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SYNTHESIS AND CHARACTERIZATION OF FLY ASH HYBRID CEMENTS WITH LIMESTONE

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Abstract

In this work, the alkaline activation of hybrid fly ash cements with additions of up to 30% Portland cement and limestone activated with NaOH, Na_2CO_3, Na_2SO_4 and $(COONa)_2$ is presented. Different activator modules (Na_2O/SiO_2) of 0.1 to 0.3 and a w/c ratio of 0.45. The results of the compression strengths tests at 28 days of curing in samples activated with Na_2SO_4 showed the highest strength, 31 MPa, with a weight proportion of fly ash: Portland cement: limestone of 60:30:10. The test cements with lower strength development were those activated with NaOH and $(COONa)_2$ with 2.4 MPa and 7.4 MPa, respectively. The limestone particle could be observed by scanning electron microscopy as the nucleation center for the reaction products and the way that the fly ash reacted by means of the alkaline activation process to form part of the reaction products.

Keywords:

Alkaline activation, hybrid cement, limestone, fly ash.

1 INTRODUCTION

Currently, the use of industrial residues such a cementitious materials has shown a great benefit both ecological and technological. By replacing cement Portland partially or totally, the residues are a viable alternative for the production of new cementants [Dembovska 2017; Kumar 2010; Bonavetti 2006]. The processes for the manufacture of these cementants may contain very different parameters depending on the material used. One of the most studied mechanisms is alkaline activation, which consists of increasing the pH levels within the pore solution at values higher than 13 [Rakhimova 2015; Ruíz 2016]. This alkaline environment produces tetrahedral stable structures from the alkali that comes from the activator. As a result, cementitious systems with hydrated silicoaluminates of C-A-S-H, N-A-S-H or some combination of both C-(N-A-S-H) or N-(C-A-S-H) are obtained which are responsible of the physical-mechanical properties of such materials

[Liew 2016; Puertas 2011; Garcia 2011].

Alkaline activated cements are clasified in different categories: slag cements, puzzolans, alumina and puzzolans with portland cement additions, commonly referred to as hybrid cements [Ankur 2016; Shi 2011]. The latter presents an attractive attention in the context of cementants for the future, since the incorporation of a source of reactive CaO (contributed by the Portland cement in a maximum of 30%) inside the mixture, allows the material to harden to environment temperature without the need of an initial thermal activation without the need of an initial thermal activation, as in the case of the alkaline activations of most industrial residues [Garcia 2016; Fernández 2013].

The addition of alkaline activators in mixtures of Portland cement with addition of an industrial residue could improve the puzzolanic potential of the latter as supplementary material and improve the properties of the cementitious systems, especially at early ages [Paris 2016]. The fly ash, as an industrial residue of low puzzolanic power is difficult to activate to be used as cementitious material. However, some researchers have used it as partial replacement in Portland cement mixtures to densify the matrix or as supplementary cement in combination with other industrial residues as blast furnace slag or metakaolin to increase its reactivity [Hermalatha 2017; Ye 2016; Shao 2016].

This work is focused in using fly ash as an alkaline activated cementitious material in hybrid systems with limestone and Portland cement additions to evaluate the microstructure and mechanical behavior of different mixture systems at room temperature.

2 EXPERIMENTAL

For this work a fly ash from a thermoelectric plant located in Rio Escondido at NAVA, Coahuila, Mexico was used as cementitious material, which according to its chemical composition is classified as type F, composed of high contents of Al_2O_3 (25.4%), SiO_2 (62.8%) and Fe_2O_3 (5.3%); along with an ordinary Portland cement type 40, mainly composed of CaO (69.9%), SiO_2 (15.7%), Al_2O_3 (3.4%) and Fe_2O_3 (3.9%) and some minor alkali; and some commercial limestone powder (CaO 97.6%) as stony material. NaOH, Na_2CO_3, Na_2SO_4 and $(COONa)_2$ were used as alkaline activators, all of them analytical grades.

Compressive strength tests were performed in an Instron 600DX universal machine. All samples were tested at 28 days of curing with three replicates by each date. For the microstructural characterization of the hybrid cements, JEOL scanning electron microscopy (SEM) under low vacuum, model JSM-6510-LV was used. The microanalysis of pallid and gold palladium-coated samples were carried out under backscattered electrons with a Voltage of 20 k. The working height was 13 mm and a spot size of 50-60.

2.1 Design of mixtures and preparation of specimens

As hybrid cementitious materials, paste systems were made (Tab. 1) with the different type of alkaline activators. As base cement, fly ash was used with a maximum of 70% of the total replacement and the remaining 30% corresponded to the Portland cement additions and limestone. In all mixtures, the water/cement ratio (w/c) of 0.45 was maintained constant and the alkaline modulus (Na_2O/SiO_2) varied from 0.1 to 0.3.

The process to make hybrid cements was performed by chemical activation. Before mixing the materials, the activator was dissolved into the water of the mixture. Subsequently, the raw materials were added to the mixture, then it was stirred at low speed for 1 minute, afterwards, the solution of the activator was dissolved in the water and it was proceeded to the stirring at high speed for 2 minutes, the mixing was stopped and the resulting paste was placed in cylindrical molds of 1 in diameter and 2 in long. The filling of the molds was carried out in two layers, the cementitious material was compacted by means of repeated blows in each cylinder. Finally, the molds were covered with rubber molds until they began to harden. After this time, they were placed in the curing room with a relative humidity of 75% and temperature of 25ºC. After 24 hours of their manufacture, the cylinders were demolded and returned to the curing room until they reached the age of 28 days of compression testing.

Tab. 1. Alkaline activation of hybrid cements

#	fly ash(%)	cement (%)	limestone (%)	w/c	Na_2O/SiO_2	NaOH	Na_2CO_3	Na_2SO_4	$(COONa)_2$
A1	70	20	10	0.45	0.3	X			
B1	70	20	10	0.45	0.3		X		
C1	70	20	10	0.45	0.3			X	
D1	70	20	10	0.45	0.3				X
A2	60	30	10	0.45	0.3	X			
B2	60	30	10	0.45	0.3		X		
C2	60	30	10	0.45	0.3			X	
D2	60	30	10	0.45	0.3				X
A3	70	20	10	0.45	0.1	X			
B3	70	20	10	0.45	0,1		X		
C3	70	20	10	0.45	0.1			X	
D3	70	20	10	0.45	0.1				X

3 RESULTS AND DISCUSSION

The results of the compressive strength of the hybrid cements at 28 days of curing are shown in Fig. 1.

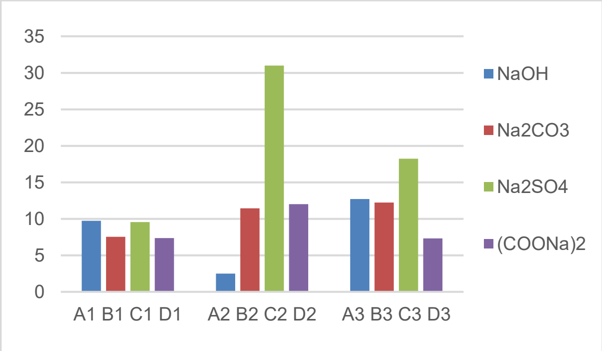

Fig. 1. Compressive strength of hybrid systems, cured at 28 days.

From all the cement tests, the ones that showed higher tendency to increase resistance were those activated with Na_2SO_4, reaching a resistance above 30 MPa in the C2 system.

This may be because an effect similar to that prevailing in Portland cements occurs in which SO_3 added as $CaSo_4$ contribute to control the reactions in initial hydrations, in the case of alkaline activated hybrid cements contribute in the condensation process and therefore accelerates activation reactions [Criado 2010]. One of the effects that can be observed in the graph is that there is a direct relationship between the compressive strength and the modulus of the activator (Na_2O/SiO_2). This can be seen by comparing module systems 3.0 (A1, B1, C1, D1) against their corresponding module 1.0 (A3, B3, C3, D3). If systems A1 and A3 for comparison, A1 has a compressive strength of 10 MPa vs 13 MPa of strength of A3. Higher strength was obtained with a smaller modulus and the same tendency could be observed in the rest of the systems, C1 shows a strength of 9 MPa and C3 a strength of 18 MPa. Although these strengths are considered as low, it is necessary to study the hydration process at later ages. It would be expected that with curing time, the compressive strengths will increase, since in most alkaline activations there is a chemical stability between the products of activation reactions at late ages, higher than 90 days of curing.

For the SEM analysis, two systems were selected: the one with higher compression strength (C2) and the one with lower strength (A2). Fig. 2(I) shows the morphology of the C2 system, taken at 1400 magnification in Fig. (II). Particles with limestone characteristics and fly ash can be clearly observed. Both participating in the activation reactions in Fig. 2(I) fly ash attached as a result of the alkaline activation can be observed, being part, mainly of the cementitious matrix and therefore with a beneficial behavior for the development of the mechanical strength.

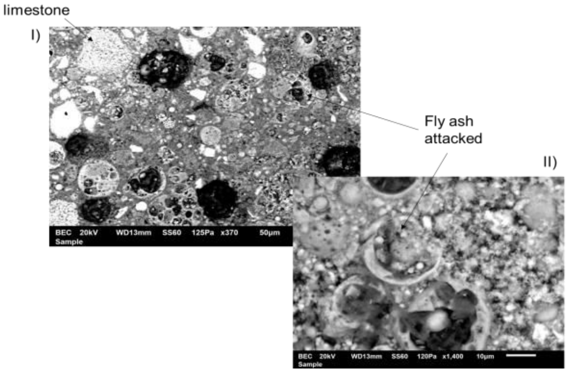

Fig. 2. Micrograph of hybrid cement (C2), at 28 days of curing.

In Fig. 2 (I) it can also be observed, the presence of limestone particles that can be acting as nucleation sites for the formation of the reaction products. Since in the edges of such particles a chemical composition rich in Ca, Si and Na was found, attributable to the formation of hydration products type C-A-S-H or C-(N-A-S-H). However, more evidence is needed to determine the type of hydration product and to analyze the systems at more advanced curing ages. In Fig. 2(II) the fly ash is observed attacked and surrounded by reaction product. The micrograph of Fig. 3, taken at 1200 magnifications shows the morphology of the hybrid cement (A2), the presence of fly ash particles that have not yet reacted can be clearly observed, which indicates that it is not part of the reaction products. This would explain the low compression strength observed in Fig. 1.

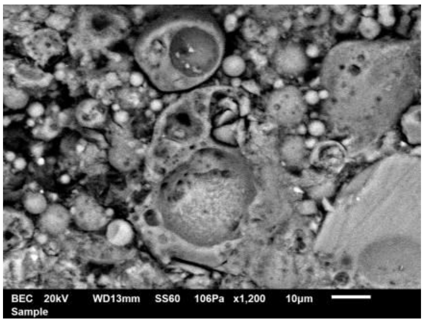

Fig. 3. Micrograph of the hybrid cement (A2) at 28 days of curing.

4 CONCLUSIONS

The hybrid cements activated with Na_2SO_4 can be considered as of higher efficiency regarding compression strength, specifically the C2 system.

The activator modulus (Na_2O/SiO_2), optimal for the efficiency of these cementitious materials, is inversely related to the compressive strength, the lower the modulus the higher strength.

The limestone in these hybrid cements contribute the formation of reaction products, acting as nucleation sites.

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