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Sustainable alkaline activation of fly ash, aluminium anodising sludge and glass residue blends with recycled aluminium etching solution

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Abstract

Introduction of new residues and wastes in the development of alkaline activated materials is a major concern regarding the spreading and dissemination of this technique. Such increase in the spectrum of available raw materials will decrease the need for long-distance transportation of the more traditional precursors that have been tirelessly used in the past two decades (e.g. fly ash, blast furnace slag). Additionally, the use of commercial activators severely hinders its environmental and financial performance, promoting the need to develop waste-based activators. In this paper, wastes from the aluminium anodising process and the production of optical lenses were combined with low-calcium fly ash, to produce binders exclusively made from wastes and residues. The performance was assessed through uniaxial compression strength tests, which were accompanied by the monitorisation of several physical properties, including temperature, pH and weight; and by a thorough microscopic analysis, including scanning electron microscopy, coupled with energy dispersive spectroscopy, and x-ray diffraction, for mineralogy characterisation. Results show that the addition of glass residue and aluminium anodising sludge to class-F fly ash optimised the final precursor, which was then successfully activated with a disposed aluminium anodizing etching solution, originally used to clean the aluminium surface, prior anodization. The inclusion of soluble silicon and aluminium in the precursor raised the compression strength after short-term curing, compared with pastes prepared only with fly ash.

Keywords: alkaline activation; glass residue; aluminium anodizing residues; fly ash; mechanical behaviour

1. Introduction

For the past decade, industrial wastes and residues have been gaining influence on civil engineering works. The potential of fly ash, ground granulated blast furnace slag, siderurgy slag, construction and demolition waste, among others, to enhance or substitute construction materials is significant. Moreover, the quantities produced are increasing exponentially, which constantly increases the difficulty in reintroducing these by-products in the production chain. Furthermore, most of the current reapplications are based on just a few commonly used materials, such as fly ash and blast furnace slag. Most of the other industrial residues still have low practical usage, which increasingly makes them a preferable research target. The novelty and potential of using these abundantly available and unused raw materials can constitute a significant breakthrough.

The process of alkaline activation (AA) of industrial wastes is a very convincing tool, that can act as a powerful lever for the implementation of the “construction with recycled and sustainable materials” paradigm (Silva et al. 2013; Hoy et al. 2016; Rios et al. 2017). Alkaline activation of fly ash is a procedure in which the grey amorphous powder produced from the coal combustion, rich in aluminium and silica, is mixed with certain alkaline activators and the resulting paste is cured under mild temperature producing hardened materials in a short period of time. The activator is based on an alkali or alkali earth metal, usually in aqueous form, which can substantially raise the pH of the mixture for the reactions to begin. The most commonly used activator solutions, when aiming strength and durability aspects, are based on sodium hydroxide and sodium silicate (Fernández-Jiménez and Palomo 2005; Palacios and Puertas 2007). However, in the industrial manufacturing of sodium silicate (or waterglass), temperatures of around 1300°C must be attained to fuse silica and sodium carbonate together, that are afterwards dissolved in water to produce an aqueous form. This is a highly polluting process, due to the high CO₂ emissions and the high energy required to cause the fusion (Larosa-Thomson et al. 1997; Brykov and Korneev 2008; Cristelo et al. 2015; Torres-Carrasco and Puertas 2015). Sodium hydroxide is one of the most versatile chemicals worldwide, although it is highly “resource intensive and energy intensive” (Hong et al. 2014). It can be obtained by several different techniques, but the mostly used is the electrolysis of sodium chloride, which implies a very significant electrical

energy consumption, including the energy consumed during the brine extraction, essential to produce sodium chloride (Lima et al. 2010). Furthermore, it also has a reasonable extra environmental damage associated with the consequent and inevitable discharge of toxic compounds associated with chlorine (Harris 1999; Hong et al. 2014). Finally, the financial cost associated with the production and thereafter market sell of these reagents can add up significantly to the overall financial burden. Hence, the replacement of the activator components by industrial residues, without technical efficiency loss and gains in terms of financial and environmental performance, is absolutely innovative and essential.

The current paper is part of an ongoing research aiming to develop alkaline binders made exclusively from industrial wastes, specifically for geotechnical applications (involving any kind of stabilisation, deep or superficial). Due to the original raw materials (i.e. wastes) and also due to the mechanical requirements of most geotechnical projects, the threshold behaviour of the mentioned binders is expectedly less demanding than that commonly established for concrete-based applications. To achieve this, a considerable effort must be made to spot, characterise and optimise industrial wastes, and especially to fulfil the activator role, since wastes and residues are already commonly used as precursors. The following industrial wastes were combined: glass residue (GP), aluminium anodizing sludge (AS) and aluminium anodising etching solution, hereafter referred to as ‘cleaning solution’ (CS), having in mind that any alkaline activated paste should comprise the following three major characteristics: high silicon content, high aluminium content and a very high initial pH.

The AS and the CS result from the aluminium processing industry. The CS was originally a strong sodium hydroxide solution that was used to clean the aluminium extrusion steel dies. After some cycles, it becomes less reactive and is thus discarded. Because it dissolves a superficial thin layer of aluminium, at the end of its life cycle it contains both sodium hydroxide and sodium aluminate. Approximately 1000 tons are produced by the Portuguese industry, every year, and its ‘hazardous waste’ status represents a cost of 80 Eur/ton, for proper landfilling. The use of the CS as an alkali activator, as well as the use of the GP as a precursor, was previously reported by the authors (Fernández-Jiménez et al. 2017), with promising results. The FA was also used as a precursor in the mentioned study, and the comparison enhanced the potential of the

GP. Other authors (Onutai et al. 2015; Ogundiran et al. 2016) have also successfully activated fly ash using this CS as an activator, although lower strength values were obtained, in comparison with the commercial activators tested. To the best of our knowledge, the first fundamental study using aluminate solution as an activator was reported already in 2002 (Phair and van Deventer 2002).

The AS is obtained after dehydration of the solution resulting from the neutralization of the acid and alkaline waste generated from the application of oxide coating on aluminium extrusions (Álvarez-Ayuso 2009), a well-known electrolytic passivation process called ‘anodising’, which culminates a series of preparation stages, including the cleaning stage that produces the CS. It possesses a high aluminium hydroxide content and, as such, previous research reported the use of this waste as an aluminium source in the production of calcium sulfoaluminate - belite cements (Raupp-Pereira et al. 2008; da Costa et al. 2016), with promising results in terms of compression strength.

The present work focusses on the assessment of the AS’s contribution for the overall behaviour of the binders developed with a combination of FA and GP, and activated with CS. The silicon and aluminium needs, which are, theoretically, fulfilled by the FA, were enhanced by the addition of GP and the AS, respectively, while the cleaning solution has already proved to effectively raise the pH of the final mixture, thus creating the required conditions to dissolve the Si and Al from the precursors. This kind of studies strongly contribute to the possible future inclusion of other types of residues and wastes in the development of alkaline activation materials, with the potential to substitute more traditional precursors – like fly ash, metakaolin or blast furnace slag; or activators, like sodium hydroxide, sodium silicate), allowing a more versatile and adaptable technique, which will thus become more appealing to the construction industry. The development of the most effective combinations was based on the uniaxial compression strength tests, while cubic specimens were submitted to different analyses, including weight, temperature and pH variation. Microstructural and mineralogical characterisation of the most performing pastes was also conducted, for curing periods up to 112 days, namely scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS), for morphology and chemical composition; and X-ray diffraction (XRD), with Rietveld refinement, for mineralogy identification and phase quantification.

2. Materials and methods

2.1 Materials

The fly ash (FA), provided by a Portuguese thermo-electric power plant and, was classified as Class F, based on its chemical composition (presented in Table 1, obtained by X-ray fluorescence, on a PHILIPS PW-1004 X-ray spectrometer) and ASTM C 618 (ASTM C618 2012). A high silica content was determined, as well as a moderate content of alumina and a very low content of calcium. The glass powder (GP) is a residue from the production of optical lenses, provided by the Portuguese company POLO. It was received in slurry form, and was milled, by hand, in a porcelain mortar and pestle, until it became a very fine powder. Its chemical composition is also included in Table 1, together with the mass loss on ignition (L.O.I.), determined up to 1000°C. Further information on this residue can be found in (Fernández-Jiménez et al. 2017). The GP revealed a very high silica content (58%) and a low aluminium content, of only 4%. Based on UNE 80103 (UNE 80103 2013), specific gravity values of 2.26 and 2.63 g/cm³ were obtained for the FA and GP, respectively, using a Le Chatelier volumenometer.

The AS, initially received in clustered pieces, was broken down in a fine powder by using a stone grinder. **Figure 1** shows the AS before and after grinding. Its chemical composition, presented in Table 1, reveals the presence of a high aluminium content (54%), but also a moderate to high sulphur content (33%). It is expected that the aluminium percentage would make the AS an ideal residue for tailor make the composition of the final mixtures, having in mind alkali activation reactions. However, the sulphur content posed an initial concern, due to the influence that it could produce on the behaviour of the final mixture, namely in terms of compression strength.

The cleaning solution was included in this research in the role of alkali activator. Is is a highly basic aqueous solution, with a density of approximately 1.3 g/cm³, capable of effectively raising the initial pH of the activator-precursor mixture (Fernández-Jiménez et al. 2017). It was used as received in the laboratory, after through homogenisation.

The elemental composition is presented in Table 2, and was determined by means of inductively coupled plasma atomic emission spectrometry (ICP-AES), on a Variant 725-ES ICP atomic emission spectrometer, with the following characteristics: plasma power of 1.40 kW, plasma gas flow of 15.00 l/min, nebulizer gas flow of 0.85 l/min and read time of 5s. The CS alkali concentration is approximately 5M, which is slightly below the sodium hydroxide concentration values usually found in similar research, i.e. approximately 8M (Xu and van Deventer 2000; Fletcher et al. 2005; Panagiotopoulou et al. 2007; Granizo et al. 2014; Cristelo et al. 2016).

Table 1: Chemical composition (wt. %) of the FA, GP and AS obtained through XRF analysis

Table 2: Chemical composition of the cleaning solution used as activator (% wt)

Figure 1: Aluminium sludge as received and dried (left) and after milled (right)

Figure 2 presents the particle size distribution curves of the glass powder and the fly ash. These curves were obtained by laser diffraction, using a Sympatec Helos BF particle-size analyser, with a measuring range between 0.9 μm and 175 μm . The particle size below 45 μm was 89.8, 76.3 and 99.2 wt% for the FA, AS and GP, respectively. This means that the percentage of AS particles above 45 μm (23.7%) was more than 2x the percentage of FA particles above this diameter (10.2%), which most likely hindered its reactivity. At the same time, all GP particles possessed a diameter lower than 45 μm .

Figure 2: Cumulative particle size and particle size distribution of the FA, AS and GP

Mineralogy was analysed with a PANalytical X'Pert Pro MPD diffractometer, with CuK α radiation, 40kV and 30mA, fitted with an X'Celerator detector and secondary monochromator. The resulting diffractograms of the original materials are presented in **Figure 3**. The scans covered a 2θ range of 5 to 70°, with a nominal step size of 0.017° and 100 s/step. The X-Ray diffractogram of the FA showed the two most significant mineral phases usually found in the material received from this power-plant: quartz and mullite. The halo between the 17 and 33 (°2 θ) angles reveals the presence of an important vitreous phase. The XRD of the AS identified Gibbsite and Thenardite (sodium sulphate phase V) as the most significant phases, and trace amounts of sodium sulphate phase III, which is a less stable version of the thenardite mineral, obtained with slightly higher temperatures (Grossi et al. 1997). The presence of an amorphous phase in the AS was also detected, between angles 15 and 25 (°2 θ). As expected, the XRD of the GP revealed a predominantly amorphous state.

Figure 3: XRD patterns of the original FA, GP and AS (G = gibbsite; M = mullite; Q = quartz; S = sodium sulphate phase III; T = thenardite)

2.2 Specimen preparation and testing

The complete list of mixtures tested is presented in Table 3. Two main groups of pastes were sequentially prepared and tested: the first group aimed at identifying the most effective activator content, while the second group aimed at defining the most effective combination between the fly ash and the remaining two precursors. For the first group, a combination of FA (75 wt%), AS (12.5 wt%) and GP (12.5 wt%) constituted the precursor phase, while the activator / precursor ratio assumed the values 0.7, 0.6, 0.5 and 0.4. These first set of experiments defined the most performing activator / precursors ratio (Ac/Pr), which was then used to prepare the pastes of the second set of experiments (FA/Pr), in which the FA content varied between 65 wt% and 85 wt%, with the other two precursors (AS and GP) filling the remaining precursor content, in equal parts.

Table 3: Identification of all the mixtures studied (Ac: activator; Pr: precursors)

Preparation of the pastes started with the dry mixing of the precursors (FA, AS and GP), for 5 min, in a Hobart counter mixer. The activator was then slowly added, and an additional mixing period of 5 min followed, to guarantee adequate homogenisation. Uniaxial compression strength tests (UCS) were carried out to assess the mechanical performance of every paste, on cylindrical specimens with 35mm in diameter and 70mm in height. Curing periods of 14, 28, 56 and 112 days were considered for both groups, in each case allowing a throughout understanding of the reactions' development with curing time. Curing temperature of 25°C and relative humidity of 60% (in a climatic chamber) were exclusively used. Each specimen was weighted and measured shortly before being tested. Results showed in this paper represent the average of three tested specimens. One specimen from each batch, obtained after the conclusion of the

respective mechanical test, was grounded to $<45\text{ }\mu\text{m}$ and frozen with an acetone / ethanol mix, to detain chemical reactions.

Additional analyses were performed, regarding weight, temperature, pH and microstructure variation, throughout the first 4 months of curing. A total of 24 cubic specimens, with 100 mm side (Figure 4), were fabricated for each of these three analyses, for each of the eight pastes. The fabrication procedure was very similar to the one described for the UCS specimens, the difference being the shape (UCS specimens were cylindrical).

Figure 4: Cubic specimens (100 mm) used for monitoring the weight, temperature and pH variation of each of the 8 pastes

The weight variation was monitored throughout the first 60 days (Ac/Pr pastes) and 112 days (FA/Pr pastes) of curing. Since none of these pastes possessed the required consistency to be demoulded during the first few days, they were weighted while still inside the respective mould, which was later subtracted to the total value. The same curing temperature of 25°C was used for both sets, while different humidity values were used for each set, namely 80% RH for the Ac/Pr pastes, and 50% RH for the FA/Pr. The different relative humidity was applied in order to increase the apparently slow rate of water loss registered for the L/S pastes, which, after 60 days, still hadn't reach a stable plateau.

One thermocouple was installed inside a cubic specimen of each of the Ac/Pr and FA/Pr pastes, in order to register the continuous temperature variation during the development of the reactions (Figure 5). The Ac/Pr and FA/Pr sets were monitored for 85 and 98

days, respectively. All the specimens were cured at room temperature, which was simultaneously recorded.

Figure 5: Setup for monitoring the temperature variation inside the specimens (the mould shown on the right was kept while the pastes didn't show the required consistency)

Variations in the pH of each of the four FA/Pr pastes were monitored using both water and calcium chloride (Minasny et al. 2011; Seguí et al. 2017), for a total of 102 days (post-fabrication). The curing conditions throughout the monitoring period were the same as those already described for the temperature variation analysis, i.e. ambient temperature, continuously monitored. For each measurement, a sample was collected from the respective, and purposely fabricated, cubic specimen.

Both the original precursors and hydration pastes were further characterized by Scanning Electron Microscopy (SEM), Energy Dispersive Spectrometry (EDS) and X-Ray Diffraction (XRD), after each predetermined curing period. The SEM analyses were performed on a *FEI Quanta 400* scanning electron microscope, with 30 kV, in low vacuum mode (1.3 mbar), avoiding the deposition of a conductive layer. The device was coupled with a EDS analyser, from EDAX, and the quantitative chemical analysis used a ZAF correction model.

3. Results

3.1 Compression strength

The average peak stress of the three specimens is shown in **Figure 6**. The four pastes presented an increase in UCS between 14 and 56 days, but mostly between 28 and 56 days curing. The highest UCS was produced by the paste with an activator / precursor

ratio of 0.5 (Ac/Pr05), after 112 days curing. Furthermore, this paste presented the higher UCS values for every curing period analysed, and inclusively doubled the UCS of the second most performing paste – Ac/Pr06 – after 112 days. The results suggest that the UCS decreases with the increase in activator content, except for the paste with the lowest liquid/solids ratio (0.4), which showed the lowest UCS values. However, this was probably a consequence of an excessively low liquid content, insufficient for an adequate and effective homogenisation of the mixture.

Another somehow surprising outcome was the slight strength reduction registered between 56 and 112 days, for all pastes, with the exception of the Ac/Pr04 paste. This might be a consequence of the initial water content, which dried with the curing process and enhanced the development of cracks. A factor supporting this hypothesis is that this strength loss decreased with the reduction of the activator / precursor ratio (i.e. with the reduction of the initial water content).

Regardless of the subtleties of some results, the Ac/Pr05 paste was clearly the most performing, and thus the activator / precursor ratio of 0.5 was chosen to proceed to the next phase.

Figure 6: Compressive strength of the Ac/Pr pastes after 14, 28, 56 and 112 days

A second phase of uniaxial compression tests followed, using a fixed liquid/solids ratio of 0.5, to assess the effect of the ratio between the fly ash and the remaining precursors. Four additional compositions were designed and tested, after 28, 56- and 112-days curing. The results are shown in **Figure 7**. The pastes with lower FA content (FA/Pr65

and FA/Pr70) showed a higher 28-day strength than the pastes with more FA in its composition (FA/Pr80 and FA/Pr85), but their strength increase rate was significantly slower from then on, and, inclusively, practically stagnated after 28 days. These results suggest that, on the medium to long-term, the increase in FA was beneficial for the production of aluminosilicate binding gel. Nevertheless, after 112 days, the highest UCS was obtained by the FA/Pr80 paste, indicating that, even for long-term curing, the inclusion of GP and AS has a positive effect on the overall mechanical performance of these pastes.

Figure 7: Compressive strength of the FA/Pr pastes after 28, 56 and 112 days

3.2 Temperature variation and humidity loss

The temperature of the Ac/Pr pastes was monitored from mid-May to mid-August, while the temperature of the FA/Pr pastes was monitored between January and March. This is an important difference, since the ambient temperature in the room, in the winter months, was artificially kept between 28 to 30°C, while in the summer months (May to September), with no artificial heating, the room temperature showed a lower average value (between 20 and 24°C). As can be seen in **Figure 8**, the temperature variation inside the Ac/Pr pastes fluctuates significantly with time, but their pattern is very similar. These variations clearly followed room temperature, which, in turn, was influenced by the season during which the monitoring occurred, i.e. between January and March. While the temperature of the pastes Ac/Pr06 and Ac/Pr04 was always very similar to the room temperature, the temperature of the pastes Ac/Pr07 and Ac/Pr05 was always 2 to 3°C lower. Regarding the FA/Pr pastes (also presented in **Figure 8**), the inside temperature of the cubic specimens followed the room temperature until day 14.

After that, the temperature of the pastes was, in general, higher than the room temperature.

Figure 8: Temperature variation of the Ac/Pr (between January and March) and FA/Pr (between May and July) pastes

Figure 9 shows the mass (i.e. water) loss of the Ac/Pr and FA/Pr pastes, normalised by the initial weight of each cubic specimen. The moulds were removed after 12 curing days, and their respective weight was considered in the data presented. A steep reduction was registered for the FA/Pr pastes after 12 days, when the exposed surface area of the specimens increased, thus increasing also the rate of humidity exchange with the atmosphere. This reduction was not so significant for the Ac/Pr pastes, because the inside temperatures of the pastes were generally lower than the temperatures for the FA/Pr pastes, as can be seen in Figure 8. These higher interior temperatures are a consequence of the higher room temperatures that were registered for the curing of the FA/Pr pastes.

The FA/Pr pastes, all prepared with the exact same initial water content, presented very similar variations through time, and achieved a plateau around day 80, after which the humidity levels inside the specimens seem to have stabilised. It is not surprising that the Ac/Pr pastes showed slightly different humidity loss rates between them, since they were prepared with different initial water contents. The Ac/Pr04, Ac/Pr05 and Ac/Pr06 curves are very similar, up to day 30. After that, the first two showed a similar decrease in mass loss rate, while the Ac/Pr06, with a higher water content, showed smaller reductions in mass loss. Of the four pastes tested, the one which presented the highest mass loss was, clearly, the Ac/Pr07, due to its higher water content.

Figure 9: Mass evolution with curing time (normalised by the initial weight of the specimens)

3.3 pH variation

As evident from **Figure 10**, which shows the pH fluctuation of the FA/Pr pastes throughout the first 98 days, there is an initial steep decrease, in the first 7 days. This is not surprising, given the specific characteristics of alkaline activation, which requires a high initial pH that inevitably will be reduced, as the reactions progress. Thereafter, only smaller variations were recorded, which appear to have occur in response to the room temperature variations. Indeed, the general trend of the pH values seems to be closely dependent on the room temperature, and every significant temperature increase or decrease produced a corresponding decrease or increase in pH, respectively. Regardless, the pH values never again reached the values registered at the beginning of the curing process, showing fluctuations between 10.5 and 11.5, after starting at almost 13. As expected, the values obtained with calcium chloride (CaCl_2) were comparatively a little lower than those obtained with water. Also noticeable is the similarity between all the curves.

Figure 10: pH variation using distilled water (a) and calcium chloride (b) of the FA/Pr pastes

3.4 Microstructure and mineralogy

Figure 11 shows the XRD diffractograms of the pastes FA/Pr65, Ac/Pr05 and FA/Pr85, after curing periods of 14, 28, 56 and 112 days. The Rietveld refinement results of the FA/Pr75 paste, showing quantitative phase analysis and quantification of the amorphous material developed, is presented in **Figure 12**. General trend lines were added to this last graphic, for general guidance regarding the evolution of each phase.

Fourteen days after activation, the amorphous content-related hump in the FA diffractogram showed a slight shift to the right, accompanied by an intensity decrease, due to the formation of some crystalline phases. However, between 14 and 112 days curing, the amorphous content clearly increased, as shown by **Figure 11** and **Figure 12**. This is probably a consequence of the formation of amorphous silica in the gel ([van Jaarsveld and van Deventer 1999](#); [Phair et al. 2000](#)).

The initial quartz was partially dissolved and included in the binding gel, while mullite, being an aluminosilicate mineral, showed a slight content increase, with curing time.

Faujasite-Na, from the zeolite family, was detected after relatively short curing periods. It was clearly present, after 56 days, in all the three pastes analysed, and a 12.7% content was even detected after 28 days, in the Ac/Pr05 paste. The synthesis of faujasite from the alkaline activation of fly ash was previously reported ([Liu et al. 2016](#)).

530

531 Thenardite was very clear after only 14 days. Being, essentially, sodium sulphate, this is
532 not surprising, given the fact that the AS has approximately 33% of SO_3 . Also not
533 surprising is the fact that the FA/Pr65 paste, with the highest AS content of the three
534 pastes, showed the most intense thenardite peaks. Based on the observation of the
535 diffractograms and, especially, on the refinement results obtained for the Ac/Pr05 paste,
536 this phase tends to reduce with curing time. As expected, given the relative percentages
537 of AS in each paste, the FA/Pr85 showed the lowest content.

538

539 Gibbsite, which is mostly aluminium hydroxide (present in the AS) was detected in all
540 three pastes, although more predominantly in the FA/Pr65. This is a consequence of the
541 higher AS content included in the fabrication of this paste. The peak intensity of this
542 mineral phase decreased with curing time, as confirmed by the Rietveld refinement of
543 the Ac/Pr05 data.

544

Figure 11: XRD patterns of the FA/Pr65 (a), Ac/Pr05 (b) and FA/Pr85 (c) pastes (F = faujasite; G = gibbsite; M = mullite; Q = quartz; T = thenardite)

Figure 12: Rietveld phase quantification

Pastes FA/Pr65, Ac/Pr05 and FA/Pr85 were submitted to SEM/EDS analysis, for a thorough morphological and microstructural characterisation, after curing periods of 28 and 112 days, and a summary of the data gathered is presented in Figure 13, Figure 14 and Figure 15, respectively. All the pastes showed evidence of developing a N-A-S-H type gel, after only 28 days.

In terms of morphology, paste FA/Pr65 showed only minimal transformations between 28 and 112 days, contrary to what can be observed for the remaining two pastes. Indeed, the morphology of the pastes Ac/Pr05 and FA/Pr85 has changed significantly during this period. The almost-intact ash particles (mostly with some slight surface dimple) which are seen after 28 days (points A), are less easily detected in the pastes Ac/Pr05 and FA/Pr85, after 112 days. This can be interpreted as a higher volume of gel, after 112 days, after a slow initial reaction (after 28 days). This evolution resulted in a more homogeneous structure for these two pastes.

Figure 13: SEM images and EDS spectra of the FA/Pr65 paste after 28 days (a) and 112 days (b)

Figure 14: SEM images and EDS spectra of the Ac/Pr75 paste after 28 days (a) and 112 days (b)

Figure 15: SEM images and EDS spectra of the FA/Pr85 paste after 28 days (a) and 112 days (b)

The main reaction product is a sodium aluminosilicate gel, as confirmed by the average gel composition (Table 4), obtained from 20 points per image (i.e. 20 points per curing period, per paste), of which only 6 are presented in each of the three sets of SEM micrographs.

Table 4: Average elemental composition (based on 20 points) of the gels after 28 and 112 days (wt.%)

This data shows also the incorporation of sulphur (S), originally present in the aluminium sludge, in the form of SO_3 . The S content decreased between 28 and 112 days in paste FA/Pr65. For pastes Ac/Pr05 and FA/Pr85, the percentage of S also increased significantly – 2.5x and 4.8x, respectively. The fact that these two pastes showed a significant strength increase, during this interval, indicates that the incorporation of S in the gel structure is not detrimental. At the same time, the fixation of sulphur ions in the structure might also indicate that it does not represent an environmental concern, although this possibility needs to be confirmed with a specific experimental campaign.

4. Discussion

Two different mechanical assessment phases were developed, to determine the optimum activator/precursor wt. ratio (phase 1) and the optimum precursor combination (phase 2). Based on the results obtained from phase 1, the compression strength (UCS) increases with the decrease of the activator/precursor content. The highest UCS results were obtained for the paste Ac/Pr05, although such optimum value might be further reduced if not for the poor homogenisation conditions encountered during the fabrication of the Ac/Pr04 paste, due to excessively low liquid content.

Phase 2 showed that the fly ash content also had an optimum value in terms of GP and AS contents. Higher FA contents (FA/Pr80 and FA/Pr85) were responsible for the highest UCS values after medium-to-long term curing, while increased GP and AS percentages (FA/Pr65 and FA/Pr70) produced the highest short-term UCS. This is an interesting result, since one of the current disadvantages associated with the

introduction of alkaline activation in civil engineering applications (if not the most relevant) is the higher curing periods required by most of the activator-precursor combinations tested, comparatively to Portland cement. Furthermore, the highest UCS obtained during phase 2 was obtained with the paste FA/Pr80, and not with the FA/Pr85, indicating that the introduction of an adequate percentage of soluble silicon (from the GP) and soluble aluminium (from the AS) has a positive effect, as opposed to using exclusively FA in a precursor role. This is likely to be caused by the introduction of the AS and/or GP, which helped to reduce the volume and number of structural pores, thus generating a more compact material (Palomo et al. 2004).

The humidity loss of the FA/Pr pastes stabilised between the 56 and 112-day curing period. This factor doesn't seem to have a clear influence on compression strength, since the UCS of two of these pastes (FA/Pr80 and FA/Pr85) increased significantly during this period.

A progressive and sub-linear reduction in the pH was observed throughout the curing process, after significant initial variations. This pattern suggests that the pH influence on the development of the binding gel is only felt during the first few days after the beginning of the reactions.

In terms of phase evolution with curing time, the general trends observed for the Ac/Pr05 paste were: decrease of the quartz, gibbsite and thenardite phases and increase in the faujasite-Na zeolite and mullite phases. The total amorphous content showed a slight increase, which is explained by the amorphous to semi-crystalline state of the aluminosilicate gel formed after activation (Yip et al. 2005). The formation of the new zeolite-type crystalline phase faujasite-Na represents an interesting development, since the formation of crystalline precipitates in the structure of amorphous silicate materials is not easily detected, due to the demanding conditions required, namely the need for an adequate water content to fully hydrate the species in solution (Duxson et al. 2007). The strength decrease registered in the pastes with a FA content of 75% or less, between 56 and 112 days, which was probably a consequence of excessive internal cracking, might be compensated, in the long-term, by further growth of fully crystalline precipitates. The transition from amorphous to semi-crystalline is common, even if it happens only after very long periods subjacent to the beginning of the reactions (Fernández-Jiménez

et al. 2006).

This study focused on the introduction of three industrial wastes – glass residue (GP), aluminium anodizing sludge (AS) and a sodium hydroxide-based aluminium etching (cleaning) solution (CS) – in the production of alkaline binders. All the combinations tested also included fly ash (between 65% and 85%), which is an industrial residue, as a precursor. The intention of using the mentioned additional precursor materials (GP and AS) was the inclusion of soluble silicon (from the GP) and soluble aluminium (from the AS), thus improving the short-term strength increase of the alkaline binder. The use of the etching solution allowed to avoid the inclusion of any commercial activator, like sodium silicate or sodium hydroxide, which would represent a significant financial and environmental cost. Apparently, the incorporation of GP and AS was beneficial for the mechanical behaviour of the composite, since it increased the total amount of soluble silicon and soluble aluminium, respectively, in the newly formed binding gel, resulting in a combination (FA/Pr80) with higher compression strength than the pastes with more FA (FA/Pr85). Even avoiding more traditional materials, the compression strength achieved was significant (in excess of 8 MPa), and more than that required for geotechnical and non-structural civil engineering applications.

4. Conclusions

The presented research aimed to assess the potential use of different wastes, produced by the aluminium anodising and optical lenses industries, as partial substitutes of thermo-electric fly ash, in the role of precursor for alkaline activation reactions. The fly ash, glass power and aluminium sludge blends were then activated with another waste, originally used to etch aluminium surface before the application of electrolytic passivation. The incorporation of these wastes, less common in alkaline activation studies, together with the more traditional FA precursor, increases the versatility of the technique, since the raw materials sources will be more effectively spread, not to mention the increase in the overall volume available.

- Results showed that there is an optimum FA/(AS+GP) ratio, after which the compression strength of the mixtures decreases, meaning that the incorporation of these wastes (AS and GP) was, indeed, beneficial.
- A decrease in the activator content showed a positive effect on the mechanical behaviour of the blends, providing it is not reduced below the ideal homogenisation value.
- The increase of GP and AS promoted a faster strength development, after short-term curing periods of 28 to 56 days; while lower GP and AS contents produced the highest strength after 112 days.
- The presence of sulphur in the resulting binding gel was not detrimental to the compression strength of the pastes.

The compression strength results obtained are well above the minimum threshold required for several geotechnical and non-structural applications, which is only possible due to the availability of silicon and aluminium in the additional precursors (GP and AS) as well as to the alkalinity levels of the CS. It is commendable that these results were obtained exclusively from industrial wastes, thus avoiding the significant financial and environmental costs of more common materials, like sodium silicate and/or sodium hydroxide.

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Conflict of Interest

The authors declare that they have no conflict of interest.

References

- Álvarez-Ayuso E (2009) Approaches for the treatment of waste streams of the aluminium anodising industry. *J Hazard Mater* 164:409–414
- ASTM C618 (2012) Standard specification for coal fly ash and raw or calcined natural pozzolan for use in concrete. *ASTM Int Annu B Stand* 1–5
- Brykov AS, Korneev VI (2008) Production and usage of powdered alkali metal silicate hydrates. *Metallurgist* 52:648–652
- Cristelo N, Miranda T, Oliveira DV, et al (2015) Assessing the production of jet mix columns using alkali activated waste based on mechanical and financial performance and CO₂(eq) emissions. *J Clean Prod* 102:447–460
- Cristelo N, Tavares P, Lucas E, et al (2016) Quantitative and qualitative assessment of the amorphous phase of a Class F fly ash dissolved during alkali activation reactions - Effect of mechanical activation, solution concentration and temperature. *Compos Part B Eng* 103:1–14
- da Costa EB, Rodríguez ED, Bernal SA, et al (2016) Production and hydration of calcium sulfoaluminate-belite cements derived from aluminium anodising sludge. *Constr Build Mater* 122:373–383
- Duxson P, Fernández-Jiménez A, Provis JL, et al (2007) Geopolymer technology: The

current state of the art. *J Mater Sci* 42:2917–2933

Fernández-Jiménez A, Cristelo N, Miranda T, Palomo Á (2017) Sustainable alkali activated materials: Precursor and activator derived from industrial wastes. *J Clean Prod* 162:1200–1209

Fernández-Jiménez A, Palomo A (2005) Composition and microstructure of alkali activated fly ash binder: Effect of the activator. *Cem Concr Res* 35:1984–1992

Fernández-Jiménez A, Palomo A, Sobrados I, Sanz J (2006) The role played by the reactive alumina content in the alkaline activation of fly ashes. *Microporous Mesoporous Mater* 91:111–119

Fletcher RA, MacKenzie KJD, Nicholson CL, Shimada S (2005) The composition range of aluminosilicate geopolymers. *J Eur Ceram Soc* 25:1471–1477

Granizo N, Palomo A, Fernández-Jiménez A (2014) Effect of temperature and alkaline concentration on metakaolin leaching kinetics. *Ceram Int* 40:8975–8985

Grossi CM, Esbert RM, Suarez del Rio LM, et al (1997) Acoustic emission monitoring to study sodium sulphate crystallization in monumental porous carbonate stones. *Stud Conserv* 42:115–125

Harris J (1999) The economic importance of chlor-alkali industry products, and alternatives to those products, to the Canadian economy. *Chemosphere* 38:2533–2548

Hong J, Chen W, Wang Y, et al (2014) Life cycle assessment of caustic soda production: A case study in China. *J Clean Prod* 66:113–120

Hoy M, Horpibulsuk S, Rachan R, et al (2016) Recycled asphalt pavement – fly ash geopolymers as a sustainable pavement base material: Strength and toxic leaching investigations. *Sci Total Environ* 573:19–26

Larosa-Thomson J, Gill P, Scheetz BE, Silsbee MR (1997) Sodium silicate applications for cement and concrete. *Proc 10th Int Congr Chem Cem Gothenbg* 3:3

Lima PR, Mirapalheta A, Henrique dos Santos Andrade M, et al (2010) Energy loss in electrochemical diaphragm process of chlorine and alkali industry - A collateral effect of the undesirable generation of chlorate. *Energy* 35:2174–2178

Liu Y, Yan C, Qiu X, et al (2016) Preparation of faujasite block from fly ash-based geopolymer via in-situ hydrothermal method. *J Taiwan Inst Chem Eng* 59:433–439

Minasny B, Mcbratney AB, Brough DM, Jacquier D (2011) Models relating soil pH measurements in water and calcium chloride that incorporate electrolyte concentration. *Eur J Soil Sci* 62:728–732. doi: 10.1111/j.1365-2389.2011.01386.x

- Ogundiran MB, Nugteren HW, Witkamp GJ (2016) Geopolymerisation of fly ashes with waste aluminium anodising etching solutions. *J Environ Manage* 181:118–123
- Onutai S, Jiemsirilers S, Thavorniti P, Kobayashi T (2015) Aluminium hydroxide waste based geopolymer composed of fly ash for sustainable cement materials. *Constr Build Mater* 101:298–308
- Palacios M, Puertas F (2007) Effect of shrinkage-reducing admixtures on the properties of alkali-activated slag mortars and pastes. *Cem Concr Res* 37:691–702
- Palomo A, Fernández-Jiménez A, Criado M (2004) “Geopolymers”: same basic chemistry, different microstructures. *Mater Construcción* 54:77–91
- Panagiotopoulou C, Kontori E, Perraki T, Kakali G (2007) Dissolution of aluminosilicate minerals and by-products in alkaline media. *J Mater Sci* 42:2967–2973
- Phair J, Deventer JSJ Van, Smith JD (2000) Mechanism of polysialation in the incorporation of zirconia into fly ash-based geopolymers. *Ind Eng Chem Res* 39:2925–2934
- Phair JW, van Deventer JSJ (2002) Characterization of Fly Ash-Based Geopolymeric Binders Activated with Sodium Aluminate. *Ind Eng Chem Res* 41:4242–4251
- Raupp-Pereira F, Ball RJ, Rocha J, et al (2008) New waste based clinkers: Belite and lime formulations. *Cem Concr Res* 38:511–521
- Rios S, Cristelo N, Viana da Fonseca A, Ferreira C (2017) Stiffness Behavior of Soil Stabilized with Alkali-Activated Fly Ash from Small to Large Strains. *Int J Geomech* 17:04016087
- Seguí Y, Angst U, Elsener B (2017) pH - monitoring in mortar with thermally - oxidized iridium electrodes. *RILEM Tech Lett* 59–66. doi: 10.21809/rilemtechlett.2017.37
- Silva RA, Oliveira D V., Miranda T, et al (2013) Rammed earth construction with granitic residual soils: The case study of northern Portugal. *Constr Build Mater* 47:181–191
- Torres-Carrasco M, Puertas F (2015) Waste glass in the geopolymer preparation. Mechanical and microstructural characterisation. *J Clean Prod* 90:397–408
- UNE 80103 (2013) UNE 80103:2013 - Metodos de ensayo de cementos. Ensayos físicos. Determinación de la densidade real. AENOR - Asoc Española Norm y Certificación

882 van Jaarsveld JGS, van Deventer JSJ (1999) The effect of the Alkali Metal Activator on
883 the Properties of Fly Ash-Based Geopolymers. Ind Eng Chem Res 38:3932–3941
884 Xu H, van Deventer J (2000) The geopolymerisation of alumino-silicate minerals. Int J
885 Miner Process
886 Yip CK, Lukey GC, van Deventer JSJ (2005) The coexistence of geopolymeric gel and
887 calcium silicate hydrate at the early stage of alkaline activation. Cem Concr Res
888 35:1688–1697
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890
891
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Table 1: Chemical composition (wt. %) of the FA, GP and AS obtained through XRF analysis

Element	FA	GP	AS
Na ₂ O	0.93	8.75	9.5
SiO ₂	55.27	58.37	0.4
Al ₂ O ₃	21.77	3.940	54.1
MgO	1.37	0.492	-
K ₂ O	2.82	4.659	-
CaO	2.85	6.128	-
TiO ₂	1.58	2.730	-
Fe ₂ O ₃	11.15	0.148	-
ZnO	0.03	2.572	-
ZrO ₂	0.05	2.155	-
BaO	0.12	2.300	-
PbO	-	5.072	-
SO ₃	1.55		33.0
P ₂ O ₅	0.70		-
CO ₂	-	-	2.4
Others	1.368	0.833	0.833
L.O.I.	6.470	1.849	-
Si/Al	2.53	14.81	-

Table 2: Chemical composition of the cleaning solution used as activator (% wt)

Al ₂ O ₃	Na ₂ O	SO ₃	H ₂ O	pH	^a [OH] ⁻	Density (g/cm ³)
7.14	12.13	1.18	79.5	≤ 14	5.3	1.30

^a Acid-base reaction with 5N HCL (Panreac S.A.)

Table 3: Identification of all the mixtures studied (Ac: activator; Pr: precursors)

Mixture ID		FA (wt%)	AS (wt%)	GP (wt%)	Ac/Pr (wt.)
Phase 1	Ac/Pr07	75	12.5	12.5	0.7
	Ac/Pr06	75	12.5	12.5	0.6
	Ac/Pr05	75	12.5	12.5	0.5
	Ac/Pr04	75	12.5	12.5	0.4
Phase 2	FA/Pr85	85	7.5	7.5	0.5
	FA/Pr80	80	10.0	10.0	0.5
	FA/Pr70	70	15.0	15.0	0.5
	FA/Pr65	65	17.5	17.5	0.5

Table 4: Average elemental composition (based on 20 points) of the gels after 28 and 112 days (wt.%)

Paste	Element	Weight percentage	
		28 d	112 d
FA/Pr65	Na	28.5	12.5
	Al	16.5	18.4
	Si	35.0	51.1
	S	10.3	5.0
Ac/Pr05	Na	14.9	19.5
	Al	18.0	16.5
	Si	49.9	38.7
	S	3.5	16.7
FA/Pr85	Na	12.4	8.7
	Al	20.1	17.9
	Si	53.8	55.5
	S	2.7	6.7

Figure01

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