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Application of the Taguchi approach for the composition optimization of alkali activated fly ash binders

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HIGHLIGHTS

- Hellenic fly ash is converted to structural material having cement-competitive strength.
- Taguchi method permitted the simultaneous optimization of several factors by conducting the minimum number of experiments.
- The alkali to aluminum ratio has the highest impact on the strength development.
- The interrelation of precursor composition, microstructure and strength is reported.

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ABSTRACT

This paper presents an experimental study carried out to optimize the mix proportions of fly ash based geopolymers, in order to achieve the maximum compressive strength. The Taguchi design methodology was applied and the experiments were designed using a L16 orthogonal array with three factors varying at four levels each. The effect of alkali content, alkali kind and silicon content in the activation solution is analyzed using mean response data and ANOVA technique. The final products were examined using XRD, FTIR and SEM. According to the results, the optimum values of the process parameters are sodium to aluminum ratio of 0.85 in the starting mixture and silicon to sodium oxide of 1.35 in the activation solution. The mean value of optimal strength is predicted as 42.6 MPa, with a tolerance of ±3.1 MPa, for a 95% confidence interval. Confirmatory experimental result obtained for the optimum conditions is 43.1 MPa.

1. Introduction

The need for construction materials with fire-resisting properties led Davidovits to the development of novel materials, named geopolymers or inorganic polymers [1]. The formation of geopolymers involves a chemical reaction between an aluminosilicate material and sodium silicate solution in a highly alkaline environment. The synthesis and chemical composition of geopolymers are similar to those of zeolites, but their microstructure is amorphous to semi-crystalline [2]. Theoretically, any aluminosilicate material can undergo geopolymerization under certain circumstances. Previous works have reported the formation of geopolymers from natural minerals [3–5], calcined clays [6,7], industrial by-products [8–11] or a combination of them [12–16].

Factors, such as the curing conditions and the composition of the precursor, strongly affect the structure and properties of geopolymers [17–19]. In addition to the nature and composition of the raw aluminosilicate material, the content of soluble Si, the kind of the alkali ion and the alkalinity of the activation solution are, according to the literature, the most significant factors [6,20–21]. Usually, the effect of synthesis parameters is studied by changing one factor at a time. However geopolymerization is a complicated and dynamic process and in the case of a full factorial design, the experiments are numerous and practically not possible to be carried out. The implementation of a multifactorial experimental designing model allows the investigation of the combining effect of selected parameters, conducting the minimum number of experiments. Taguchi has developed a parameter design method based on orthogonal arrays (OA), which provides a simple and efficient tool for optimizing parameters in complicated systems [22]. The Taguchi method has been used in various industrial fields and research areas and lately it has been also applied in concrete design [23–26].

The application of multifactorial experimental designing models for studying geopolymerization is still very limited. Previous

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works have reported the design of fly ash based bricks [27], fly ash concrete [26], alkali activated cement [28,29] or multi component systems based on alkali activation [30,31].

In this work the Taguchi experimental designing model was applied in order to study the effect of selected synthesis parameters on the strength development of fly ash based geopolymers.

2. Experimental

2.1. Materials and methods

Fly ash used for the geopolymer synthesis comes from the power station at Megalopolis, Greece and its chemical composition is presented in Table 1. This fly ash can be characterized as cementitious and pozzolanic mineral admixture (category II, according to RILEM classification) or as normal pozzolan (category IV). It can also be characterized as Type F according to ASTM C 618, as the sum of the oxides $SiO_2 + Al_2O_3 + Fe_2O_3$ is greater than 70%. The material consists mainly of quartz (SiO_2) and feldspars ($NaAlSi_3O_8$), while anhydrite ($CaSO_4$), gehlenite, cristobalite and maghemite (Fe_2O_3) are found in smaller quantities. Fly ash was previously ground and its mean particle size (d_{50}) was approximately 20 μm. This is a typical fineness of fly ash when used in construction technology (as main constituent in blended cements).

The geopolymer samples were prepared using an aqueous activation solution containing alkali (Na, K) hydroxide and commercial water silica solution. The activation solutions were stored for a minimum of 24 h prior to use, to allow equilibrium. The raw material and the activation solution were mechanically mixed (standard mortar mixer: Controls 65-L0005) to form homogenous slurry which was transferred to 50 mm cubic molds and mildly vibrated. In all mixtures the ratio $m_{\text{solids}}/m_{\text{liquids}}$ was kept to 2.6. The specimens were left for 2 h at ambient temperature before they were cured at 70 °C for 48 h and left to be cooled for 24 h. These curing conditions were found to be optimal in a previous work [17]. Their compressive strength (Wykeham Farrance uniaxial testing machine, load rate: 2400 ± 200 N/s according to EN 196-1) was measured 7 days after the thermal curing (10 days after the mixture preparation) and their structure was examined using XRD, FTIR and SEM.

X-ray powder diffraction patterns were obtained using a Siemens D-5000 diffractometer, CuK_{a1} radiation (λ = 1.5405 Å), operating at 40 kV, 30 mA. The IR measurements were carried out using a Fourier Transform IR (FT-IR) spectrophotometer (Perkin Elmer 880). The FTIR spectra in the wavenumber range from 400 to 4000 cm^{-1} were obtained using the KBr technique. The pellets were prepared by pressing a mixture of the sample and dried KBr (sample: KBr approximately 1:200) at 8 tons cm^{-2}. The microstructure of the samples was studied using a JEOL JMS-5600 SEM and an OXFORD LINK ISIS 300 microanalyser.

2.2. Experimental design

The aim of a parameter design experiment is to identify and design the settings of the process factors that optimize a chosen quality characteristic and are least sensitive to noise (uncontrollable) factors. When many factors/inputs/variables must be taken into consideration, the Taguchi method is a structured approach for determining the "best" combination of inputs to produce a product with optimized properties. The Taguchi method utilizes orthogonal arrays from design of experiments theory to study a large number of variables with a small number of experiments. Using orthogonal arrays significantly reduces the number of experimental configurations to be studied. Furthermore, the conclusions drawn from small scale experiments are valid over the entire experimental region.

The results of the experiments were treated using the analysis of variance (ANOVA), in order to determine the percent contribution of each factor on the compressive strength of geopolymers. ANOVA is a standard statistical technique to quantitatively estimate the relative contribution of each parameter on the overall measured response and to express it as a percentage. The percentage contribution of each factor is the ratio of its sum of squares to the total sum of squares.

The factors selected to be investigated are: (i) the molar ratio R/Al in the starting mixture (R: Na, K). (ii) the molar ratio Na/(Na + K) in the activation solution and (iii) the Si content in the activation solution $[Si]/R_2O$. The experimental design involved their variation in four levels (for example R/Al levels are 0.50, 0.85, 1.20 and 1.50), while their variation range (for example R/Al varies from 0.50 to 1.50) was selected according to physical and chemical restrictions. The variation levels of the selected parameters are presented in Table 2.

Table 1
Chemical composition of Hellenic fly ash (% w/w).

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	L.O.I.
47.86	23.54	7.15	10.56	2.28	1.58	–	2.50	4.30

Table 2
Parameters and their variation levels.

Parameters	Level 1	Level 2	Level 3	Level 4
Alkali to aluminum ratio, R/Al	0.50	0.85	1.20	1.50
Alkali species, Na/(Na + K)	0.00	0.35	0.70	1.00
Silicon content in activation solution, $[Si]/R_2O$	0.00	0.70	1.35	2.00

These factors were selected based on previous literature [17–21] and our preliminary studies. The alkalies participate in the formation of the aluminosilicate network playing a charge-balancing role. The molar ratio R/Al connects the alkalinity of the activation solution to the Al content of the raw material. If this ratio is much lower than 1, the incorporation of Al in the geopolymer network is constrained. In case of ratios much higher than 1 there will be an excess of free alkalis in the final product, leading to carbonation effects. In this study the R/Al ratio was varied from 0.5 to 1.5. The kind of alkali ion is connected to the dissolution of the aluminosilicate material as well as the polycondensation of the geopolymeric gel. Na favors the dissolution of the raw material, while potassium, due to its larger size, favors the formation of less ordered structures, having a positive effect on the formation of the amorphous geopolymeric network. The ratio Na/(Na + K) was used as a variable in order to evaluate the effect of the kind of alkali on the geopolymerization. This ratio was varied from 1 (only Na in the activation solution) to 0 (only K in the activation solution). At the early stages of dissolution, Al dissolves in preference to Si forming an initial, weakly bonded and Al-rich gel. The presence of soluble Si is crucial for the formation of an aluminosilicate gel [32]. The ratio $[Si]/R_2O$ was chosen as a variable because the dissolution of Si in an alkaline solution is connected with the alkalinity of the solution. This ratio was varied from 0 (no soluble Si in the activation solution) to 2 which is the solubility limit of Si in an alkaline solution [33].

A full factorial design requires the conduction of 64 experiments (3 factors, 4 levers per factor, experiments = $\#\text{levels}^{\#\text{factors}} = 4^3 = 64$). The application of a L16 orthogonal array, based on Taguchi method and shown in Table 3, reduces the number of experiments to 16.

3. Results and discussion

Table 4 shows the synthesis parameters as defined by Taguchi model and the compressive strength of the corresponding geopolymers. Three specimens for each experiment were prepared and tested under compression. It must be noted that use of three specimens to measure compressive strength is the common case in the literature and in the practice. When one or more results within the three individual results varies by more than ±10% from the mean, these results are discarded and new specimens are prepared. Table 4 also presents the maximum% variation from the mean and the standard deviation of the measurements.

The effect of each parameter on the development of compressive strength is presented in Fig. 1, which has been based on the exploitation of the data of Table 1. For example the compressive

Table 3
L16 (4^3) standard orthogonal array.

Experiment no.	R/Al	Na/(Na + K)	$[Si]/R_2O$
1	1*	1	1
2	1	2	2
3	1	3	3
4	1	4	4
5	2	1	2
6	2	2	1
7	2	3	4
8	2	4	3
9	3	1	3
10	3	2	4
11	3	3	1
12	3	4	2
13	4	1	4
14	4	2	3
15	4	3	2
16	4	4	1

* Variation level according to Table 2.