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Alkali-activated cement using slags and fly ash

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ABSTRACT: Alkali Activated Cements (AAC) are a very convenient alternative to common binders as waste materials like slag and fly ash are included in their production. In this paper, a response surface method is used to optimize an AAC made with fly ash, steel slag, sodium silicate and sodium hydroxide. For this purpose, an experimental plan contemplating 26 mixtures was developed, which included compression and flexural strength tests. The experimental data was then analyzed using regression analysis and ANOVA. The results indicate that the sodium hydroxide/sodium silicate solution ratio is the most relevant variable, followed by the ratio between the two solid components (slag and fly ash).

1 INTRODUCTION

Most binders used worldwide in the construction industry are based on Portland cement. However, society is more and more concerned about environmental issues, and the production of clinker involves a high amount of carbon dioxide (CO_2) released to the atmosphere, estimated as 5% to 8% of the overall CO_2 released to the atmosphere (Scrivener & Kirkpatrick, 2008). Therefore, there is an ongoing research effort targeting the development of more sustainable binders (Juenger et al., 2011). In particular, the use of waste materials is highly encouraged, since it allows an increase in resource efficiency, while contributing also to enhancing the circular economy.

The alkaline activation technique is particularly adequate to create binders based on residues, such as fly ash or ground granulated blast furnace slag, which constitute very effective options due to their amorphous aluminosilicate microstructure. It consists on a reaction between aluminosilicate materials and alkali or alkali-based earth substances, such as sodium (Na) or potassium (K), or an alkaline earth ion, such as calcium (Ca). The reactions can be summarized in the following sequence. First, there is the destruction, by the high hydroxyl (OH-) concentration in the alkaline medium, of the Si-O-Si, Al-O-Al and Al-O-Si covalent bonds present in the vitreous phase of the original semi-amorphous aluminosilicate (i.e. the precursor). The Si and Al ions are released into the solution as they become available and; at the same time, the alkaline cations—usually Na+ or K+, depending on the activator—compensate the excess negative charges associated with the modification of the aluminium coordination during the dissolution phase. The resulting products accumulate for a period of time, forming an ion-rich solution, which finally precipitates and reorganizes into more stable and ordered Si-O-Al and Si-O-Si structures. If calcium is predominant, relatively to the sodium or potassium, the dissolved Al-Si ions will diffuse from any solid surface, which favours the production of a C-S-H gel phase. Otherwise, the Si and Al ions will be able to accumulate around the nuclei points, sharing all the oxygen ions and forming a Si-O-Al and Si-O-Si three-dimensional structure (the formation of Al-O-Al is not favoured). The resulting product

is an amorphous alumina-silicate gel, which evolves, with curing time and crystallization, from an Al-rich phase to a Si-rich phase. The crystallization, starting almost immediately after the precipitation, is responsible for the hardening of the gel, which eventually matures into alkaline cement, with pre-zeolite as secondary products (Fernández-Jiménez et al., 2005).

The precursor should always be submitted to a previous thermal treatment, capable of inducing the loss of constituent water and the subsequent re-coordination of the aluminium and oxygen ions, transforming an originally crystalline structure into an amorphous one, more susceptible to further chemical reactions. The relative presence of calcium in the precursor and/or in the activator is very important, since the speed of the reactions is highly dependent on the type of aluminosilicate gel being formed, either N-A-S-H or C-S-H. The former needs longer periods in order to mature into a stable and reliable matrix, while the latter has curing/developing periods similar to those obtained with cement-based binders (Dombrowski et al, 2007; Garcia-Lodeiro et al., 2013).

In some cases, constrains related with short deadlines often require tight construction periods, which hinders the use of alkali activated low calcium (class F) fly ash, based on the mentioned slower reaction kinetics of the N-A-S-H gel, when compared with the C-S-H gel. However, in the presence of enough calcium, the two systems are very compatible, and several studies have focused on the characterisation of their interaction and coexistence (Garcia-Lodeiro et al., 2009, 2011; Puligilla & Mondal, 2013). For this reason, in this work a mixture of low calcium fly ash and slag (very rich in calcium) was used to produce an alkaline activated cement (AAC) joining N-A-S-H and C-S-H gel. A central composite design was carried out to mathematically model the influence of mixture parameters and their coupled effects on compression strength and flexural strengths.

2 MATERIALS

2.1 *Slag*

The slag was collected at the Megasa Steel Industry of Maia, Portugal. This facility produces different types of slags some of them certified to be used in concrete as stone replacer. In this case, a white slag was used, which does not have, at the moment, any known application. Since this waste material is rich in calcium (Table 1) it was considered suitable for the production of alkaline activated cement.

2.2 *Fly ash*

The fly ash was collected at the PEGOP thermoelectric power plant at Pego, Portugal. It is classified as type F according to ASTM standard C 618 (ASTM, 2012) due to its low calcium content, as can be observed in the chemical composition presented in Table 2. The loss on ignition value was not specifically determined for the present fly ash, but it should be around 2.59, according to Cristelo et al. (2012) that has worked with a fly ash from the same thermoelectric power plant.

2.3 *Alkaline activator*

The alkaline activator solution was prepared by sodium hydroxide and sodium silicate. The sodium hydroxide was obtained in flake form, with a specific gravity of 2.13, at 20°C, and with

Table 1. Composition of the slag (wt%).

Element	SiO_2	Al_2O_3	CaO	MgO	MnO	Fe total	Cr_2O_3	Others
Slag	23.5	6.6	54.9	8.5	0.4	1.1	0	5

Table 2. Composition of the fly ash (wt%).

Element	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	TiO_2	MgO	Na_2O	SO_3	Others
Fly ash	54.84	19.46	10.73	4.68	4.26	1.40	1.79	1.65	0.7	0.5

95–99% purity. It was then dissolved in water up to the desired concentration. The sodium silicate was already in solution form with a specific gravity of 1.5 and SiO_2/Na_2O ratio of 2 by mass.

3 EXPERIMENTAL PLAN

3.1 *Design of experiments*

Response surface methods offer statistical design of experiment tools that lead to peak process performance. A precise map based on mathematical models is produced which can put all the responses together via sophisticated optimization approaches leading to the discovery of the best option (for example, meeting the required specifications at minimal cost).

These methods are very interesting for mixtures composed by several ingredients, as it is the case of the AAC, to determine the best performing combination. This is often achieved by changing the quantity of each ingredient, at a time, following the traditional one-factor-at-a-time approach. However, this methodology does not account for the interactions between variables which might be estimated using full factorial designs, symbolized mathematically as N^K, where N is the factorial design level and K is the number of variables. A three-level factorial design provides a good prediction. However, as K increases, the number of runs becomes excessive (e.g. with 5 factors, 243 runs are needed). For that reason, it is more convenient to use a two-level factorial design and try to improve it. Nevertheless, when approaching the optimum level of response, a two-level factorial design no longer provides sufficient information to adequately model the true response surface. Such difficulty can be overcome if center and axial points are added to the two-level factorial design, and thus a composite design is obtained, adequately suited to response surface methods (Anderson and Whitcomb, 2005). In this work, a face-centered composite design was used, which means that the axial points are at the center of each face of the factorial space.

3.2 *Key mixture parameters and experimental region*

Input variables for the present work could be the amount of each ingredient of the AAC, namely fly ash, slag, sodium silicate and sodium hydroxide. However, there are abundant works in the literature (e.g., Hardjito et al., 2004; Kupwade-Patil and Allouche, 2013; Cristelo et al., 2013; Rios et al., 2016) reporting correlations between certain parameters and mechanical properties of the AAC such as unconfined compression strength or elastic stiffness. These parameters generally involve: a parameter that relates the quantity of fluid in the mixture; a parameter relating the two solutions of the activator (the sodium silicate and the sodium hydroxide) and the sodium hydroxide concentration. In this work, another parameter was necessary, relating the amount of slag and fly ash. The selected variables can then be summarized as follows:

A. SS/(SS+SH) where SS means sodium silicate and SH means sodium hydroxide;
B. E/(E+C) where E means slag and C means fly ash
C. S/L where S is the solids weight (slag + fly ash) and L is the fluid weight (the activator made by SS and SH)
D. SH conc, meaning the sodium hydroxide concentration in molal

Please note that to apply the described response surface method it was necessary that the variables were continuous and without math indeterminations when some of the ingredients were null. The first variable (SS/(SS+SH)) range was defined between 0 and 1, where 0 corresponds to an activator only composed by sodium hydroxide and 1 to an activator only composed by sodium silicate. The second variable (E/ (E+C)) range was defined between 0.1 and 1 where 1 corresponds to a mixture without fly ash. Since the mixtures without slag were slow to harden they were removed from the plan. The third variable (S/L) range was defined between 1.5 and 2.5, based on preliminary tests. Finally, the sodium hydroxide concentration varied between 5 and 12 molal, as currently found in the literature (Xu and van Deventer, 2003; Cristelo et al., 2013; Phummiphan et al., 2016). To facilitate the paper reading, these variables were named as A, B C and D. This lead to an experimental plan of 26 mixtures.

3.3 *Specimen's preparation and test methods*

To prepare the specimens, the solids (fly ash and slag) were first dry mixed and the solutions for the activator was also prepared. The sodium hydroxide pellets were dissolved in water to the desired molal concentration and let to cool down up to room temperature. Then, the sodium hydroxide was mixed with the sodium silicate solution according to the desired ratio (SS/(SS+SH)). Finally, the solids and the activator were mixed together in an automatic mixer for 10 minutes and molded in beams of $40 \times 40 \times 160$ mm^3 according to the ASTM D 1632 (2007). After two days, the specimens were consistent enough to be demolded, and so they were stored in a temperature controlled room at 20°C, to cure up to 14 days. After the curing period, the specimens were then tested for flexural strength, using three-point loading tests, according to ASTM D 1635 (2012). After leveling the surfaces, the two pieces resulting from the flexural test were also tested for unconfined compression, following the ASTM standard D 1633 (2007).

4 RESULTS

The results of unconfined compression strength (fc) and flexural strength (ffl), at 14 days, were then analyzed, namely, to fit models using regression analysis and ANOVA and to validate the models by examining the residuals for trends. Table 3 presents the results of the estimated models (both in terms of actual and coded values of mixture parameters), including the residual error term (ε), along with the correlation coefficients. In both cases, a variable transformation was used, as indicated in Table 3, in order to stabilize the response variance and improve the fit of the model to the data.

The estimates of the model coefficients, in terms of coded values, give an indication of the relative significance of the mixture parameters on each response. Higher values indicate greater influence of the mixture parameter in the response and on the other hand, a negative value reflects a response decrease to an increase in this parameter.

In this case, it is clear that A is the most important input variable for both response variables. This means that the relationship between the sodium silicate and the sodium hydroxide has a major effect on the mechanical behavior of the AAC. In fact, the quantity of sodium silicate will determine the amount of soluble silica incorporated in aluminosilicate gel, with

Table 3. Fitted numerical models in terms of actual and coded values of mixture parameters.

	Actual values		Coded variables	
Response variable	Log (fc)	√ ffl	Log (fc)	√ ffl
model terms	estimate	estimate	estimate	estimate
independent	−3.63262	+0.20951	+0.72	+1.44
× A	+2.10471	+0.87407	**+0.74**	**+0.66**
× B	−1.67121	+0.53578	−0.16	−0.10
× C	+3.59636	+0.30146	+0.21	+0.15
× A × B	+1.23311	+0.79508	+0.28	+0.18
× A × C	−0.27647	NS	−0.069	NS
× B × C	+0.35146	NS	+0.079	NS
× A^2	−0.74928	NS	−0.19	NS
× B^2	NS	−1.05356	NS	−0.21
× C^2	−0.80865	NS	−0.20	NS
residual error, ε *				
mean	0	0	0	0
standard deviation	0.13	0.17	0.13	0.17
$R^2/R^2_{adjusted}$	0.98/0.97	0.94/0.92	0.98/0.97	0.94/0.92

(NS) non-significant terms; (*) error term is a random and normally distributed variable.

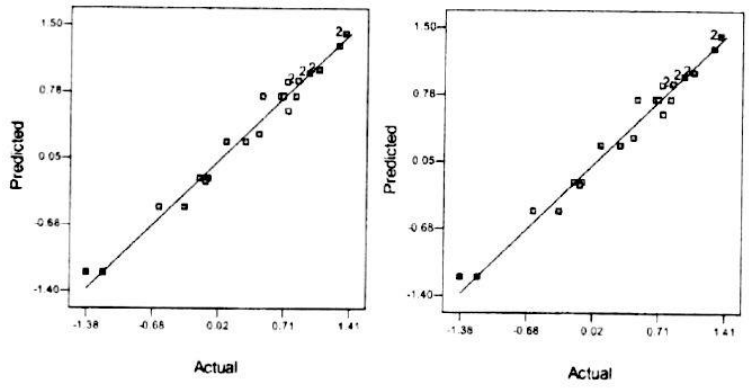

Figure 1. Relationships between predicted and experimental values for the two transformed response variables: a) Log(fc); b) √ ffl.

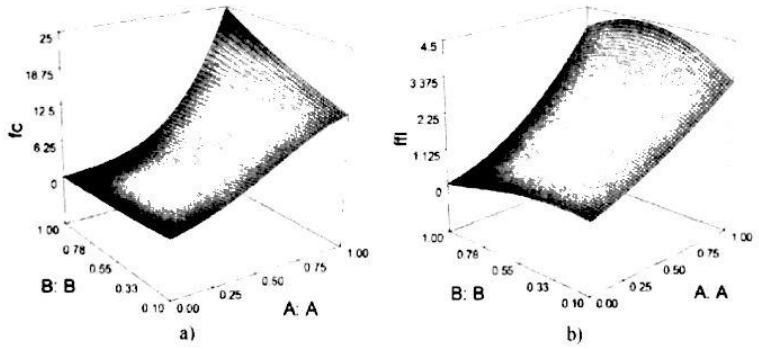

Figure 2. Response surfaces for each response variable: a) Log(fc); b) √ fl.

implications on the structure of the resulting gel (Silva et al., 2007). The second most important variable is the slag/ash ratio, which defines the amount of calcium present in the mixture and thus controls the relative amount of C-S-H and N-A-S-H gels formed, as explained above.

The numerical models presented in Table 3 are well adjusted to the experimental data, as expressed by the R^2, but also by the relationships between predicted and experimental values presented in Figure 1.

The 3D response surfaces associated to the proposed models are presented in Figure 2 for the two most important input variables (A and B), while keeping C = 2 and D = 8.5, which are the center values for these variables. From these surfaces, it is clear that higher values of A and B lead to higher compression and flexural strength values.

5 CONCLUSIONS

The paper presents the use of a response surface method to optimize an alkaline activated cement made by fly ash, slag, sodium silicate and sodium hydroxide. Design of experiments approach was very useful to define the experimental plan and also to analyze the results. Testing a total of 26 mixtures it was possible to obtain a numerical model of the two response variables which were very well adjusted to the experimental data. These models indicated that the best mixture composition is obtained by increasing the two most important variables: the ratio between the two solutions of the activator, and the ratio between the two solids (fly ash and slag).

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