Synthesis of alkaline cements based on fly ash and
metallurgic slag: optimisation of the $\text{SiO}_2/\text{Al}_2\text{O}_3$
and $\text{Na}_2\text{O}/\text{SiO}_2$ molar ratios using the response
surface methodology

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Abstract

During the present work, different binders were synthesized by alkaline activation of fly ash (FA) and a mixture of 75% fly ash and 25% metallurgical slag (FASLG). Two different curing periods, of 7 and 28 days, were considered. A Variance Analysis (ANOVA), conducted to assess the effectiveness of the Response Surface Methodology that was used to structure the study, revealed that this was capable to predict, with very satisfactory precision, the maximum compression strength values of the pastes considered. By optimising the independent variables, defined as the $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O}/\text{SiO}_2$ molar ratios, 28-day uniaxial compression strength (UCS) values of 44.3 MPa and 28.5 MPa were predicted, for the FA_{28} and FASLG_{28} , respectively. The experimental results showed UCS values of $\text{FA}_{28} = 41.5$ MPa and $\text{FASLG}_{28} = 22.1$ MPa, confirming the validity of each model. R-square values of 81.4% (FA_{28}) and 75.0 % (FASLG_{28}) are an effective measure of the experimental variability associated with the estimation of new observations, which can be further reduced if more variables are controlled and included in the model.

Keywords: alkali cements; response surface methodology; compression strength; fly ash, metallurgic slag

1. Introduction

The use of industrial residues or by-products as a source of raw materials for the fabrication of binders is partially generated by the necessity to decrease the environmental impact associated with their landfilling. This is the case of a significant proportion of the worldwide production of fly ash, which is either included in the production of cements or stored in deposits designed for hazardous residues. The fly ash resulting from the combustion of coal, produced in powerplants across the world, has usually some dangerous elements in its composition, like As, Cr, Hg, Ni, Pb or Ti. According with studies from Neupane et al (2013) [1], once the fly ash is deposited in a landfill, these dangerous elements can more or less easily leachate into the phreatic water. The worldwide production of fly ash was estimated at approximately 780 million tonnes annually [2]. Moreover, this number is not expected to suffer any significant decrease in the near future, mostly due to the relatively low cost of fossil fuels, especially in countries with large coal deposits, like China, USA, India and Australia [3]. Therefore, the burning of coal for energy production is a habit that will most probably endure for the next decades. Nonetheless, fly ash has been moderately reused in several applications, like cement and concrete production, as a filling material in earth works, in mining operations, in agriculture, in road and railway pavements, or in soil stabilisation. More recently, it has become the single most successful precursor in alkali activation reactions, aiming the fabrication of alkaline cements. In 2013 alone, from the 50 million tonnes of fly ash produced in the US, approximately 40% was reintroduced in the economy through different applications, of which the traditional cement industry was responsible for 11 million tonnes [3]. However, this apparently successful application should also be evaluated considering the fact that, according to Huang et al (2017) [4] – whom has studied the life cycle of municipal solid waste

incineration fly ash under 4 different reuse scenarios (landfill after stabilisation; reuse as raw material in cement kiln; reuse as aggregates in bricks; reuse as alkali in the Waelz process) – the inclusion in cement kiln proved to be the second least interesting option, in terms of life-cycle environmental impact and cost-benefit relationship, superior only to landfilling.

The use of fly ash to synthesize alkaline cements and geopolymers has seen a substantial increase in the last 5-10 years, especially due to the abundance and tailored qualities of this residue. Among these qualities are the high percentages of aluminosilicates (SiO_2 and Al_2O_3), essential elements for the formation of the 3-dimensional structure of any alkali-activated product, and especially their high level of amorphization, resulting from the high calcination temperatures.

The most effective experimental work design techniques have a wide application range, making it a very versatile tool for many scientific areas. They possess a very significant potential in most engineering fields, helping the planning of the production processes of new components or the optimisation of those processes, associated with existing components [5]. In this study, the Response Surface Methodology (RSM) was used, through the software *Minitab* (v17), allowing the estimation of the optimum values of the dependent variables, the definition of the most effective compositions and an adequate support of the decision-making process.

The present paper aims to synthesize simple (fly ash) and binary (fly ash and metallurgical slag) alkaline cements, using the RSM to optimise the $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O}/\text{SiO}_2$ molar ratios. The quality control was achieved by uniaxial compression strength tests. X-ray diffraction (XRD), infrared spectroscopy (FTIR) and back-scattering electron microscopy (BSEM), were used to confirm the molar ratios in the resulting gels.

2. Materials and methods

2.1. Materials

The fly ash (FA) was provided by the Portuguese thermo-electric power plant ‘Central do Pego’ and, based on its chemical composition was classified as Class F (ASTM C 618 [6]). Metallurgical slag (SLG), resulting from the treatment of liquid steel in ladle furnaces, was also used. The general aspect of both precursors is depicted in Figure 1. Two different mixtures were defined based on these two residues: FA (100%FA) and FASLG (75% FA + 25% SLG).

Figure 1: General view of the FA (a) and the SLG (b)

The chemical composition of these three materials, obtained by X-ray fluorescence (XRF) on a PHILIPS PW-1004 X-ray spectrometer, is presented in Table 1, together with the mass loss on ignition (L.O.I.) up to 1000°C. The main components of the FA are silica (54.8%) and alumina (21.6%), with a calcium content of just 1.7%. On the contrary, the SLG shows a very significant calcium content (49.48%). Table 2 shows the FA reactive content of SiO₂ and Al₂O₃ evaluated by chemical attack.

The activator solution, used for the fabrication of the compressive strength test specimens, was composed of sodium hydroxide (SH) and sodium silicate (SS). The

former was supplied in pellets, with a specific gravity of 2.13 at 20°C (99 wt.%), which was then dissolved in water to pre-determined concentrations. The sodium silicate had a unit weight of 1.464 g/cm³ at 20°C, a SiO₂/Na₂O weight ratio of 2.0 (molar oxide ratio of 2.063) and a Na₂O concentration in the solution of 13.0%. Deionised water was used in every mixture prepared during the work presented. The proportions of the sodium hydroxide and sodium silicate were defined based on the SiO₂/Al₂O₃ and Na₂O/SiO₂ molar ratios, which were pre-determined using the response surface methodology.

Table 1: Chemical composition of the precursors (% wt)

Element	FA	SLG
Na ₂ O	1.18	0.13
SiO ₂	54.77	18.79
Al ₂ O ₃	21.57	7.39
MgO	1.87	5.41
K ₂ O	2.56	0.03
CaO	1.68	49.48
TiO ₂	1.01	-
Fe ₂ O ₃	7.33	10.07
SO ₃	-	3.42
Others	1.41	-
L.O.I.	6.47	-
Si/Al	2.53	-

Table 2: FA reactive content obtained by 1% HF chemical attack (% wt)

Bulk	63.17 ± 1.30
Reactive SiO ₂	42.60 ± 0.80
Reactive Al ₂ O ₃	20.57 ± 0.50

2.2. Fabrication and testing procedures

Two distinct groups of mixtures were prepared, based on the precursor composition. Thus, the precursor of the mixture FA was 100% fly ash; while the precursor of the binary mixture (FASLG) was composed of 75 wt% fly ash and 25 wt% slag. The complete RSM process used to determine the several precursor/activator combinations is described further ahead.

Preparation of the FASLG mixtures started with the dry mixing of the solids (FA and SLG) during 5 min in a Hobart counter mixer. After this initial homogenization period,

the activator, which was prepared with distilled water, 4 to 6 hours prior, was slowly added. An additional mixing period of 5 min followed, in order to guarantee an acceptable homogenisation. The activator temperature at the time of the mixing was $25^{\circ}\text{C} \pm 1^{\circ}\text{C}$. Immediately after the mixing process, the homogenized paste was compacted inside cubic stainless-steel moulds, with 40 mm. The general aspect of the moulded specimens can be seen in Figure 2.

Figure 2: General view of some of the moulded specimens

The moulds were then left inside a climatic chamber, under temperature and relative humidity of 25°C and 50%, respectively, for 48h. After this period, necessary for the specimens gain some consistency, they were demoulded and stored again in the climatic chamber until the end of each respective curing period of 7 or 28 days. Each specimen was weighted and measured shortly before being tested.

A servo-hydraulic testing machine fitted either with a 25 kN or 50 kN capacity load cell, with a resolution of 0.006 kN, was used for the uniaxial compression strength tests. These were carried out under monotonic displacement control, at a rate of 0.4 mm/min, and the peak load was obtained. Results showed in this paper represent the average of three tested specimens.

2.3. Analytical characterisation techniques

The mineralogy was examined by a *PANalytical X'Pert Pro* diffractometer with $\text{CuK}\alpha$ radiation, fitted with an *X'Celerator* detector and secondary monochromator. The scans covered a 2θ range of 10 to 80° , with a nominal step size of 0.017° and 100 s/step. The Infrared spectra were acquired using a Thermo Scientific Nicolet iS50 FTIR spectrometer, resorting to an ATR (Attenuated Total Reflectance) accessory with a diamond crystal. The instrument was controlled by the Omnic software package, version 9.2.28, from Thermo Fisher Scientific Inc. A spectrum range of 1600 to 400 cm^{-1} was defined, with a resolution of 4 cm^{-1} and 128 accumulations per spectrum. The spectra were corrected for background interferences, using a baseline to "normalize" the data before comparison. The material was previously milled in a mortar for 20 minutes. BSEM analyses were performed on a JEOL JSM 5400 scanning electron microscope (20 kV), in low vacuum mode (1.3 mbar), avoiding the deposition of a conductive layer. The device was fitted with a solid-state BSE detector and an X-ray energy dispersive analyser (EDX) – Oxford LINK-ISIS – using a ZAF correction model for quantitative chemical analysis.

2.4. Experimental work design using RSM

For the present study, central composite designs (CCD) were developed. This is the most common approach when the aim is to find the functional relationship between the factors and the response, meaning that mathematical connections are established between the response variable and the independent variables. In this case, these independent variables are the molar ratios $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O}/\text{SiO}_2$. For each of the CCD developed (both with a k value of 2), a total of 13 runs were obtained, comprising 4 points for the hypercube, 5 central points and 4 axial points. Table 3 presents the

levels considered for each independent variable, and for each of the two mixtures analysed.

Table 3: Levels for each independent variable

Variable	Level	FA	FASLG
SiO ₂ /Al ₂ O ₃	Lower (-)	4.5	5.1
	Upper (+)	5.5	6.1
Na ₂ O /SiO ₂	Lower (-)	0.1	0.1
	Upper (+)	0.2	0.2

3. Results and discussion

For most of the synthesized binders, either simple or binary, the strength increases with curing time (between 7 and 28 days) was clear, which is a consequence of the precipitation of the reaction products. According to several authors [7–9], a metastable binding gel, rich in Al, precipitates during the initial stages. With curing time, the precipitated gel has an increasingly higher Si content, forming more stable and larger silicate chains, with a subsequent increase in strength. Furthermore, the use of sodium silicate on the activator's composition, as a source of soluble silica, improves the kinetics of the polymerisation [10,11], since it allows the initial gel to have a more balanced Si/Al ratio. Therefore, more of this 'stronger' gel is included in the final matrix, with clear benefits in terms of mechanical behaviour.

3.1 The response surface statistical model

In order to develop the response surface model, the commercial software "Minitab", version 17, was used. When the response trend can be modelled with a linear function of the independent variables, the model is a first order polynomial. When some curvature is required, the level of the polynomial needs to increase. In this case and based on the previous experience of the authors with similar experimental data, a

quadratic polynomial was used. Indeed, the relation between the mechanical strength of the polymerised gel and the initial $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O}/\text{SiO}_2$ molar ratios is usually not linear. On the contrary, depending on the composition of the precursor and the properties of the activator, there is always a peak strength value, corresponding to a certain combination of molar ratios, after which an inflexion of the results is clear. This is valid only if assuming that all the remaining controllable variables, with any kind of influence on the mechanical response (e.g. curing conditions), are kept constant [12–15].

The analysis of variance (ANOVA) between each of the variables ($\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O}/\text{SiO}_2$), their respective effects (linear, quadratic and of interaction), and the mechanical strength determined after different curing periods, can be seen in Table 4. The adequacy of the model was assessed using a lack-of-fit test (F-test), which was made for a significance level of 0.05. With this test it is possible to observe if, during the regression, each parameter achieves a considerable influence on strength (if its P-value is lower than 0.05).

Table 4: ANOVA results for mixtures FA and FASLG, for 7- and 28-days curing

Mixture	Term	7 days curing				28 days curing			
		Value	F	P	Signif.	Value	F	P	Signif.
FA	Constant	-152.7	-	-	-	717	-	-	-
	Si/Al	42.9	21.04	0,002	yes	-247.7	30.91	0.00	yes
	Na/Si	412	0.01	0,909	no	-1616	91.5	0.00	yes
	$(\text{Si}/\text{Al})^2$	-	-	-	-	20.79	7.1	0.013	yes
	$(\text{Na}/\text{Si})^2$	2415.0	17.62	0,003	yes	-	-	-	-
	Si/Al*Na/Si	-227.7	8.86	0,018	yes	355.7	34.14	0.00	yes
	F-test	-	4,29	0,094	no	-	1.74	0.186	no
	SD	1.913	-	-	-	3.1337	-	-	-
	$R^2\text{Adj}$	78.39%	-	-	-	83.57%	-	-	-
	$R^2\text{Pred}$	31.47%	-	-	-	81.39%	-	-	-
FASLG	Constant	-369.0	-	-	-	-1433.0	-	-	-
	Si/Al	54.1	18.83	0.002	yes	478.0	3.28	0.092	no
	Na/Si	2479.0	3.22	0.111	no	1159.0	9.56	0.008	yes
	$(\text{Si}/\text{Al})^2$	-	-	-	-	-41.57	21.73	0.00	yes
	$(\text{Na}/\text{Si})^2$	-4137.0	10.04	0.013	yes	-3371.0	13.23	0.003	yes

Si/Al*	-235.0	1.83	0.213	no	-10.8	0.02	0.895	no
Na/Si								
F-test	55.92	0.59	0.690	no	0.938	0.10	0.758	no
SD	4,3423	-	-	-	2.974	-	-	-
R ² Adj	71.37%	-	-	-	80.31%	-	-	-
R ² Pred	47.43%	-	-	-	75.03%	-	-	-

Si/Al = SiO₂/Al₂O₃ and Na/Si = Na₂O/SiO₂

Based on the ANOVA, the most adequate equations to estimate the mechanical strength of each binder, after each curing period, are formulated (Eq. 1 to 4). The proposed models provided a satisfying approximation of the value, supporting that prediction on the controlled variables, SiO₂/Al₂O₃ and Na₂O/SiO₂ (from this point forward referred to as Si/Al and Na/Si, respectively, unless otherwise stated). R-squared values of 78.4% (7 days) and 83.6% (28 days) were obtained for mixture FA; and values of 71.4% (7d) and 80.3% (28d) were obtained for FASLG. The shape of the models is also presented in Figure 3.

$$M1_7 = -152.7 + 42.9 \cdot \frac{Si}{Al} + 412 \cdot \frac{Na}{Si} + 2415 \cdot \left(\frac{Na}{Si}\right)^2 - 227.7 \cdot \frac{Si}{Al} \cdot \frac{Na}{Si} \quad (1)$$

$$M1_{28} = 717 - 247.7 \cdot \frac{Si}{Al} - 1616 \cdot \frac{Na}{Si} + 20.79 \cdot \left(\frac{Si}{Al}\right)^2 + 34.14 \cdot \frac{Si}{Al} \cdot \frac{Na}{Si} \quad (2)$$

$$M2_7 = -369 + 54.1 \cdot \frac{Si}{Al} + 2479 \cdot \frac{Na}{Si} - 4137 \cdot \left(\frac{Na}{Si}\right)^2 - 235 \cdot \frac{Si}{Al} \cdot \frac{Na}{Si} \quad (3)$$

$$M2_{28} = -1433 + 478 \cdot \frac{Si}{Al} + 1159 \cdot \frac{Na}{Si} - 41.57 \cdot \left(\frac{Si}{Al}\right)^2 - 3371 \cdot \left(\frac{Na}{Si}\right)^2 - 227.7 \cdot \frac{Si}{Al} \cdot \frac{Na}{Si} \quad (4)$$

Figure 3: Response surface for mixtures FA (a) and FASLG (b), strength prediction model at 7- and 28-days curing

3.1.1 Mixture FA

Based on the ANOVA of the experimental design (Table 4), all the quadratic and interaction effects of the 7 days curing data were significant, except for the linear effect of the Na/Si variable, which presented a P value of 0.909 (> 0.05). This can be interpreted as considering that the strength of this mixture, after 7 days curing, is mainly related with the Si/Al variable. As can be observed in the response surface plot, presented in Figure 3a, the best mechanical performance should be obtained with molar ratios $\text{SiO}_2/\text{Al}_2\text{O}_3 > 5.0$ and $\text{Na}_2\text{O}/\text{SiO}_2 = 0.1$ (the minimum value considered). According to several authors [14,16], low $\text{Na}_2\text{O}/\text{SiO}_2$ molar ratios, in alkaline activation of fly ash, produce lower mechanical properties, due to an insufficient dissolution of the precursor material resulting from the low NaOH concentration. This ratio is partially controlled by the content of soluble silicon, which is provided by the sodium silicate

with the aim of favouring the initial steps of the poly-condensation process. This silicon content is thus subjected to a second variable control, i.e. the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, which only increases the complexity of the task of defining the optimum mixture composition. Nevertheless, it is not surprising that the maximum strength was obtained for the minimum $\text{Na}_2\text{O}/\text{SiO}_2$ value, since this minimum value corresponds to an increase in the soluble Si content, much needed at the beginning of the reactions [16,17].

Regarding the 28 days curing period, the ANOVA results show that the two variables, as well as their linear, quadratic and interaction effects, are significant (Table 4). This is interpreted as a sign that both variables considered in this study assume a significant proportion of the responsibility for the mechanical strength of the mixtures. The shape of the response model for the FA mixture at 28 days, presented in Figure 3 a, corroborates this interpretation, by showing a clear area of maximum values for a particular combination of the ratios (in this case, for $\text{SiO}_2/\text{Al}_2\text{O}_3 > 5.0$ and $\text{Na}_2\text{O}/\text{SiO}_2 = 0.2$), instead of a scattered distribution of the results. It was already stated that higher NaOH concentrations, in alkaline activation of fly ash, potentiates the dissolution of the precursor, which generates a higher quantity of aluminosilicate gel and, consequently, promotes the cross-linking of the silicate chains which are responsible for the microstructure that controls the mechanical behaviour [18,19]. With the increase in NaOH concentration, time becomes an increasingly important factor, since the initial stages of the reactions occur at a faster pace and the surface of the ash particles are dissolved more rapidly. According with the model presented by Fernández-Jiménez et al (2005) [8], fly ash particles can be divided in three different groups: massive spheres, cenospheres and pleuroospheres (with hundreds of particles in their interior). These particles are progressively dissolved, with time, by the alkaline attack, increasing the amount of reaction products and, thus, the volume of binding gel. The formation of such

products occurs mainly between days 7 and 28 [14], which explains the FA's lower strength values presented by the response surface model, at 7 days curing.

3.1.2 Mixture FASLG

The 7-day curing ANOVA results for the FASLG mixtures (Table 4), revealed that the linear effect of the variable Na/Si and the interaction between the variables Si/Al and Na/Si were non-significant (P values of 0.111 and 0.213, respectively), for this curing period. As already mentioned, for the 7-day FA mixtures a non-significant Na/Si linear variable indicates that the variable Si/Al is the most influential for the strength development, for this curing period. Consequently, the importance of the availability of soluble silica during the first stages of the reaction is clear, which is controllable by the addition of sodium silicate. With the increase in soluble silica, it is possible to improve the mechanical strength, even when the dissolution rate of the precursor is still low (although it should be remembered that, in the present study, the Al content, also very important during the first stages [9,20], is exclusively provided by the precursor, and thus the Al content can't be adjusted without dissolution).

The non-significance of the interaction between the variables Si/Al and Na/Si suggests that, in terms of experimental control, other variables are contributing, to some extent, to the final compressive strength result. Such variables (e.g. the soluble Si, Al and Ca content of the precursor; the Ca content relatively to the Si and Al contents) were not controlled due to various reasons, either because they could not be experimentally assessed, or simply because we are unaware of their importance. Is it known that the addition of a significant Ca content, provided by the SLG, increases the complexity of the structural matrix formed after the alkaline activation, namely associated with the formation of two different types of gel: N-A-S-H (resulting from the dissolution of the fly ash) and C-A-S-H (from the dissolution of the high Ca content slag) [21] the latter

with a Ca/Si molar ratio lower than the ratio presented by a Portland cement gel, due to the structural inclusion of aluminium tetrahedrons in its silicate chains [22]. In short, although the slag content was kept constant throughout the experimental campaign, the CaO/SiO₂ molar ratio interacted with the variable considered (SiO₂/Al₂O₃ and Na₂O/SiO₂), hence influencing the microstructure and the strength development of the alkaline cement synthesized [23].

Regarding the 28 days curing period, the ANOVA results show that the linear effect of the variable Si/Al (P-value of 0.092) and, especially, the interaction between the Si/Al and Na/Si variables (P-value of 0.895), are statistically non-significant. Experimentally, and similarly to the model developed for the 7-days curing period, the interaction between these two variables is not the only influencing the mechanical response, since the Ca/Si ratio of the SLG, among other factors, was not considered in this study. However, for the 28-days model Figure 3 b, an optimum zone, in terms of mechanical results, is very clear. This zone is centred around the point Si/Al = 5.6 and Na/Si = 0.15 and presented UCS values around 25 MPa. According to other authors [24,25], it is plausible that, with this specific composition, the necessary conditions for the reaction products resulting from the FA (N-A-S-H gel) and SLG (C-A-S-H), precipitate and coexist, in an optimised combination. The moderate NaOH concentration in the system, together with a limited Ca content, should induce a partial substitution, in the predominant N-A-S-H gel, of the Na⁺ ions by the higher valence Ca⁺⁺ ion. This would modify the N-A-S-H gel without totally degrading it, promoting the formation of a gel with a hybrid microstructure of the type (C,N)-A-S-H.

3.1.3 Optimisation

The statistics package *Minitab* (v17) was used to interpret the experimental data and optimise the independent variables – SiO₂/Al₂O₃ and Na₂O/SiO₂ – for each of the two

mixtures, and specifically for the curing period of 28 days. Figure 4 shows the variation of the compression strength (dependent variable) of each mixture, signalling the maximum theoretical UCS. According to other authors [24], the optimisation was based on a desirability function (d), which assumes any value between 0, when the dependent variable is outside the predefined acceptable region; and 1, when such variable is inside this acceptable region. Therefore, the values for the independent variables were chosen according to the highest d value for each mixture, i.e. $d = 1$ (FA₂₈) and $d = 0.929$ (FASLG₂₈).

Figure 4: Optimization of the independent variables

The theoretical optimised results and the experimental results, regarding the response variable, are compared in Figure 5. Both the FA₂₈ and FASLG₂₈ achieved experimental values very close to those predicted by the numerical model. From the R^2 Pred values, presented in Table 4, the RSM was capable to predict, based on the experimental variability, approximately 82% and 75% of the new observations for mixtures FA₂₈ and FASLG₂₈, respectively. Therefore, it appears that the RSM was less efficient in predicting the formulation incorporating fly ash and slag, which might be related with

the fact that, in this case, there are two different precursors involved, thus increasing the uncertainty associated with the following factors:

- Characteristics of the materials, namely the different reactive percentages of each of the main elements relevant in alkali activation reactions, like Si, Al and Ca.
- Their respective optimum curing conditions – low-calcium fly ash and high-calcium slag are known to yield optimum results under different curing temperature [23,26]; and optimum activation conditions – since the initial alkalinity range of both types of precursors is significantly different, with the low-calcium precursor requiring a higher initial pH, during the dissolution stage, than the high-calcium precursor, which excels in less alkaline environments [27].

Figure 5: Theoretical and experimental compressive strength

The relation between R^2_{Adj} and R^2_{Pred} values can give a fairly approximate idea of how precise was the model in representing the experiment. According to some authors [5,24], if the difference between these two values is less than 20%, than the developed

RSM can be regarded as effective. Based on this concept and because the difference between R^2_{Adj} and R^2_{Pred} were 0.19% and 5.28%, for the FA₂₈ and FASLG₂₈, respectively, then it can be assumed that these models were indeed very effective.

3.2 Microstructural characterisation

Figure 6 shows the FTIR spectra of the original materials and the optimised pastes produced from FA (FA) and FA+SLAG (FASLG), after 7- and 28-days curing. Several changes in the microstructure of the pastes can be observed, relatively to the original precursor. The spectrum of the FA presents a main band around 1035 cm^{-1} , which is associated with asymmetric Si-O-Si or Si-O-Al stretching vibrations, confirming some crystallinity of the material. Other relevant signals are those centred around 782 cm^{-1} and 446 cm^{-1} , which are associated with Si-O (quartz) functional groups; and at 555 cm^{-1} , which usually corresponds to bending vibrations of Al-O-Al bonds (octahedral aluminium associated to mullite) [16,25–27]. The synthetization of the pastes produced microstructural changes that were captured by the infra-red technique. One of the most significant was the shift of the main band of the original FA (1035 cm^{-1}) to lower wave lengths, which is attributed to a structural reordination motivated by the precipitation of the reaction products. The shift of the main band depends of several factors, mainly the composition of the precursor, the type of alkaline activator and the curing conditions [25].

Figure 6: IR spectra of the precursor FA and FA and FASLG optimised mixtures

Comparing the spectra of the FA after 7- and 28-days curing, it is possible to assume that the shift of the main band of the paste with 7days (FA₇), between 1035 cm⁻¹ and 1009 cm⁻¹, is mostly attributed to the incorporation of soluble silicon from the waterglass, since the 7-day period was probably not enough to dissolve all the precursor. This is confirmed in the FA₇ spectrum, in which the quartz and mullite bands (782, 446 and 555 cm⁻¹) did not present any meaningful changes, in comparison with the original FA. In the FA₂₈ spectrum it is possible to observe how the main band has shifted to a lower wavelength of approximately 992 cm⁻¹, which is attributed to the precipitation of aluminosilicate gel, as a result of the alkaline activation reactions. This is corroborated by the fact that the bands at 782, 446 and 555 cm⁻¹ have almost disappeared, as a result of the dissolution promoted by the activator. In both the FA₇ and FA₂₈ spectra is visible the formation and growing of new bands, around 861 and 1450 cm⁻¹, which are usually assigned to C-O functional groups, possibly resulting from the

development of different types of carbonate minerals, like calcite and carboaluminate [28–30].

Regarding the optimised FASLG FTIR spectra, very similar observations can be made to those already discussed for the FA pastes. However, a significant difference was found, in the main band of the synthesized material, which presented higher wavelength reductions than the FA-based paste. This is believed to be caused by the presence of slag prompting the formation of a main band around 974 cm^{-1} , due to the asymmetric stretching of Si-O bonds between silicon tetrahedron condensate in Q2 units, thus indicating that the synthesis of the FASLG paste promoted the simultaneous formation of C-A-S-H and N-A-S-H type gels, which, under thermodynamic equilibrium, can generate a hybrid gel more known as (N,C)-A-S-H [22,31,32].

BSEM/EDX was used to perform a quantitative analysis of the reaction products from the optimised FA (Figure 7) and FASLG (Figure 8) mixtures. The effect of curing time on the FA mixture is very clear, with several unreacted particles appearing after 7 days, most of them with Na covering and attacking their surface (points A) or their nucleus (points B). After 28 days, the number of unreacted FA spherical particles is significantly lower, and the mass of aluminosilicate (N-A-S-H) gel is spread-out. At the same time, after 28 days the appearance of cracks on the gel, or on the gel-particle interface, is also very evident, suggesting some type of shrinkage cracking. However, even after 28 days, some unreacted particles, without any signs of Na ‘attack’, can still be found (points C). The most relevant aspect of mixture FASLG Figure 8 was the concentration of Ca in very specific locations (points D), after 7 days curing, which appear to be spread through the matrix, after 28 days. Thus, a hybrid aluminosilicate gel was formed, with significant contributions from sodium and calcium. Several unreacted particles, with no apparent Na ‘attack’ can be seen after 7 and 28 days (points C).

Figure 7: BSEM images of the 7d optimised FA paste, after 7 (a) and 28 (b) days curing

Figure 8: BSEM images of the 7d optimised FASLG paste, after 7 (a) and 28 (b) days curing

The ternary diagrams presented in Figure 9, obtained during the BSEM analysis on gel points, show higher contents of CaO in the FASLG mixture, which is not surprising, given the original composition of both precursors. It is possible that this higher incorporation of CaO in the gel can interfere significantly with the planned $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O}/\text{SiO}_2$ ratios, thus altering the final composition of the gel. Also relevant is the higher Na_2O content in the FASLG mixture, compared with the FA mixture. Finally, the SiO_2 and Al_2O_3 contents are very similar for both mixtures, the exception being the

FASLG after 28 days, when the CaO content clearly affected the overall composition of the mixture.

Figure 9: Ternary diagrams of FA (a) and FASLG (b) mixtures, after 7- and 28-days curing

5. Conclusions

The Surface Response Methodology is a very powerful tool to plan the formulation of alkaline binders. By controlling the independent variables, $\text{SiO}_2/\text{Al}_2\text{O}_3$ y $\text{Na}_2\text{O}/\text{SiO}_2$, it was possible to corroborate the experimental evidence concerning the non-linearity of the response variable (uniaxial compression strength - UCS), regarding the influence of the independent variables. For each alkaline binder thus fabricated, there are

combinations of values that the independent variables can assume, conducing to the best possible final result (maximum UCS)

The ANOVA, performed on the experimental FA and FASLG data, showed that, for the first 7 days curing, the variable $\text{Na}_2\text{O}/\text{SiO}_2$ is statistically non-significant, with respective P values of 0.909 and 0.111. This is a clear indication that the $\text{SiO}_2/\text{Al}_2\text{O}_3$ variable is the main responsible for this short-term strength development, for both types of mixture. After 28 days curing, and for the FA mixture both variables, as well as their interaction, are statistically significant, showing the higher UCS for $\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.5$ y $\text{Na}_2\text{O}/\text{SiO}_2 = 0.2$. For the FASLG mixture, also after 28 days curing, the $\text{SiO}_2/\text{Al}_2\text{O}_3$ variable and the $\text{SiO}_2/\text{Al}_2\text{O}_3$ y $\text{Na}_2\text{O}/\text{SiO}_2$ interaction are not statistically significant. This is probably related with the fact that a third variable - CaO/SiO_2 , not included in the present study, has also a very important role in the alkaline activation of high-calcium gel precursors. Nevertheless, the higher UCS values were obtained around $\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.6$ y $\text{Na}_2\text{O}/\text{SiO}_2 = 0.15$.

After 28 days, the chosen independent variables were optimised based on the experimental data. The most effective values observed, for each type of mixture, were used to maximise the response variable (UCS). The theoretical results predicted by the RSM were 44.3 MPa (FA) and 28.5 MPa (FASLG), while the experimental campaign yielded maximum values of 41.5 MPa and 22.1 MPa, respectively. By implementing the response surface methodology, it is possible to predict, with a very satisfactory precision, the mechanical behaviour of the FA mixture (81.4%), while the precision for the FASLG mixture behaviour was slightly lower (75.0%). This decrease is not surprising, given the fact that an influential variable was not included in the study.

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