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SUPERSULFATED CEMENTS BASED ON VOLCANIC RAW MATERIALS

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Abstract

Research efforts worldwide have focused on developing alternative binders that would help to reduce the Greenhouse gas emissions associated to the production of Portland cement. Various raw materials, natural or byproducts, have been studied for the development of several types of binders. One of those greener cements are the so called supersulphated, which are commonly formulated using about 80% blast furnace slag and a source calcium sulphate and an alkaline activator that is commonly clinker of Portland cement. This paper presents results from an investigation on a novel supersulphated-type binder which contains at least 60% volcanic pumice; the sulphatic activators were hemihydrate and waste anhydrite, while the alkaline activator was portland cement (PC). The Taguchi method was used for the experimental design, which included variation in the composition of the binder and curing temperatures within the range of 20 to 60°C; a selection of 4 factors using 2 and 3 levels led to an orthogonal array L18 (2^1x3^3). The compressive strength was the response variable. After 28 days, the optimal composition showed 20.16MPa for a paste made of 70%pumice-20%PC-10%Anhydrite cured for 22 h at 60°C then at 20°C. In general, the pastes showed a trend towards higher strengths. The effect of higher curing temperatures and higher PC content were favorable for the strength. The microstructures showed that the pumice reacted although not very actively. Thermal analysis evidenced the formation of C-S-H, ettringite and gypsum. Some of mortars were cured under water and showed strength stability, which further evidenced the formation of C-S-H. A general discussion on the effects of the experimental parameters on strength and reaction products will be discussed.

Keywords:

supersulphated cements; volcanic materials; sulphatic activation; new alkaline binders.

1 INTRODUCTION

The use of alternative cements, based on industrial byproducts or natural pozzolans provides significant energy savings and a reduction in the emission of greenhouse gases. One type of alternative binder that have been extensively used are the supersulfated cements, which can be regarded as low energy and low CO_2 emissions. Supersulphated binders are commonly based on 70-85% blastfurnace slag 10-20% calcium sulfate and about 5% activator, which is usually clinker (Taylor 1997; Bijen 1981; Dutta 1990; Erdem 1993; Gruskovnjak 2008; Mehrotra 1982). Slags rich in Al_2O_3 are suitable for supersulphated cements, with a minimum content of 14 to 15% (Kühl 1908).

The objective of this research is to study the mechanical properties and hydration products of supersulphated binder based on a natural pozzolan of volcanic origin called, i.e. pumice; with two sources of calcium sulfate hemihydrate and anhydrite with Portland cement as alkaline activator. In order to optimize the research work while ensuring a robust study, the Taguchi design of experiments method was implemented. Statistical analysis of the results was also conducted by analysis of variance (ANOVA) of Signal to Noise Ratio to determine the main effect of each of the factors. Finally the confirmatory test was performed under optimal conditions.

2 EXPERIMENTAL AND MATERIALS

2.1 Materials

The natural pozzolan used was a volcanic material type Pumice (PM) from the mexican state of Veracruz, located in the Physiographic Province

Plateau Neovolcánica. The pozzolan was ground in a ball mill to a Blaine 5000 cm^2/g; the content of glass phase was of 87%. Two sources of calcium sulphate were used for the sulphatic activation, namely commercially available hemihydrate (HH) and a byproduct from hydrofluoric acid production anhydrite (AN). The alkaline activator was a Portland cement 30R (30MPa at 28 days).

Tab. *15* presents the chemical composition of the starting materials as obtained by X-ray fluorescence.

Tab. 15: Composition chemical of starting materials: Pumice (PM), Compound Portland Cement (CPC), Hemihydrate (HH) y Anhydrite (AN).

Material	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	Na_2O	Cl
PM	68.730	14.010	2.500	1.640	0.340	0.024	5.453	3.690	0.107
PC	17.740	3.970	3.649	62.710	1.360	4.452	1.090	0.443	
HH	0.939	0.199	0.081	39.700	0.583	51.690			
AN			0.109	43.830	0.042	55.450			

2.2 Fabrication of specimens

The factors (variables) and levels were selected based on previous experiences with supersulphated binders in the lab, Tab. 16 shows the details. The factors were Type of calcium sulphate (Type of CS); Tab. *17*.

Cubes of pastes of 25.4 mm per side were prepared using a water/solids ratio=0.45; the blends were mixed for 3 min in a blender with planetary movement. The specimens were left to set for 22 h at 20, 40 and 60°C, after demolding these were isothermally cured at 20 ºC in air up to 28 days. The compressive strength results were analyzed to define the optimum conditions, under the quality characteristic “the bigger the better” (Equation 1) (Setyo Hadiwidodo 2010).

$$S/N = -10\log_{10}\left[\frac{1}{n}\sum_{i=1}^{n}\frac{1}{Y_i^2}\right] \quad (1)$$

amount of Pórtland Cement (%PC), amount of calcium sulphate (%CS), curing temperature (CTemp). An orthogonal array L18 (2^1x3^3) was selected, the 18 trials condition are described in

Where: y_i= Results of experiments, observations or quality characteristics, n= Number of repetitions.

Tab. 16: Factors and levels selected for the design of experiments.

Factors	Levels		
	1	2	3
Type SC	HH	AN	
% PC	10	15	20
%SC	5	10	15
CTemp	20°C	40°C	60-20°C

Tab. 17: L18 orthogonal array (2^1x3^3).

Trial number	Type CS	% PC	% CS	CTemp
P-01	HH	10	5	20
P-02	HH	10	10	40
P-03	HH	10	15	60-20
P-04	HH	15	5	20
P-05	HH	15	10	40
P-06	HH	15	15	60-20
P-07	HH	20	5	40
P-08	HH	20	10	60-20
P-09	HH	20	15	20
P-10	AN	10	5	60-20
P-11	AN	10	10	20
P-12	AN	10	15	40
P-13	AN	15	5	40
P-14	AN	15	10	60-20
P-15	AN	15	15	20
P-16	AN	20	5	60-20
P-17	AN	20	10	20
P-18	AN	20	15	40

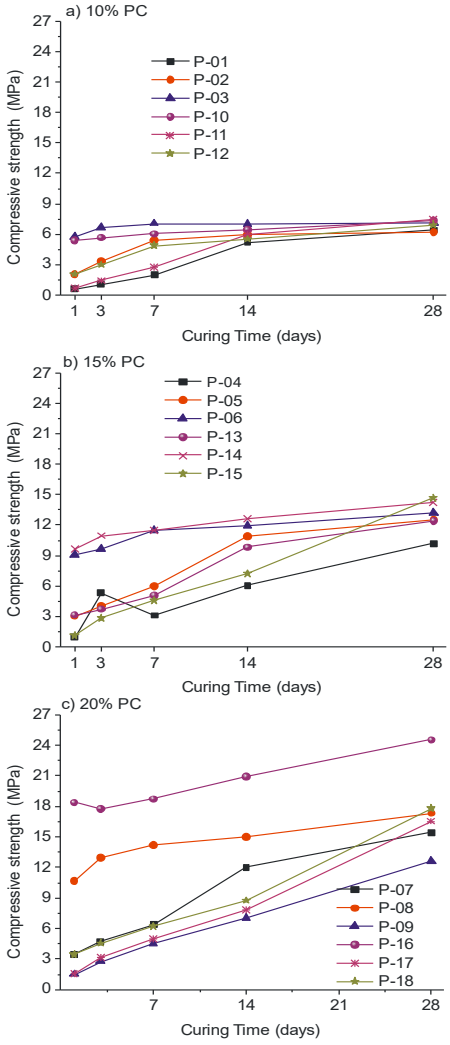
2.3 Characterization

The compressive strength of pastes were determined for up to 28 days using a hydraulic automatic press with a load rate of 300 N/s. Fragments of the crushed cubes were dried by submerging in methanol for 72 h to stop the hydration reactions; the specimens were further dried in a vacuum chamber to 38ºC. Some Samples were selected for analysis by X-ray diffraction (XRD) using a CuKα source radiation, the analysis conditions were a sweeping range of 10-80° 2θ with a step of 0.03° 2θ with 3s per step. Pieces of specimens were mounted in resin, ground and then polished for microstructural studies by scanning electron microscope (SEM) operated at 20 keV.

3 RESULTS

3.1 Compressive strength

The results of compressive strength vs time are shown in Fig. 14 divided in 3 groups as a function of the %PC. It was generally seen that the strength increased with higher %PC; also higher temperatures accelerated the reactions and favored the strength since the early ages. In Fig. 14a) it is observed that trials 03, 10 and 11 had the highest strength; sample 11 reached up to 7.45 MPa, while curing at 60°C for 24h (trials 03 and 10) resulted in more of than 70% of the 28 day strength since 1 day.



Tab. *17.*

Fig. 14: Compressive strength vs curing.

For pastes with 15%PC (Fig. 14b) the highest strength was registered by trials 06, 14 and 15. Trial 15 was cured at 20°C and while it had a relatively slow strength development, it reached the highest 28 days values of 14.6 MPa. Curing at 60°C for 24h (trials 06 and 14) had a favorable effect since day one. On the other hand, for pastes with 20%PC (Fig. 14c) showed a similar pattern as before, in that curing at 60°C for 24 h notably favored early strength, trial 16 reached about 18MPa after 1 day and 24.5 MPa after 28 days. Trial 17 with 70%pumice, 10 anhydrite and 20%PC cured at 20°C showed increased its strength over time, with a clear trend towards higher values.

3.2 Optimization

Calculations of the signal to noise (S/N) allowed to determine of the optimum conditions. Fig. 15 shows the main effects on each level of the factors; the optimal conditions for each factor are those with the higher S/N, highlighted in red. The optimal condition was identified as 20%PC-10%AN-70%PM cured under the regime of 60-20 ºC. The predicted strength at such conditions according to equations 2 and 3 (Roy, 1990) was calculated as of 20.63 ± 1.15 MPa with a confidence level of 90%. The confirmation experiment was carried out in the lab and resulted in a compressive strength of 20.16 MPa, which matched the predicted value and indicated that the experimental work was performed adequately.

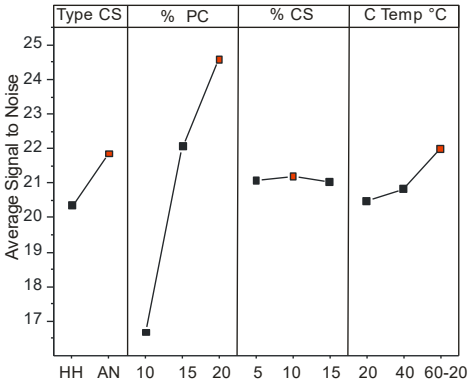


Fig. 15: Main effects of the signal to noise (S/N).

The percentage contribution of each factor was determined by Analysis of Variance (ANOVA) analysis of the S/N, the results are presented in

Tab. 3: (ANOVA) of Signal to Noise Ratio

.Factor	Degrees of freedom	Sum of squares	Contribution factor
Type SC	1	10.218	4.600
% PC	2	195.392	87.90
%SC	2	0.057	0.030
CTemp	2	7.503	3.380
Error	10	9.130	4.090
Total	17	222.300	100.000

The most important factor was the %PC with 87.900%.

$$Y^2_{expected} = 1/MSD \quad (2)$$

Where:

MSD= Mean square deviation from the target value of the quality characteristic

$$C.I. = \pm \sqrt{F(1, n_2)} \times V_e / N_e \quad (3)$$

Where:

F (1, n_2)= F value from the F Table at a required confidence level and at DOF 1 and error DOF n_2

V_e= Variance of error term (from ANOVA)

N_e= Effective number of replications

N_e= Total number of results

(or number of S/N ratios)/ DOF of mean (=1, always) + DOF of all factors

3.3 X-ray diffraction (XRD)

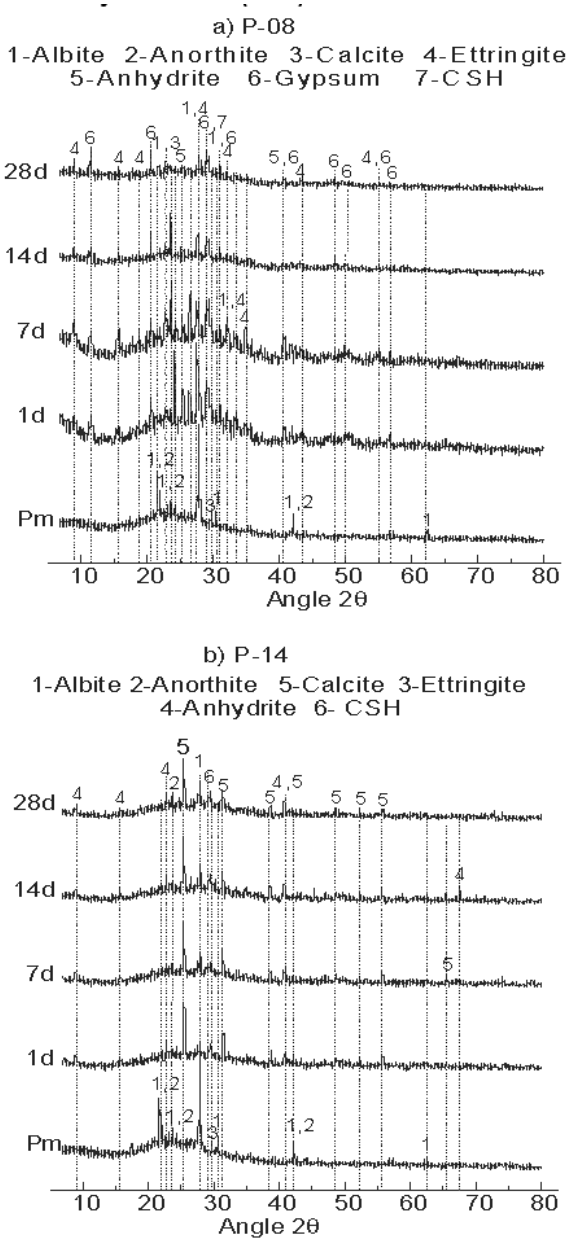


Fig. 16: X-ray diffraction patterns of two trials.

Fig. 16 presents the X-ray diffraction patterns of the trial 08 and 14. The paste with 20%PC showed intense formation of gypsum, ettringite and C-S-H from 1 day; however, the intensity of reflections decreased after 14 days. For the paste with 15%PC the main phases detected were ettringite, anhydrite and C-S-H from one day and after 14 days the intensity of the peaks decreased. The crystalline phases of the pumice, namely albite and anorthite, persisted after 28 days, which indicated that such phases were stable and did not participate in any hydration reactions. For both pastes, the amorphous hump in the XRD patterns of the pumice, shifter to the right, indicating the formation of amorphous reaction products of different composition.

3.4 Scanning electron microscopy

Fig. 17 presents the microstructures of pastes P-08 and P-14 after 28 days of curing. The images were obtained using backscattered electron imaging. The pastes showed a relatively dense matrix of hydration products, which had embedded of unreacted or partially reacted Pumice particles and grains of

partially reacted Portland cement. The pumice particles did not show rims of hydration products, which suggest a reaction controlled by a dissolution under the sulphatic and alkaline environment to form cementitious products.

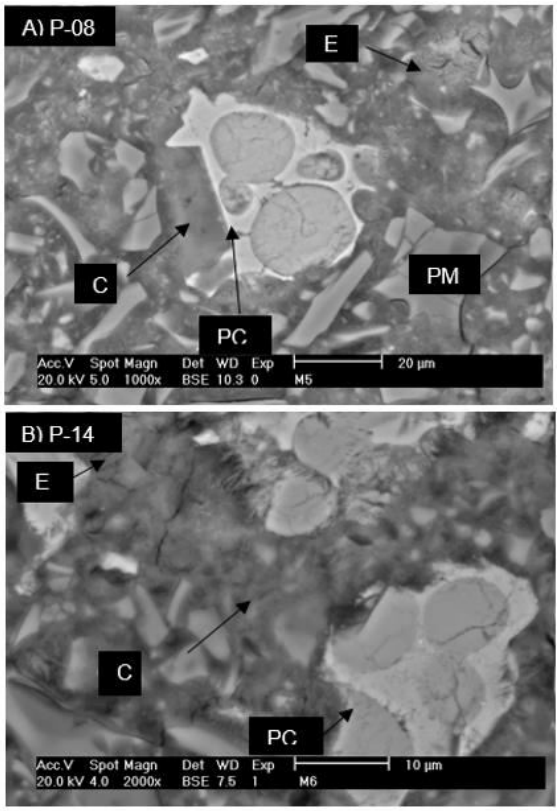


Fig. 17 : SEM microstructures of the systems A) P-08 and B) P-14 at 28 days. (PM= pumice; C= matrix hydration products CSH; CP= Portland cement; E= ettringite).

4 CONCLUSIONS

- Pumice is a suitable raw material to formulate alternative supersulphated binders
- The compressive strength development is favored by the increased amount of PC in the binder.
- Heat treatment curing at 60°C for the first 22 h favored early strength; the highest 28 day strengths were also for the pastes cured with such regime.
- Better strengths were observed when anhydrite was used in the formulation as compared to the use of hemihydrate.
- The main hydration products formed were gypsum, ettringite and C-S-H; unreacted anhydrite remained in some formulations.
- The Taguchi method proved a useful tool for the experimental design and investigations in these novel cements.
- The statistically predicted optimal strength was corroborated experimentally, which indicated that the experimental work was consistently carried out.

5 ACKNOWLEDGMENTS

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