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Supersulfated binders based on volcanic raw material: Optimization, microstructure and reaction products

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HIGHLIGHTS

- Volcanic materials are useful precursors to formulate supersulfated binders.
- C-S-H and ettringite are the main hydration products.
- 20% Portland cement contents favor strength, CaSO4 is essential to improve strength.
- Anhydrite is better to improve strength than hemihydrate.
- The statistically predicted 28 and 90 days strengths were experimentally confirmed.

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ABSTRACT

The characterization and optimization of supersulfated binders based on a volcanic material was carried out by Taguchi orthogonal array experimental design, investigating the effects of four factors: type of calcium sulfate, % calcium sulfate, %Portland cement and initial curing temperature. The binders increased strength over time. The statistically defined optimum formulation was: 70%volcanic material-10%Anhydrite-20%Portland cement and curing 22 h at 60 °C then at 20 °C; the predicted and confirmed 28-day strength was 20.2–20.6 MPa; optimum conditions are discussed for other ages. The microstructures and chemical composition of hydration products (EDS) and XRD indicated the formation of C-S-H and ettringite as the main hydration products.

1. Introduction

The environmental impact caused by the production of Portland cement (PC) can be ameliorated by the use of alternative green cements, such as the supersulfated cements (**SSC**), which were proposed by Kühl in 1909 using granulated blast furnace slag, activated with sulfates and an alkaline source [1]. **SSC** would normally consist of up to 90% blast furnace slag, 5–15% calcium sulfate and 5–15% of an alkaline activator mainly Portland cement or clinker, Fig. 1 shows some compositions reported in the literature [2–7]. Nonetheless, other natural raw materials could also be activated, such as silicoaluminous pozzolanic volcanic glassy rocks, i.e. volcanic ashes (VA) and pumice (PM), among others [8]. PM retains a glassy structure after a rapid cooling of the magma in contact with the atmosphere; such amorphous structure is prone to chemical activation by alkalis and sulfates, so ionic species of Si and Al solubilize and further re-condense to form cementitious compounds. The volcanic materials have been used in the manufacture of various kinds of blended cements as shown in Fig. 1, such as blends with up to 50% PC [9–12], lightweight concrete production [13–17]; PM has also been investigated as a precursor for alkali activated cements [18,19].

On the other hand, few reports were found regarding the use of volcanic materials in cementitious blends involving calcium sulfates, Portland cement, clinker or lime; nonetheless, such studies described formulations that do not fall within the compositional ranges of a supersulfated-like cements; Fig. 1 includes some compositions from various reports on binders with high or very high contents of calcium sulfate or alkaline activator [10,20–22].

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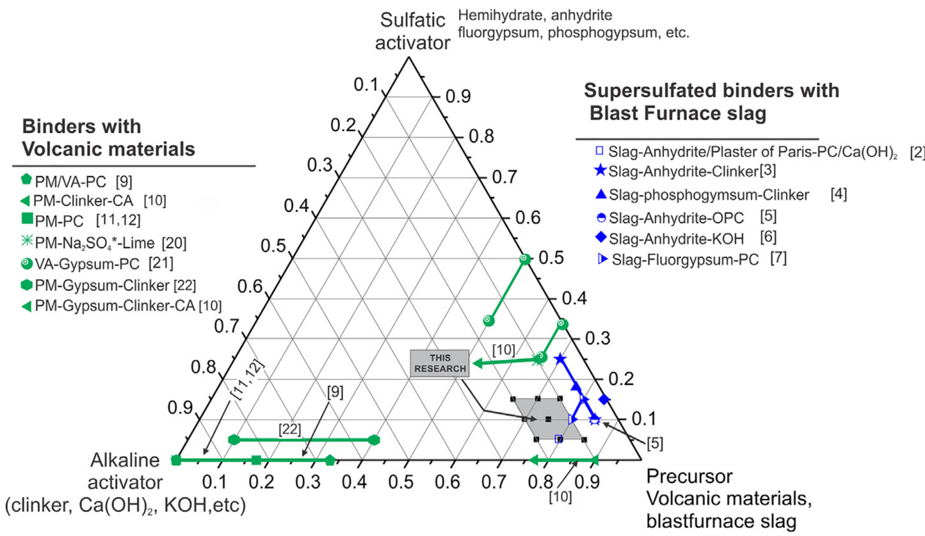

Fig. 1. Compositions from other studies of blended cements fabricated with volcanic materials and supersulfated cements based on slag.

Given the abundant resources of volcanic materials worldwide and in Mexico, the investigation of **SSC** cementitious materials seems a promising area in the search for alternative sustainable cements. Comprehensive studies for new cements on the simultaneous analysis of the effects of various factors and levels can be highly demanding of time and resources for full or fractional factorial experimental designs as a result of the preparation of many experimental trials in order to analyze a significant number of combinations of factors and their levels [23]. One statistical alternative method that has been used to optimize processes is that developed by Taguchi, who proposed the use of a set of orthogonal arrays (OA); this results in the use of simpler designs of experiments with a considerable reduction in the number of trials while maintaining statistical significance. The Taguchi method has been successfully used widely in various fields of engineering. Previous research on cementitious materials using the Taguchi method include:, cement-based grouts [24], design of brick of fly ash [25], mortars containing marble dust and glass fiber [26], activated binders [27], new binders of glass-limestone [28], geopolymers [29,30], fired bricks [31], etc.

The purpose of this research is to present a set of results from a wider investigation on supersulfated binders based on Pumice. The Taguchi method was implemented to study a set of parameters known to influence the reactivity of similar binders based on blastfurnace slag, and to determine the optimum conditions to maximize strength. In order to elucidate the mechanisms of reaction, the type and composition of hydration products, as well as the potential of the pumice based supersulfated cements, the formulations of the experimental layout were characterized for up to one year and statistically optimized formulations were characterized for up to 90 days by electronic microscopy, microanalysis, elemental X-ray mapping, X-ray diffraction and strength.

2. Materials

A natural pozzolan, volcanic pumice (**PM**), from the Mexican state of Veracruz was mechanically activated for favored the hydration reactions [32] to a Blaine fineness of 500 m^2/ kg. Two sources of calcium sulfates were used for chemical activation, namely $CaSO_4 \cdot ½H_2O$ (**HH**, commercial hemihydrate) and a byproduct of anhydrite $CaSO_4$ (**An**); the alkaline activator was Portland cement CPC30R (**PC**) [33]. The main oxides chemical composition of the starting materials is shown in Table 1. Pozzolanic activity was determined by a chemical method proposed by Luxan et al. [34], which evaluates the electrical conductivity of a solution saturated in $Ca(OH)_2$ in which the pozzolana is evaluated; the pumice showed of variation in conductivity of 0.50–0.6 (mS/cm), which according to the method corresponds to a variable pozzolanicity. On the other hand, the strength activity index was evaluated for the PM after 7 days as per ASTM C311, this resulted of 61%, which is under the requirements set by ASTM C628 [35]. These data indicates that the PM should show a pozzolanic behavior under average. The particle size distribution of the PM is shown in Fig. 2, observed that median size of the particles were of about 12 µm.

3. Experimental

3.1. Design of experiments by Taguchi method

The selection of experimental factors and their levels was based on previous reports of blastfurnace slag **SSC** [2–4], as well as on laboratory preliminary tests run with PM. The experimental design comprised four Factors: type of calcium sulfate ($C\underline{S}$), calcium sulfate content (%$C\underline{S}$), content of Portland cement (%PC) and initial curing temperature (ICT); Table 2 presents the levels for each Factor. A full factorial experimental design would require 54 trials; nonetheless, by using the Taguchi Orthogonal Arrays [23] an L_{18} ($2^1 \times 3^3$) array was selected, which led to the 18 trials listed in Table 3. Fig. 1 depicts the compositions investigated relative to previous studies involving volcanic materials and slag as precursors, as well as sulfates and alkaline activators. The trials were prepared in random order to reduce the influence of noise factors.

3.2. Preparation of specimens

The powders were dry mixed before the preparation of pastes; the blends of powders and water were mixed for 3 min and the paste placed in polymeric cubic molds of 2.54 cm per side. The water/solids ratio was fixed at 0.45 and no superplasticizers were used. After the initial 24 h of curing, the specimens were demolded and placed in plastic containers in isothermal chambers at 20 °C in air for ageing and testing.

3.3. Characterization

The compressive strength was followed for up to 360 days, the reported values represent the average of four cubes. The hydration reactions were stopped by immersing pieces from the mechani-