

# **CHEMICAL COMPOSITION CORRECTION OF ALUMINOSILICATE MATERIALS TO ENHANCE THEIR CONDITIONS AS PRECURSORS FOR ALKALINE ACTIVATION**

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### Abstract

Alkaline activation is under great attention as a useful process for producing other sort of binders than Portland cement. The great majority of the researchers are mainly focussed in low calcium alumino-silicates, such as metakaolin, fly ashes, and more recently mine tailings. Fewer works are available where the use of other kind of alumino-silicates is considered. However, in these cases, very rarely the chemical composition of such alumino-silicates when used as precursor materials allows the obtaining of a complete reaction with an alkaline solution. The development of the alumino-silicate gel structure mainly depends on the Si/Al ratio of precursor materials. Consequently, a major part of alumino-silicate materials although having rich content in alumina or silica cannot be used as precursor materials, unless adjustments of their chemical compositions are made. This paper presents a research work, which intends to demonstrate the feasibility of alkaline activation of most alumino-silicate materials by adding other source materials of different chemical composition in adequate proportions. The study was carried on two different volcanic ashes by adding some quantities of waste water sludge and glass powder. The results obtained in terms of mechanical performance and chemical stability demonstrated that alkaline activation was clearly improved in such blended materials. This could favour the alkaline activation of a larger range of materials, for example, those having negative environmental impacts.

### 1. Introduction

During the last thirty years, a great attention has been taken towards the knowledge and understanding of a new kind of materials obtained by the alkaline activation of alumino-silicates that represent a major part of all solid inorganic environment. Several research groups all around the world are committed to the study of properties and capacities of the related final reaction products that cover a bigger range of abilities when compared with current products made of ordinary Portland cement. Alkali activated materials, also designated as geopolymers, present a high standard of mechanical behaviour, resist quite well to common aggressive conditions like acidic environments or high temperatures, possess adequate freeze-thaw resistance, exhibit low shrinkage and moreover they are relatively easy to process not involving any special preparation or specific basic ingredients [1, 2].

It is known that the most suitable raw materials for this type of reaction are alumino-silicates (Al-Si) that have undergone a previous thermal treatment, naturally or artificially caused, enabling the formation of an amorphous state, at room temperature, that could favour chemical combinations [3]. Fly ash, blast furnace slag or metakaolin are Al-Si materials with adequate composition to be alkaline activated, giving place to binder materials that harden quite fast at ambient temperature, presenting very good engineering properties after activation [4].

It is also understood that the chemical composition of basic materials is of great importance because a certain level of relative abundance of some species during activation is necessary in order to promote the reaction pattern that could end in final products capable of presenting the general performance that it is recognized to those novel materials [5].

Alumino-silicates are mainly constituted by silica ( $\text{SiO}_2$ ) and alumina ( $\text{Al}_2\text{O}_3$ ), but they have normally associated others species as calcium, sodium or potassium oxides ( $\text{CaO}$ ,  $\text{Na}_2\text{O}$ , and  $\text{K}_2\text{O}$ ) that seems to favour the reaction [6, 7]. Other species, like iron oxide ( $\text{Fe}_2\text{O}_3$ ), at a certain point, may interfere with the reactive mechanisms provoking a loss of characteristics [8].

Several authors [9] refer and implicitly confirm, some composition range limits proposed by Davidovits between the most important species in order to promote the best conditions for alkaline activation. The following range limit ratios based on the chemistry of zeolites, have been appointed so far [10]:

$$\begin{aligned} 3.30 < \text{SiO}_2/\text{Al}_2\text{O}_3 < 4.50, \\ 0.80 < \text{M}_2\text{O}/\text{Al}_2\text{O}_3 < 1.60, \\ 0.20 < \text{M}_2\text{O}/\text{SiO}_2 < 0.80, \end{aligned} \tag{A}$$

where cation  $\text{M} = \text{Na}$  or  $\text{K}$ .

It must be said that these limits are only used for the solid components, which are referred as precursors, being easily recognised that only very few, if any, of the common Al-Si materials available in nature obey completely, in terms of their chemical compositions, to those molar relations. In consequence this drastically diminishes the range of materials to be used in this technique if one considers their use without further improvements. Therefore, it is implied that a chemical correction is necessary to place the raw precursor materials into the right composition being adequate to reactivity.

Until now very little work has been published about the ways or methods that can be used to enhance the chemical composition and reactivity of Al-Si source materials by the use of chemical compounds of a certain nature able to modify the relative abundance and character of the concerned species. A method of joint geopolymerization of three source materials, i.e., fly ash, kaolinite, and albite has been proposed relatively recently. The results show that the compressive strength (as a measure of the extent of reaction) of the formed geopolymer is greatly increased when these three minerals undergo geopolymerization together [11]. More recently, a feasibility study using fly ash to modify mine tailings characteristics to be used as construction material through geopolymerization has been carried on. Considering the extremely high Si/Al ratio of the mine tailings, class F fly ash was used to modify the Si/Al ratio. Addition of fly ash to mine tailings resulted in higher compressive strength of alkaline activated materials. The improving effect of adding fly ash to mine tailings was mainly due to the decrease of Si/Al ratio of the mix reaching the range of the optimum Si/Al ratio, as authors concluded [12].

Thus, the aim of this work is to demonstrate the feasibility of alkaline activation of most alumino-silicate materials by adding other source materials of different chemical composition in adequate proportions. It shows that using non-expensive natural occurring compounds as corrective materials to general Al-Si materials can enhance their reactivity for geopolymerization and consequently, the mechanical strength of final products.

This study was carried on two different volcanic ashes, which by themselves do not react or poorly react under usual alkaline conditions. By adding some quantities of waste water sludge or other sort of residues, the results improve quite consistently. This new approach of using a mixture of different alumino-silicate materials to adjust its chemical composition could favour the alkaline activation of a larger range of materials, including waste materials of several kinds that may cause very negative impacts on the environment.

## 2. Effective $\text{SiO}_2/\text{Al}_2\text{O}_3$ Range Mixing Ratios for Alkaline Activation

Sodium in alkaline activation is generally added through the activator, but at the same time, silica is a major component of sodium silicate (which is also part of the activator). The mixture of the liquid activator with solid precursors causes a distortion of the chemical composition that has to be taken into account. In fact, for the overall composition and  $\text{SiO}_2/\text{Al}_2\text{O}_3$  adequate range ratios, all components present in alkaline mix solution should be considered, in our opinion. The fact that the activator is rich in silica and in sodium oxide has a great influence in the final composition of products obtained by alkaline activation. This is specifically true when the solid precursor has a substantial amount of sodium or a low level of alumina, originating distortions on the effective  $\text{SiO}_2/\text{Al}_2\text{O}_3$  mixing ratios, if the activator components are not taken into account.

Taking into account, Davidovits [13] range limit ratios (A) and his recommendation that liquid activator must obey to a specific molar ratio  $\text{SiO}_2/\text{M}_2\text{O} = 1.85$  (where  $\text{M} = \text{Na}$  or  $\text{K}$ ), it is herein proposed that the above mentioned ratios (A) could be adjusted to the following effective range limit ratios for alkaline activation:

$$\begin{aligned} 4.86 < \text{SiO}_2/\text{Al}_2\text{O}_3 < 5.90, \\ 1.50 < \text{M}_2\text{O}/\text{Al}_2\text{O}_3 < 2.42, \\ 0.31 < \text{M}_2\text{O}/\text{SiO}_2 < 0.41. \end{aligned} \tag{B}$$

These effective range limit ratios (B) are simply obtained by joining both concepts (solid relations - (A) and the molar ratio  $\text{SiO}_2/\text{M}_2\text{O} = 1.85$ ). It must be said, as far as our experience indicates, that the best results in terms of mechanical performance are obtained with compositions, whose ratios lay somewhere in between the referred limits that must be considered as a compositional target for the activation range itself [14].

The proposed framework is not a new idea, only a new way of presenting an established reference that has the advantage of allowing an easy method of controlling the global composition, without distortions. In this work, those effective range limits are used to study the stoichiometry of compositions and to quantify the chemical correction of two materials that by their own could not be activated otherwise.

### 3. Experimental Work

#### 3.1. Alumino-silicate basic materials

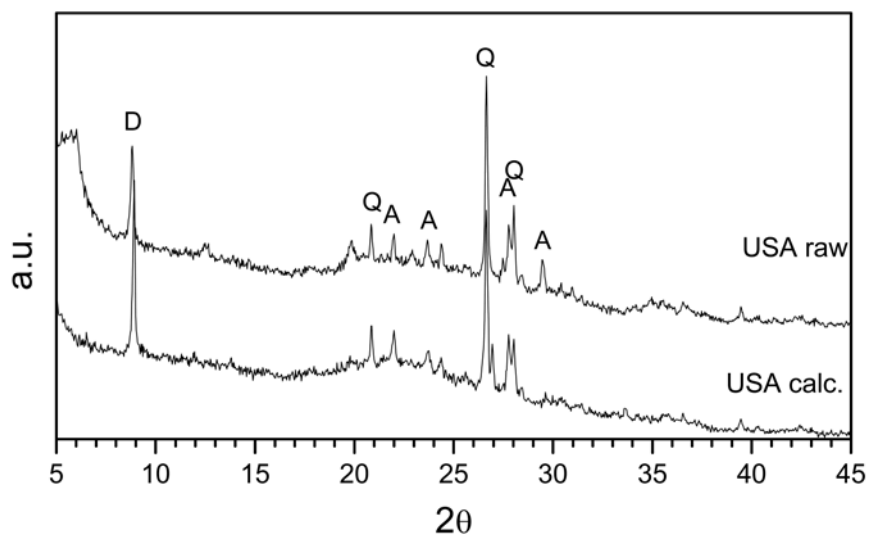
Two different materials were considered as alumino-silicate geopolymeric basic precursor with a chemical handicap in terms of the relative abundance of some species: (a) a volcanic ash from the Cape Verde island of Sto. Antão, named herein CVP; and (b) a volcanic ash from Liton on the plains of North Dakota, on the USA, named in the following as NDVA. Their chemical compositions are presented in Table 1.

**Table 1.** Chemical composition of CVP and NDVA volcanic ashes

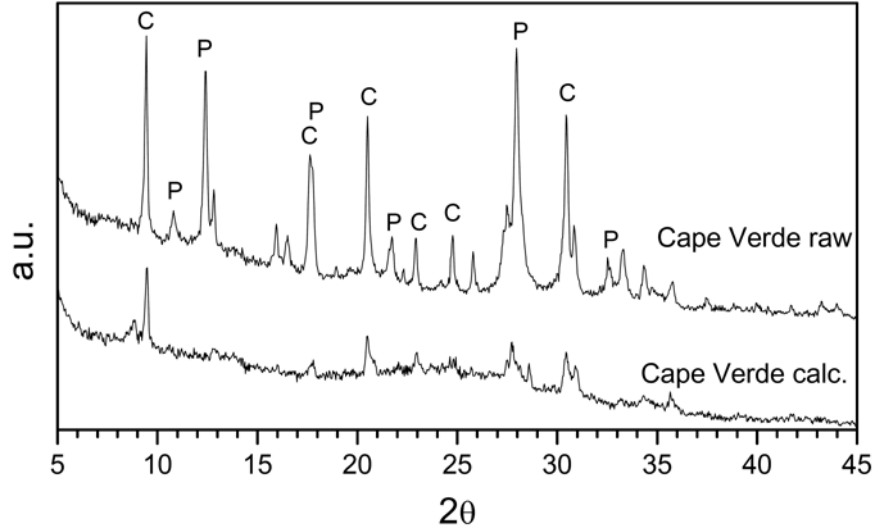
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	K <sub>2</sub> O
CVP	54.32	21.65	2.55	1.39	1.08	0.31	6.08
NDVA	68.89	15.44	2.86	2.05	1.34	0.01	3.13
	Na <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	MnO	SrO	LOI	
CVP	8.68	0.21	0.03	0.00	0.01	3.42	
NDVA	2.55	0.31	0.12	0.06	0.02	1.51	

The loss on ignition (LOI) was determined by TGA and the chemical analysis was performed by XRF analysis. Both materials were previously calcined at 750°C during 2 hours to promote the dehydroxilation. One could suppose that volcanic ashes, due to their thermal history, have a general amorphous nature. Nevertheless, after the elapsing of several millions of years, it is certain that some components have been rehydrated giving place to various types of minerals. Considering the chemical stability of those minerals, the thermal treatment was necessary to enhance the activation potential of both ashes.

XRD spectra of the materials (raw and calcined) as shown on Figures 1 and 2 have in common a visible halo of amorphism (between 10 and 38° 2 $\theta$ ), beyond several crystalline phases of albite (A), quartz (mulite and cristobalite) (Q), dicktite (D) in NDVA ashes, or phillipsite (P), and chabbazite (C), two well-known zeolites, in CVP ashes, and other impurities collected during time.



**Figure 1.** XRD spectra for NDVA.

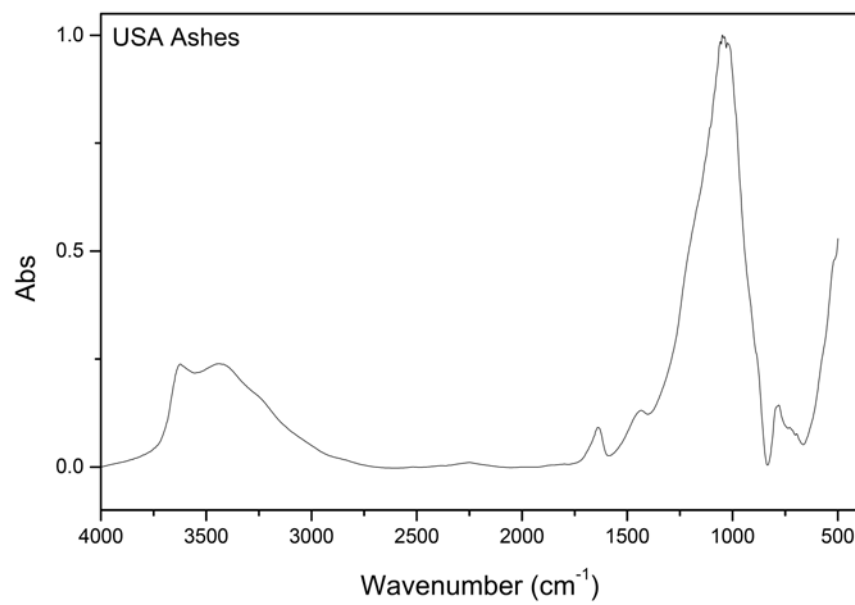


**Figure 2.** XRD spectra for CVP.

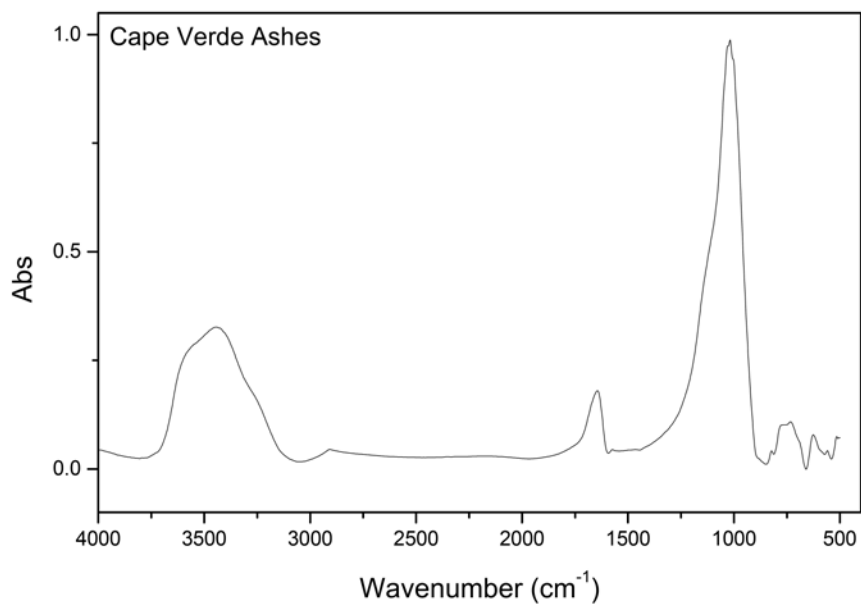
NDVA ashes present a smaller amount of crystalline phases and the amorphism halo is well defined, even in the raw material. The Cape Verde ashes due to re-hydration process present the above mentioned zeolite forms, which after calcination almost disappear when structural water is lost. The presence of absorbed water was, so far, confirmed by FTIR (infra-red spectroscopy). The spectra of Figures 3 and 4 clearly indicate the presence of hydroxyl OH on the band of  $3500\text{cm}^{-1}$ , in raw ashes (not calcined).

According to the chemical compositions of Table 1, composition ratios for both precursors are presented in Table 2. It is easily seen that almost all of the ratios are out of the Davidovits reference range limits (A). Although CVP material has a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  (in short Si/Al) ratio that is well within the range limit, Na/Al and Na/Si ratios are well outside the range limits. On the other hand, NDVA volcanic ash composition ratios are all clearly distant of range limits.





**Figure 3.** FTIR spectrum of USA ashes.



**Figure 4.** FTIR spectrum of CV ashes.

**Table 2.** Main composition ratios of CVP and NDVA volcanic ashes

	$\text{SiO}_2/\text{Al}_2\text{O}_3$	$\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$	$\text{Na}_2\text{O}/\text{SiO}_2$
CVP	4.27	0.15	0.66
NDVA	7.59	0.27	0.036

By applying the methodology described in Section 2, the Si/Al, Na/Al, and Na/Si effective mixing ratios for alkaline activation are indicated in Table 3. Identical conclusions are drawn when comparing ratios of Table 3 with the effective range ratio limits (B) herein proposed. However, by considering ratios presented in Table 3, it is possible to understand not only the need for a correction in alumino-silicate precursor compositions but also how it is advisable to make it, including the activator itself as one possibility.

**Table 3.** Effective ratios of CVP and NDVA volcanic ashes

	$\text{SiO}_2/\text{Al}_2\text{O}_3$	$\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$	$\text{Na}_2\text{O}/\text{SiO}_2$
CVP	5.10	1.30	0.25
NDVA	8.83	1.17	0.13

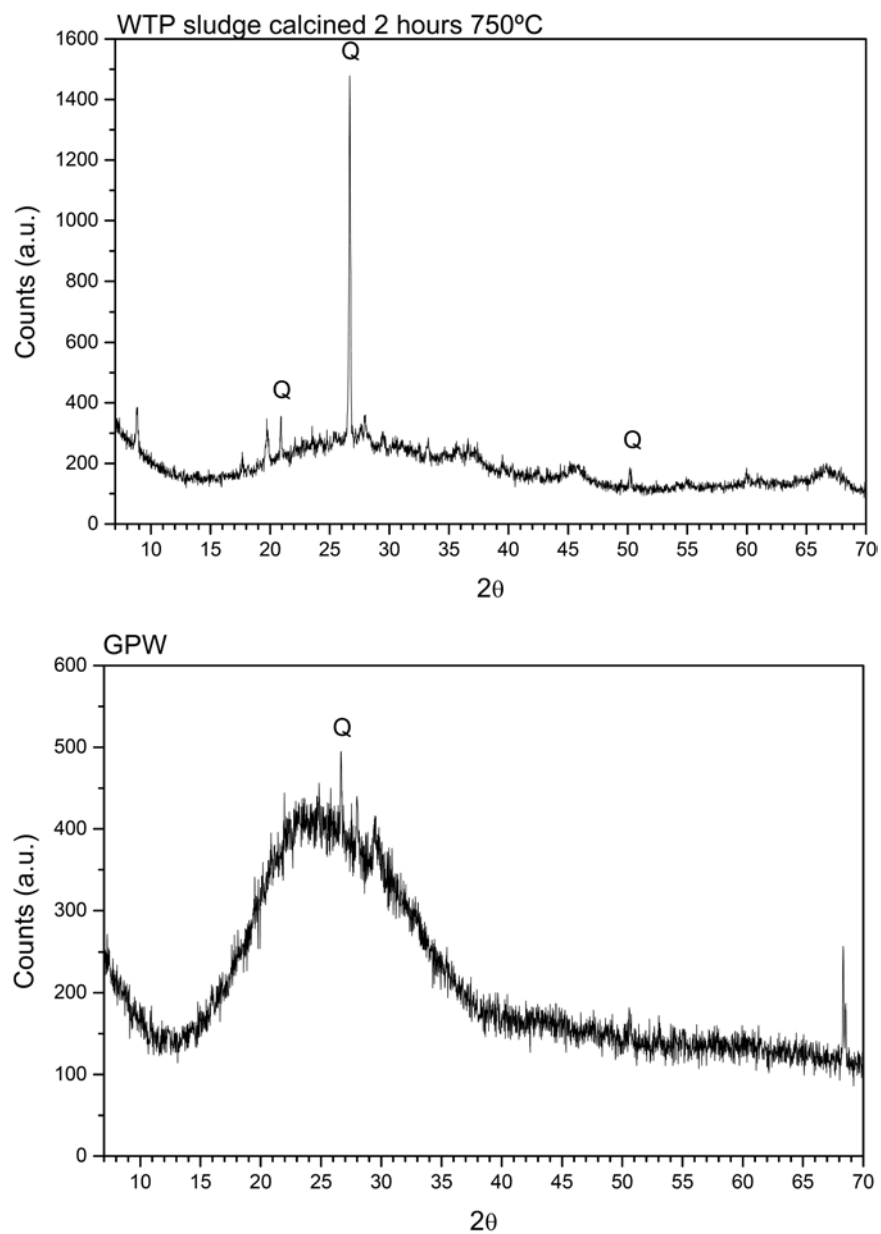
### 3.2. Additional corrective materials

Both volcanic materials have little quantity of aluminium and sodium and a correction of silica content seems also necessary. This correction can be made by blending additional materials to the basic alumino-silicate precursor materials. Beyond the theoretical possibility of using pure chemical compounds, existing natural or waste residue materials, rich in the critical species that could compensate the composition of the volcanic ashes, were considered instead. Thus, waste residue mud obtained from water treatment plants (WTP), which are  $\text{Al}_2\text{O}_3$  rich (aluminium sulphate is used in the treatment process as a flocculent), was considered as a corrector of alumina content. On the other side, glass powder (GPW), silica and sodium oxide rich, was also considered as a corrective compound. Their chemical compositions are indicated in Table 4 and Figure 5 shows the XRD spectra of both species as well.

Additionally, WTP mud was calcined at 750°C for 2 hours to increase degree of its amorphous phases. GPW was not heat treated since it is amorphous by nature. Finally, sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) from commercial source was also considered additional, since it is a powerful way of correcting the need for a higher amount of  $\text{Na}_2\text{O}$ .

**Table 4.** Chemical composition of corrective materials

	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{CaO}$	$\text{MgO}$	$\text{SO}_3$	
WTP	20.59	56.33	4.79	0.45	0.32	11.22	
GPW	68.06	0.42	0.16	9.11	4.14	< 0.03	
	$\text{K}_2\text{O}$	$\text{Na}_2\text{O}$	$\text{TiO}_2$	$\text{P}_2\text{O}_5$	$\text{MnO}$	$\text{SrO}$	LOI
WTP	0.58	0.11	0.11	0.56	0.26	< 0.04	2.11
GPW	0.26	11.86	< 0.03	< 0.03	0.00	0.00	1.08



**Figure 5.** XRD spectra (WTP and GPW).

### 3.3. Basic mix compositions and results

Before any corrective measure was taken, alkali activation trial mixes of both CVP and NDVA precursors were made in order to establish a starting reference that would be useful later to allow comparisons and detect possible gains. Specimens of first trial mixes were prepared following a standard composition: - 1 part of raw geopolymeric precursor (CVP or NDVA) for 2 parts of granite aggregate (0-6.3mm) and 0.6 parts of an alkaline activator (ACTV) composed of sodium silicate and sodium hydroxide in which molar ratio Si/Na equals 1.85.

For the first trial mixes, none of the samples have got hardened after several days at room temperature, nor even when temperature was increased in a climatic chamber up to 65°C with 98% RH for 24 hours. It was also verified that curing at 65°C for 24h at 98%RH was not sufficient as the specimens were not completely dry. Thus, the curing process was completed at room temperature for 4 days more [15].

The same mix composition was repeated, for identical curing conditions, in second trial mixes using calcined geopolymeric precursors. In this case, an apparent certain level of activation was obtained, based in mechanical strength results (Table 5), but no significant. In these conditions, it was noticed that NDVA composition seems to favour slightly higher mechanical strength results than CVP compositions.

**Table 5.** Mechanical strength of alkaline mortars using calcined materials

	Flexo-Traction (ASTM - C - 348 - 97)	Compression (ASTM - C - 348 - 97)
CVP	0.96–1.23MPa	2.87–3.10MPa
NDVA	2.40–2.44MPa	3.75–3.86MPa

### 3.4. Corrected mix compositions and results

Basic mix compositions were then corrected with additional materials referred in Subsection 3.2 taking into account the resulting effective range limit ratios (B). Thus, CVP basic composition was corrected by

adding WTP mud, GPW powder, sodium carbonate (SC) and by increasing of sodium hydroxide concentration (up to 20 molal). The final composition mixture, the percentage of each additional material, Si/Al, Na/Al, and Na/Si effective mixing ratios, as well mechanical strength results are presented in Table 6.

**Table 6.** Mechanical strength of alkaline mortars using corrected materials (CVP)

Si/Al	Na/Al	Na/Si	Composition mixture (g)					Results (MPa)	
			CVP	SC	GPW	WTP	ACTV	Flex.	Comp.
4.853	1.89	0.39	80	10	10	10	75	2.13	12.68

Mixing procedures, in this case, were first preceded by mixing and milling together solid precursors (basic and corrected materials) for about 1 hour by means of a ball mill in order to achieve a good level of homogeneity. Afterwards, the solid corrected precursors were sieved through a 125 micra mesh and finally mixed with alkaline solution. The corrected composition is now within the specified effective range ratio limits and the mechanical strength results obtained after activation has increased accordingly as expected.

The same procedures were repeated for NDVA ashes. Basic composition was also corrected with SC, WTP, and a higher concentration of NaOH (20 molal). The final composition mixture, the percentage of each additional material, Si/Al, Na/Al, and Na/Si effective mixing ratios, as well mechanical strength results are presented in Table 7.

**Table 7.** Mechanical strength of alkaline mortars using corrected materials (NDVA)

Si/Al	Na/Al	Na/Si	Composition mixture (g)					Results (MPa)	
			NDVA	SC	GPW	WTP	ACTV	Flex.	Comp.
5.53	1.75	0.32	70	15	0	15	60	4.54	19.24

#### 4. Conclusion

This paper presents a methodology of chemical composition correction of aluminosilicate materials to enhance its conditions as precursors for alkaline activation. As the case study, certain residues like glass powder from industry waste-pits (rich in Na and Si oxides) and aluminium rich mud from water treatment plants can be used as chemical correctors to promote alkaline activation of other alumino-silicate materials that by themselves do not react.

The experimental work carried on demonstrates that the two volcanic ashes being fine grinded and mixed with corrective materials in studied proportions, may react in a quick and substantial way when submitted to alkaline conditions, provided the adequate final composition is considered. The same principle can be applied to other types of Al-Si, whose chemical compositions present Si/Al, Na/Al, and Na/Si ratios outside the alkaline activation range.

Ashes from Cape Verde present an overall result in terms of mechanical behaviour that is roughly 65% of those coming from Liton in the USA. The reason for that difference, certainly not uncommon, was not in the scope of this work that only pretended to enhance the synergetic use of different materials with different composition to obtain results that otherwise were not possible.

As demonstrated in this work, chemical composition correction of certain alumino-silicates seems to be used to broaden the range of potentially useful raw materials for alkaline activation. Thus, alkaline activation of most abundant alumino-silicate materials, like volcanic fly ashes, can be achieved by adding other source materials of different chemical composition in adequate proportions. Glass powder and water treatment plant mud seem to be adequate and inexpensive corrector of the compositions.

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