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► **To cite this version:**

Sylvain Louvel, Mariane Audo, Nassim Sebaibi, Mohamed Boutouil, Moussa Gomina. Alkali activated mortars formulation optimized by an experimental design. 37èmes Rencontres Universitaires de Génie Civil, Jun 2019, Nice, France. pp.69-73. hal-02394211

**HAL Id: hal-02394211**

**<https://hal.science/hal-02394211>**

Submitted on 6 Dec 2019

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# Alkali activated mortars formulation optimized by an experimental design

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## ABSTRACT

The worksites of "Grand-Paris" will generate high amounts of excavated lands, without few recovery routes. One of them could be to use those excavated lands into alkali activated materials, based on ground granulated blast furnace slag. The study herein presented concerns the feasibility of using various untreated soils originating from Normandy (France) as the granular skeleton in alkaline activated granulated blast furnace slag-based mortars. The use of experimental designs allowed to optimize the binding phase, by varying the composition of the activation solution, for sand and slag-based mortars. The impact of hardened properties of materials was thus studied.

**Keywords:** Alkali activated concrete; untreated soils; ground granulated blast furnace slag (GGBFS); experimental design

## 1 | INTRODUCTION

Alkali activated concretes based on ground granulated blast furnace slag are today one of the most preferred alternatives to Portland cement-based concrete. Indeed, these new materials have two main advantages, allowing to reduce their carbon impact: the use of industrial by-products and the reduction of the use of Portland cement, whose production is highly CO<sub>2</sub> emitting [1], [2].

Moreover, the use of local resources for material formulation would further reduce these environmental impacts.

The study herein presented concerns the feasibility of using various untreated soils originating from Normandy (France) as granular skeleton in alkaline activated blast furnace slag-based mortars.

The use of experimental designs allowed to optimize the binding phase by varying the composition of the activation solution (concentration, molar ratios, etc.) [3], [4]. After optimizing the formulation for sand and slag-based mortars, the impact of hardened properties of materials was thus studied.

## 2 | MATERIALS

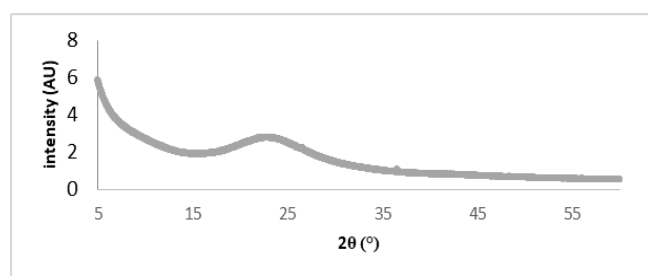
Ground blast furnace slag (GBFS) were provided by ECOCEM. GBFS composition is given in table 1.

**Table 1 | GBFS composition**

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO
wt%	37	11	43	9

0-2 mm siliceous sand provided by SACAB was used in the studied mortars.

Silica (>99% purity), supplied by NORD-HUMIDITE, and sodium hydroxide (>98% purity), supplied by LABBOX, were used as chemicals for the activation solution production. X-ray diffraction of silica is presented on figure 1 and bulging around 20° 2θ confirm its amorphous state.



**Fig. 1 | X-ray diffraction pattern of used silica obtained on Xpert Cu-Kα, presented as a function of 2θ.**

Osmoseis-purified water was produced by an ELGA PURELAB apparatus.

## 3 | METHODS

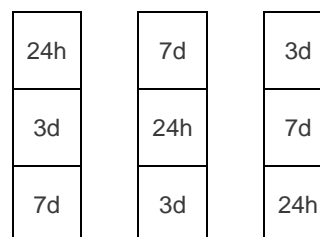
### 3.1 Preparation of the sodium silicate solution

Activation solutions were prepared by adding sodium hydroxide to osmosis-purified water. After partial cooling, ground silica was added. The mixture was kept under continuous stirring for at least 24 hours until perfect dissolution of the silica and equilibrium state between species was obtained [5].

### 3.2 Realization and conservation of specimens

900 g of GGBFS and the activation solution (quantity defined by the experimental design, see paragraph 3.3) were mixed for 90 s at small speed. 2700 g of sand was then added and mixed for 90 s at small speed, followed by 90 s at high speed. The mortars were cast in 4\*4\*16 molds. 6 specimens were cast per formulation.

All specimens were then stored for 24 hours at 20 °C and 95% of relative humidity. After this period, each specimen was sawn into three pieces, following a latin square model presented in figure 2.



**Fig. 2 | Latin square model for specimens sawing**

After 24 hours, half of the specimen series continued to be stored at 20 °C and 95% of relative humidity, while the other half was stored underwater at 45 °C.

For each series, compressive strengths were measured at 24 hours, 3 days and 7 days after the specimens being cast.

### 3.3 Description of the experimental design

The experimental design is a centered composite factorial experimental design. It was selected to study the impact of first- and second-order parameters and their interactions [3]. It was chosen to study three parameters with three levels for each parameter, directly related to the activation solution:

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- The mass percentage of solid in the solution (wt%);
- The molar ratio Na<sub>2</sub>O/SiO<sub>2</sub> in the solution;
- The mass ratio H<sub>2</sub>O/GBFS.

Table 2 presents the equivalence between the normalized values and the effective values. The detailed design of experiments is presented in table 3. The  $\alpha$ -value was set to 1.682 and the center point was repeated six times in order to evaluate the repeatability of the experiment [3].

Table 2 shows the results of the mechanical compression tests at 3 days. Each value represents the average compressive strength of three pieces.

The statistical analysis of the results was carried out using Xlstat and Matlab softwares.

**Table 2 |** Equivalence between normalized notation and chemical solution parameters

	$-\alpha$	-1	0	+1	$+\alpha$
wt%	16.59	20.00	25.00	30.00	33.41
n <sub>SiO<sub>2</sub></sub> /n <sub>Na<sub>2</sub>O</sub>	0.16	0.50	1.00	1.50	1.84
m <sub>H<sub>2</sub>O</sub> /m <sub>BGFS</sub>	0.33	0.40	0.50	0.60	0.67

**Table 3 |** Chemical solution properties and mechanical results for all formulations at 3 days

Order of fabrication	Formulation	Chemical solution properties			Mechanical result at 3 days	
		wt%	n <sub>SiO<sub>2</sub></sub> /n <sub>Na<sub>2</sub>O</sub>	m <sub>H<sub>2</sub>O</sub> /m <sub>BGFS</sub>	$\sigma_{45^\circ\text{C}}$	$\sigma_{20^\circ\text{C}}$
		x	y	z	MPa	MPa
20	I	-1	-1	-1	15.55	12.88
5	II	+1	-1	-1	4.03	7.09
6	III	-1	+1	-1	52.04	30.20
17	IV	+1	+1	-1	24.93	53.76
7	V	-1	-1	+1	30.45	22.32
1	VI	+1	-1	+1	76.89	16.94
16	VII	-1	+1	+1	16.18	11.00
10	VIII	+1	+1	+1	46.30	32.99
2	IX	0	0	0	60.66	47.72
15	X	0	0	0	65.56	46.93
19	XI	0	0	0	60.32	42.56
3	XII	0	0	0	62.36	44.68
12	XIII	0	0	0	52.18	47.94
4	XIV	0	0	0	57.08	51.36
13	XV	$-\alpha$	0	0	33.89	30.09
9	XVI	$+\alpha$	0	0	38.15	54.14
18	XVII	0	$-\alpha$	0	30.24	60.37
11	XVIII	0	$+\alpha$	0	42.27	44.53
8	XIX	0	0	$-\alpha$	2.11	2.76
14	XX	0	0	$+\alpha$	33.85	40.79
21	XXI	1.56	-0.23	-0.55	Presented in table 4	
22	XXII	0.02	0.42	0.06		
23	XXIII	0.29	1.61	1.45		

#### 4 | RESULTS AND DISCUSSION

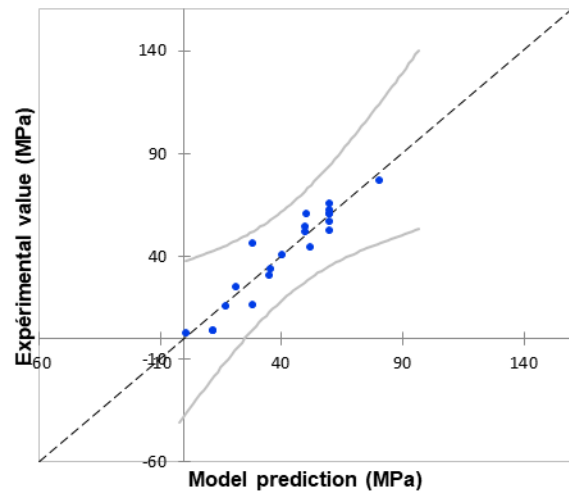
3-days compressive strength results showed an efficient activation of the GGBFS, as strengths as high as 77 MPa could be obtained, with a 45 °C curing. This will allow a large range of applications for the geopolymer binder.

As many studies have already shown, the results presented in table 3 show that thermal curing resulted in an increase of mechanical strength for most formulations. The analysis of the compressive strength results allowed the determination of a model equation at 3 days for both storage conditions (Eq. 1 and Eq. 2). Figure 3 and figure 4 present the distribution of experimental values compared to the predicted values at 3 days and for both curing conditions.

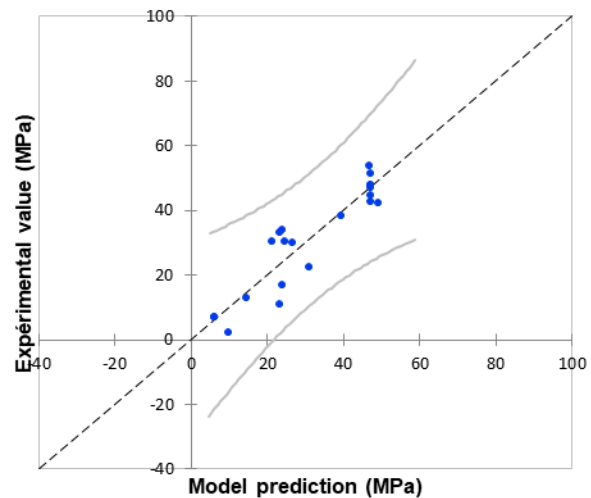
$$\sigma_{45^\circ\text{Cure}} = 59.76 + 4.22x + 0.59y + 11.67z - 5.99x^2 - 3.00y^2 - 13.87z^2 - 5.78xy + 12.60xz - 10.02yz \quad (\text{Eq. 1})$$

$$\sigma_{20^\circ\text{Cure}} = 46.93 + 3.81x + 8.25y + 4.12z - 4.94x^2 + 4.19y^2 + 10.66z^2 + 7.60xy + 0.37xz - 4.46yz \quad (\text{Eq. 2})$$

A quite good fitting between experimental and calculated data is observed. Indeed, R<sup>2</sup> are 0.83 for storage at room temperature and 0.90 for storage at 45°C respectively, which highlights the relevance of the studied parameters. At a level of confidence of 95%, the statistically influent parameters (p<0.05) are, for both equation z, x<sup>2</sup>, z<sup>2</sup>, and yz. Those results are not surprising, because one of Fernández-Jiménez conclusion is that the concentration of the solution is a significant parameter on compressive strength [6]. Moreover, concerning the z parameter, Kamaloo *et al.* mentioned that high water quantities in metakaolin-based geopolymers conduct to bad mechanical strenghts [7]. This phenomenon is also well-known for Portland cement concretes.



**Fig. 3 |** Experimental compressive strength as a function of model prediction after curing at 20°C for 3-day. The grey color curves delimits 95% confidence domain.



**Fig. 4 |** Experimental compressive strength as a function of model prediction after curing at 45°C for 3-day. The grey color curves delimits 95% confidence domain.

Figure 5 and figure 6 show visualizations of the mechanical results at 3 days, according to the 3 parameters of the experimental design. Although this modeling allows a better visualization of the interactions between the 3 parameters, outlier values can be observed at the edges of the model, for example in figure 3, -61.6 MPa for a point with  $x=1.65$ ,  $y=-1.65$  and  $z=1.65$ .

Nevertheless, this model allows to predict the experimental conditions for maximizing the compressive strength. If we reduce our confidence to the bounds -1, 1 for each parameters, this maxima should be obtained for  $x=1$ ,  $y=1$  and  $z=-0.6$  for 20 °C cure and 45 °C cure, for theoretical compressive strengths of 61.68 MPa and 57.43 MPa respectively.

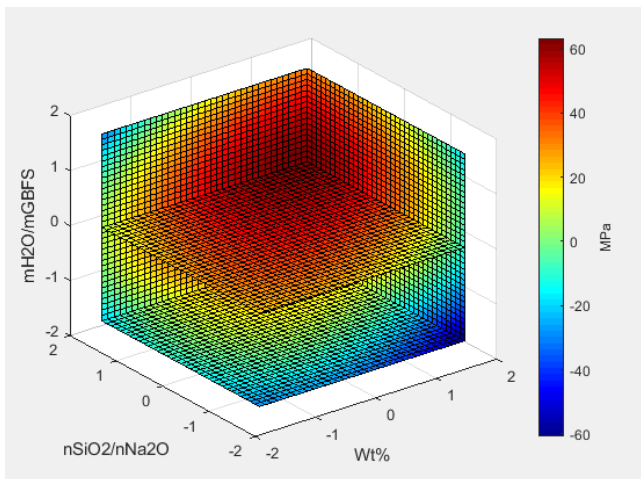


Fig. 5 | Predictive model after 3 day at 20°C.

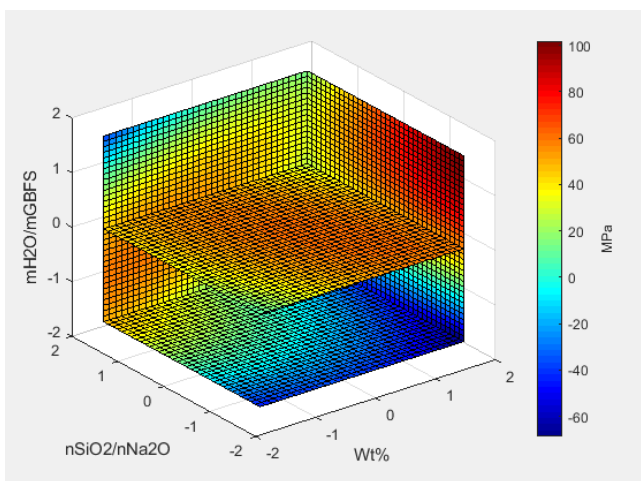


Fig. 6 | Predictive model after 3-day at 45°C.

To validate the model, three random formulations were tested and their results are presented in table 1. Table 4 presents predicted values and mechanical results for formulations XXI, XXII and XXIII.

Table 4 | Predicted value and mechanical result for tested formulations at 3 days

	Formulation	XXI	XXII	XXIII
	Distance to origin	1,44	0,42	2,19
45 °C	Predicted value (MPa)	30,84	59,92	20,59
	Mechanical result (MPa)	46,93	62,72	59,08
	Relative error (%)	-52,17	-4,67	-186,94
20 °C	Predicted value (MPa)	29,63	49,90	26,91
	Mechanical result (MPa)	36,01	44,90	37,35
	Relative error (%)	-21,53	10,02	-38,80

The results demonstrate that further away the formulation is from the central point ( $x=y=z=0$ ), the more false the predicted values are, with a maximum of relative error for the formulation XXIII of -187%. However this is not surprising, considering the outlier values presented before.

In addition, other parameters than compressive strengths must be studied in order to get the optimal GGBFS-based geopolymer: fresh state properties and environmental impacts. Indeed, the activation solutions can present high viscosity depending on concentration and  $SiO_2/Na_2O$  molar ratio [8], which can be prejudicial for fresh-state geopolymers properties. Also, even if the GBFS present a low environmental impact (as they are made of industrial by-products), the activation solution is based on chemicals with a higher environmental impact. Nevertheless, it must be kept in mind that activation solution environmental impact can be easily reduced by using by-products such as waste glass or rice hull [9], [10].

Thus, a balance between sufficient workability, high-enough compressive strength and low environmental-impact should be obtained to get the optimal material.

## 5 | CONCLUSIONS

The method of optimizing a formulation of an alkali-activated material by using an experimental design limited the number of casts to only 20, when a complete design would have required 125 ( $5^3$ ). This process was used to obtain quickly and easily, equations for a predictive model. However, the model equations remain difficult to apply outside the values of the experimental design, with outlier values at the limits of the models.

This methodology was firstly applied to 3-days compressive strength. Later, it will also be applied to other parameters, such as fresh-state fluidity, 5-days and 7-days compressive strength, and  $CO_2$ -eq emissions.

This method made it possible to determine the optimal formulation of an activation solution, allowing a binding phase with good mechanical properties. Subsequently, a new granular skeleton based on untreated soil will be used to observe the differences between this material and the optimized material.

The use of that type of resource could then be applied on sites such as those in "Grand Paris", which are likely to generate large quantities of excavated land, currently without any recovery routes.

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