Fig. 1. Compressive strengths of $\text{AAP}_{600^\circ\text{C}}$ and $\text{AAP}_{700^\circ\text{C}}$ at 7 and 28 days.

Table 1

Parameters MAS-NMR experiment.

Nucleus	Field Strength	Transmitter frequency MHz	n/2 pulse width (μs)	Relaxation delay (s)	Scans	Spinning speed KHz	reference
²⁹ Si	7.1	59.63	5	5	11524	8	TMS
²⁷ Al	7.1	78.21	6	5	4168	8	AlCl ₃ ·6H ₂ O
³¹ P	7.1	121.49	3	5	1024	8	Fluorapatite

Fig. 2. XRD diffractograms of (A) untreated PWW and calcined at 600 °C and 700 °C (B) PWW_{600°C} and AAP_{600°C} at 7 and 28 days (C) PWW_{700°C} and AAP_{700°C} at 7 and 28 days.

F: carbonate fluorapatite (PDF#:00-002-0833), H: heulandite (PDF#:01-076-2214), P: palygorskite (PDF#:00-029-0855), C: calcite (PDF#:00-002-0629), G: gypsum (PDF#:00-021-0816), Q: quartz (PDF#:01-070-2535), Ph: phlogopite (PDF#:00-079-2364), Cs: C₂S (PDF#:00-023-1042), A: anhydrite (PDF#:00-003-0368).

calcination at 600 °C the pattern presents the decrease of the reflection of heulandite, calcite and palygorskite. The reflection of the gypsum disappears and other appear correspond to the anhydrite. At 700 °C, the powder shows the disappearance of palygorskite. The reflection of heulandite and calcite decrease more. The pattern displays also new phases like the phlogopite and C₂S. At the two-calcination temperature the reflections of carbonate fluorapatite and quartz remain stable.

After alkali activation, the patterns of the AAP_{600°C} presented in Fig. 2B, with the cutoff of the y-axis because of the higher intensities of quartz, indicating the consumption of the palygorskite, heulandite and anhydrite but the carbonate fluorapatite and quartz remain unaltered after the alkali activation. The curves show also the halo centered at about 29° (2Theta) displaying the formation of the disordered reaction product characteristic of alkali activated materials [33,39,42,44]. The AAP_{700°C} present also the same behavior showed by the AAP_{600°C}. it exhibits the diminution of all the reflection correspond to the calcite, phlogopite, heulandite, C₂S and anhydrite and indicates also the non-reactivity of quartz [33,44] and carbonate fluorapatite in alkali medium. While, as displayed in Fig. 1 the two samples present a different mechanical strength at 7 and 28 days, which point out that the two PWW react differently after alkali activation. In this case the AAP need to be investigated with other technics to understand more their chemical behavior.

3.3. Solid state magic angle spinning nuclear magnetic resonance

The ²⁷Al, ²⁹Si and ³¹P MAS-NMR of the precursors at different temperatures are presented in Fig. 3A and Fig. 5A and Fig. 4B respectively. The results are discussed in detailed in a previous work [43]. The patterns of ²⁷Al nuclei (Fig. 3A) present 2 environments 4-coordinated noted ^{IV}Al and 6-coordinated noted ^{VI}Al which show a difference after thermal treatment. The patterns of the ²⁹Si (Fig. 4A) nuclei present different environments of the silicon presented in the different phases of the PWW. The ³¹P nuclei (Fig. 5A) displays one peak corresponds to the phosphorus presented in the carbonate fluorapatite. This peak did not show a difference with the calcination temperature. Table 2 presents the ²⁹Si, ²⁷Al and ³¹P MAS-NMR peaks of the PWW at 25 °C, 600 °C and 700 °C.

The solid-state NMR was designed also to understand the reactivity of the PWW_{600°C} and PWW_{700°C} after the alkali activation (AAP) at 7 and 28 days.

3.4. ²⁹Si-NMR spectroscopy of the AAP

Comparing the spectra of AAP_{600°C} and AAP_{700°C} at 7 and 28 days with that of calcined PWW, an important shift of the spectrum is detected. The obtained spectrum, fitted peak and the deconvoluted results of AAP_{600°C} and AAP_{700°C} are presented in Fig. 6 and Fig. 7 respectively.

As can be seen from Fig. 4B, the curves (²⁹Si MAS-NMR) of AAP_{600°C} at 7 and 28 days show an important shift compared to the inactivated powder PWW_{600°C}. It displays a chemical shift between -75 and -107 ppm. The curves show the consumption of the framework with no bonded Al correspond to Q⁴(0Al) at -111 and -113 ppm. The peaks which correspond to the heulandite phase -95 and -101 ppm assigned to Q⁴(2Al) and Q⁴(1Al) respectively were also consumed. The Q³(mAl) environment of the palygorskite presented by the peaks at about -91 and -96 ppm were also altered and new peaks were detected, indicating the formation of new phases during the curing time, while the peak at -107 ppm corresponds to Q⁴(0Al) related to the structure unit from quartz remain constant indicating its low reactivity.

Upon the alkali activation of PWW_{600°C} new signals between -75 and -100 ppm appear as presented in Fig. 6. These peaks are assigned to new environments of Si with 3 clear groups. First group of chemical shift has occurred from -75 ppm to -81 ppm, second group from -83 ppm to -87 ppm and a third group of chemical shift from -91 ppm to

Fig. 3. ^{27}Al MAS-NMR of the PWW (A) at different temperatures, (B) $\text{PWW}_{600^\circ\text{C}}$ and $\text{AAP}_{600^\circ\text{C}}$ at 7 and 28 days, (C) $\text{PWW}_{700^\circ\text{C}}$ and $\text{AAP}_{700^\circ\text{C}}$ at 7 and 28 days.

Fig. 4. ^{29}Si MAS-NMR of the PWW (A) at different temperatures, (B) $\text{PWW}_{600^\circ\text{C}}$ and $\text{AAP}_{600^\circ\text{C}}$ at 7 and 28 days, (C) $\text{PWW}_{700^\circ\text{C}}$ and $\text{AAP}_{700^\circ\text{C}}$ at 7 and 28 days.

Fig. 5. ^{31}P MAS-NMR of the PWW (A) at different temperatures, (B) $\text{PWW}_{600^\circ\text{C}}$ and $\text{AAP}_{600^\circ\text{C}}$ at 7 and 28 days, (C) $\text{PWW}_{700^\circ\text{C}}$ and $\text{AAP}_{700^\circ\text{C}}$ at 7 and 28 days.

–102 ppm related to Q^1 , $\text{Q}^2(\text{mAl})$ and $\text{Q}^4(\text{mAl})$ with m between 0 and 4 or else $\text{Q}^3(\text{mAl})$ respectively [42,45,46]. The reaction of $\text{PWW}_{600^\circ\text{C}}$ after alkali activation was complexed. The results of ^{27}Al MAS-NMR show that two different type of reaction products can be detected. The first product is the highly crosslinked framework silicate N-A-S-H, with the incorporation of Ca-modified geopolymer gel noted (C, N)-A-S-H that has a 3-D structure characterize with Q^3 and Q^4 Si sites [42,44,47]. The second is C-S-H/C-(A)-S-H gel has a 2-D chain silicate structure with Q^1 and Q^2 Si sites [45,46]. The samples show with the increase of the curing time a narrowing of the resonance which explains the increased ordering within the 2 different formed gels.

The ^{29}Si -NMR of the $\text{AAP}_{700^\circ\text{C}}$ at 7 and 28 days are presented in Fig. 4C. The curves show an important shift compared to the unactivated $\text{PWW}_{700^\circ\text{C}}$. The $\text{AAP}_{700^\circ\text{C}}$ spectra display new peaks in a new region between –76 and –93 ppm compared to the unreacted phosphate washing waste demonstrated in Fig. 7.

After alkali activation, the curves present also 3 clear groups. First group with a chemical shift centered at about –72 ppm suggestion the presence of isolated tetrahedral Q^0 within the reaction products. This peak can also refer to the C_2S phases. However, according to many authors [42,48–50], after alkali activation, C_2S reacts and generates new phase. The second group was at between –75 ppm and –85 ppm correspond to Q^1 (chain end group) and Q^2 (middle chain group) denoted the newly formed phase of C-S-H [44,51]. The third group of peaks presented between –87 ppm and –97 ppm. Based on the data reported in the literature [39,46,52,53] the shift at about –87 ppm correspond to $\text{Q}^4(4\text{Al})$ and the shift from –90 ppm to –97 can correspond to Q^3 and $\text{Q}^4(\text{mAl})$ tetrahedral silica surrounded by 3, 2 or 1 alumina units [39,42,49,54]. The activation of $\text{PWW}_{700^\circ\text{C}}$ displays also 2 different types of reactions. The main reaction is the formation of 3D N-A-S-H in which Ca displace Na ions and leads to the formation of (C, N)-A-S-H gel [52]. The second reaction is the formation of the

Table 2²⁹Si, ²⁷Al and ³¹P MAS-NMR of PWW at different temperatures (25 °C, 600 °C and 700 °C).

	Assignment	25 °C	600 °C	700 °C
²⁹ Si	Q ³ (mAl)	Palygorskite –92,	Palygorskite –91,	–
	Q ³ (1Al)	–97 ppm	–96 ppm	Phlogopite
	Q ⁴ (2Al)	–	–	–86 ppm
	Q ⁴ (1Al)	Heulandite-K	Heulandite-K	Heulandite-K
	Q ⁴ (0Al)	–93 ppm	–95	–95 ppm
	Q ⁴ (0Al)	Heulandite-K	Heulandite-K	Heulandite-K
	Q ⁰	–101 ppm	–101	–10 ppm
	Quartz	Quartz	Quartz –107	Quartz
	–107 ppm	–107 ppm	Framework (0Al)	–107 ppm
	Framework	–111, –113	–111, –113	Framework
²⁷ Al	(0Al)-112, –113	–	–	(0Al)-112
	–	–	–	C ₂ S –71 ppm
	Al _{oct}	Palygorskite	Palygorskite	Phlogopite 2 ppm
	Al _{tet}	3 ppm	3 ppm	–
		Palygorskite	Palygorskite	Heulandite
		54 ppm	54 ppm	56 ppm
³¹ P		Heulandite	Heulandite	
		58 ppm	56 ppm	
	Carbonate	Carbonate	Carbonate	
	Fluorapatite	Fluorapatite	Fluorapatite	
	2.6 ppm	2.6 ppm	2.6 ppm	

C–S–H/C–(A)–S–H gel.

3.5. ²⁷Al-NMR spectroscopy of AAP

The ²⁷Al NMR provided additional information about the environment of the Al nuclei in the new formed materials. The spectra of the PWW uncalcined and calcined at 600 °C and 700 °C presented in Fig. 3A, show 2 environments correspond to the Al(IV) and Al(VI). After calcination the curves exhibit a decrease of the 6-coordinated Al and an increase of the 4-coordinated Al and this was explained by the start of dihydroxylation of the palygorskite [43]. The 4-coordinated Al corresponds to the heulandite and also to the palygorskite present in the powder at 25 °C and 600 °C. At 700 °C the 2 environments correspond to the aluminum present in the heulandite and the phlogopite phases.

The ²⁷Al MAS-NMR spectra of the AAP_{600°C} and AAP_{700°C} are presented in Fig. 3B and 3C respectively. The AAP_{600°C}Al MAS-NMR spectrum reveals the presence of both tetrahedrally and octahedrally coordinated aluminum. The 6-coordinated Al appeared to be unaffected by the alkali activation. It can be seen from the data in Table 3 that the intensity of those peaks did not show also a big difference from 7 to 28

days. In contrast, the AAP_{700°C} presents a tetrahedrally coordinated aluminum with highest intensity. While the octahedrally aluminum makes a chemical shift to 3.6 ppm and 1.77 ppm at 7 and 28 days respectively and the intensity of those peaks dropped clearly compared to the PWW_{700°C} as Table 3 shows.

The difference of the intensity of the two environments of Al can be explained differently. First the presence of Al(VI) in the AAP_{600°C} with the high intensity could be related to the low geopolymerization degree in the samples. Secondly the availability of Al (VI) from the phases present in the PWW_{600°C} is limited by the nature of these phases. In this case the palygorskite which present the octahedrally environment of aluminum is the phase that can show a limited or negligible contribution to the activation reaction. However, based on the results of the XRD in Fig. 2B and according to Wango et al. [55], at higher alkali medium the palygorskite is consumed and presents other new phases. The third hypothesis is that the Al(VI) are forming individual phases [56].

The ²⁷Al MAS-NMR spectra of the AAP_{700°C} shows that most of the aluminum is tetrahedrally coordinated. The curves present the transformation of Al(VI) to Al(IV) which indicates that aluminum is incorporated in the new formed phases. The curves show also a peak with low intensity and sharper shape at around 3.6 ppm and 1.7 ppm at 7 and 28 days respectively. The attribution of those peaks is not clearly determined in the literature, but it can be assigned to the hydrated crystalline phases [51,57] or is attributed to Al(VI) linked to Mg in a spinel-type structure [47,58].

The ²⁷Al MAS-NMR spectra of each AAP_{600°C} and AAP_{700°C} cured at 7 and 28-days exhibit high resonance from 30 to 70 ppm and centered at approximately 55 ppm, which assigned to four-fold coordinated Al namely q4(4Si) in a significant disordered tetrahedral environment [39, 42,59]. In this case it is the formed amorphous N–A–S–H/(N, C)–A–S–H gel.

The ³¹P MAS-NMR spectra presented in Fig. 5B and 5C show the phosphorus environment in the fluorapatite. It is clearly that the environment did not present a chemical shift after alkali activation. These results indicate that the fluorapatite did not react after alkali activation [14] and confirm the results of the XRD.

3.6. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR)

ATR-FTIR spectra collected of the PWW calcined at 600 °C and 700 °C and activated powders cured at 7 and 28 days are presented in Fig. 8A. As discussed in the previous work [43], the FTIR spectra show 2

Fig. 6. Deconvolution curves of AAP_{600°C} at A) 7 and B) 28 days.

Fig. 8. FTIR of the (A) PWW, PWW_{600°C} and PWW_{700°C} (B) PWW_{600°C} and AAP_{600°C} at 7 and 28 days PWW_{700°C} and AAP_{700°C} at 7 and 28 days.

presence of the 3D network (N-A-S-H), (N,C)-A-S-H and 2D (C-S-H) and also a small particles of zeolite that was not spread with high quantities in the formed sample.

From Table 4, it was clearly shown that the elemental composition of AAP_{600°C} and AAP_{700°C} in zone1 and zone2 respectively, was dominated by silicon, calcium, sodium and aluminum. The AAP_{700°C} exhibit also the C-S-H phase as a separate phase following the hydration of the C₂S [48].

The zones3 and zones1+3 of AAP_{600°C} and AAP_{700°C} respectively show the particles of fluorapatite that stayed no reacted after activation which confirm the XRD and MAS-NMR results. Small amount of zeolites was displayed in the SEM-EDS analysis that did not appear in the XRD diffractometer.

4. Discussion

Exploring the obtained results XRD, MAS-NMR, FTIR, SEM-EDS and DSC-TG [13], analysis of the AAP_{600°C} and AAP_{700°C}, it was clear that the alkali activation of the 2 precursors leads to the formation of new phases which affect the compressive strength of the obtained materials.

The present study was designed to determine first the effect of the calcination process on the mineralogical composition of the PWW. As described in previous work [43] the calcination affect significantly the phases of the PWW. As one of interesting finding in this study is the role of Al present in the PWW_{600°C} and PWW_{700°C} was different. The two precursors present a 4-coordinated Al and 6-coordinated Al with different population but the results provide that the 6-coordinated Al did not react with same way. After activation, the AAP_{700°C} was characterized with 4-coordinated Al at about 55 ppm with an important intensity after the consumption of the most of 6-coordinated Al. This environment indicating the higher silicon surrounded Al, q4(4Si) environment [39, 49,56], means that one aluminum is surrounded by for silicon. This state describes the position of Al within the 3D network. However, the population of the 6-coordinated Al for AAP_{600°C} was higher compared to the AAP_{700°C} and did not show a significant change from 7 to 28 days. As aluminum is one of the elements that plays an important role in the alkali activated materials. The difference of compressive strength presented in Fig. 1 can be first explained by the role of Al in the 2 powders following the calcination and the activation process. According to Chao, Roosz and Duxon [57,63–65] aluminum and the rate of its release throughout the reaction cause the higher compressive strength of the obtained materials.

The difference of the compressive strength and its variation from 7 to 28 days for the 2 samples may be explained by the fact that also the amount of the reactive calcium present in the 2 precursors was not the same. The Ca cation is present in different phases (Anhydrite, Calcite and Heulandite in PWW_{600°C} and Anhydrite, Calcite, Heulandite and C₂S in PWW_{700°C}). The difference of those phases from 600 °C to 700 °C were their reactivity. The heulandite and calcite were altered after calcination with decomposition of heulandite and decarbonation of calcite. Those phenomena were significantly important at 700 °C than 600 °C. Based on the literature [42,54,63], the calcium has a positive effect on the compressive strength and this behavior depends on the amount and the form in which it is present. The Ca cation in this case plays two functions; replace Na cation by ion exchange like the phenomena presented in the clay or zeolite [40,49,66] for the N-A-S-H/(N,C)-A-S-H or forming other phases like C-S-H or C-(A)-S-H. The presence of the different phases caused by the reaction of Ca cation in alkali medium can explain the evolution of the compressive strength of the 2 samples [67].

Based on the FTIR analysis the main band at 995 cm⁻¹ of AAP_{600°C} was at higher wavenumber compared to the AAP_{700°C} which appear at 965 cm⁻¹. This band displays the Si-O-T where T is a tetrahedrally coordinated cation and the incorporation of a large T: Al and Ca will shift the band toward lower wavenumber [40]. These results confirm that more Al and Ca are present in the formed gel of AAP_{700°C} than in the AAP_{600°C} [60,66,68]. Making a relation between the results, the increase of reactive calcium in the powder leads to the increase of the incorporation of Al within the new phases [45,46].

Table 4

The average elemental compositions of the different zones presented in Fig. 9.

	Wt.% Zone	Silicon (Si)	Calcium(Ca)	Sodium(Na)	Aluminum(Al)	Oxygen(O)	Phosphorus(P)
AAP _{600°C}	Zone1	20	12.42	13	2.31	42	–
	Zone2	60	–	–	–	37	–
	Zone3	6	34.2	5.8	–	35.8	10.2
AAP _{700°C}	Zone1+3	4.2	55	2.5	–	25.5	5.65
	Zone2	19.8	12.8	10.7	2.9	43.5	–
	Zone4	35	2.89	3.6	6.8	45.2	–
	Zone5	61.3	–	–	–	35	–
	Zone6	33.07	38.4	2.03	–	19.9	–

Fig. 9. SEM observation of the AAP_{600°C} (A, B) and AAP_{700°C} (C, D) at 28 days.

This system can be described as follow. The alkali activation of *PWW*_{600°C} and *PWW*_{700°C} conduct to dissolution of different sources of silicon and aluminum (heulandite, palygorskite and phlogopite) and other sources of calcium (anhydrite, calcite and C₂S) to give different species ($\text{SiO}_2(\text{OH})_2^{2-}$ or $\text{SiO}(\text{OH})_3^-$, $\text{Al}(\text{OH})_4^-$, Ca^{2+} , SO_4^{2-} [61,67]. Interaction between all these species generate two types of reaction. the precipitation of N-A-S-H gel or the C-S-H gel. Furthermore, the study displays the presence of other ions from the dissolution as the Mg^{2+} , K^+ and Na^{2+} are incorporated in the formed gels.

5. Conclusion

The aim of this study is to investigate the reactivity and reaction products of alkali-activated phosphate washing waste calcined at two different temperatures 600 and 700 °C. The results show that:

- The calcination temperature has an important effect on the reactivity of the phosphate washing waste PWW.
- The alkali activation of the *PWW*_{600°C} and *PWW*_{700°C}, generate two types of reactions confirmed by the MAS-NMR and SEM-EDS analysis which are the formation of the 3D network N-A-S-H/(C,N)-A-S-H gel and the C-S-H, C-(A)-S-H gel.
- The activation demonstrates the consumption of all the aluminosilicate phases (Heulandite, palygorskite and phlogopite) and calcium

from anhydrite, C₂S and calcite. It shows also that the fluorapatite and quartz did not react after activation.

- The role of active calcium and aluminum present in the 2 powders can explain the difference of the compressive strength of the two mortars.

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