High volume fly ash concrete activated with naoh, sodium sulfate and limestone

Elaboración de concretos con altos reemplazos de cenizas volantes y activación con naoh, sulfato de sodio y caliza

DOI: http://doi.org/10.17981/ingecuc.18.1.2022.17

Artículo de Investigación Científica. Fecha de Recepción: 15/12/2020. Fecha de Aceptación: 28/08/2021.

Dimelsa Salazar-Carreño
Fundación Centro de Desarrollo Tecnológico-CENTREK. Bogotá, D.C. (Colombia)
dimelsasalazar@gmail.com

Rafael Guillermo García-Cáceres
Universidad Pedagógica y Tecnológica de Colombia-UPTC. Sogamoso (Colombia)
rafael.garcia01@uptc.edu.co

Alejandra Santa
Alienergy S.A.S. Sogamoso (Colombia)
geopolimeros@alienergy.com

To cite this paper
D. Salazar-Carreño, R. García-Cáceres & A. Santa, "High volume fly ash concrete activated with naoh, sodium sulfate and limestone," *INGE CUC*, vol. 18, no. 1, pp. 243–250, 2022. DOI: http://doi.org/10.17981/ingecuc.18.1.2022.17

Resumen

Introducción— Las grandes cantidades de cenizas volantes que se obtienen como subproducto de la combustión del carbón en las termoeléctricas han generado preocupación por su impacto ambiental, por ejemplo, en Colombia este residuo representa la cantidad de 6 millones de toneladas al año. Dentro de las estrategias de solución está el aprovechamiento de este residuo en procesos industriales. El residuo cuenta con propiedades puzolánicas útiles en industrias como la del cemento y concreto.

Objetivos— La presente investigación tiene como objetivo evaluar la resistencia a la compresión a diferentes edades de concretos con reemplazando cemento por ceniza volante de 40%.

Metodología— Se utilizó la activación alcalina con NaOH y activación con sulfato de sodio y caliza, en diferentes proporciones.

Resultados— Los resultados mostraron que la activación mejora el desempeño de la ceniza.

Conclusiones— Se lograron obtener mejores propiedades mecánicas que sin activación.

Palabras clave— Concreto; Cenizas Volantes; Activación; NaOH; Silicato de Sodio; Caliza

Abstract

Introduction— The large quantities of fly ash obtained as a by-product of coal combustion in thermoelectric power plants have generated concern about its environmental impact; for example, in Colombia this waste represents 6 million tons per year. One of the solution strategies is the use of this residue in industrial processes. The residue has pozzolanic properties useful in industries such as cement and concrete.

Objectives— The objective of this research is to evaluate the compressive strength at different ages of concrete by replacing cement with 40% fly ash.

Methodology— Alkaline activation with NaOH and activation with sodium sulfate and limestone, in different proportions, were used.

Results— The results showed that activation improved the performance of the ash.

Conclusions— Better mechanical properties were obtained than without activation.

Keywords— Concrete; Fly Ash; Activation; NaOH; Sodium Sulfate; Limestone

I. Introduction

The cement industry generates large amounts of CO^2, the main cause of global warming, due to de-carbonization of limestone and the burning of fuel for furnaces, in which clinker is obtained [1]. According to the ACAA, only in the United States, the production of fly ash is above 50 million tons per year and an increasing rate of 2.6% per year is projected to 2033. These quantities show the waste polluting potential.

Fly ash can be used as a supplementary cementitious material in the production of Portland cement [2]. The research about the development of cement produced through the replacement of High Volumes of Fly Ash (HVFA), goes back to the eighties [3], which focuses on looking for the best physical mechanical characteristics of concrete HVFA in laboratory in order to establish a conceptual base of its economic- environmental potential for a further evaluation in industrial application. Its use has been spread since it contributes to lessen greenhouse gas emissions effect. Studies have shown that the synergy between fly ash and cement allow the development of a good quality concretes, which possess appropriate mechanical properties and high durability. Fly ash physical-chemical properties area a determinant factor for its use and are given by both the type of coal they come from and for the operating conditions of the power generation plant [4].

To achieve higher replacements of cement by fly ash in concrete, several types of activators have been studied in order to accelerate the chemical reactions that result in improvements in its mechanical characteristics. On one hand, alkaline activation has been used as a catalyst of the reactions of amorphous and short-ordered phases in fly ash looking for higher initial compressive strengths. OH-ions promote de-polymerization of the aluminosilicate network, and consequently allow the formation of new compounds that result in an increase of the concrete mechanical properties [5]. The most common alkaline activators used are sodium and potassium hydroxide, silicates and carbonates [6]. On the other hand, sulfate ion is a catalyst for the formation of zeolites, compounds which promote the compressive strength of concrete when fly ash is used, to this respect, sodium sulfate use is very common [7].

Spanish and English researchers [8] studied the alkaline activation effect with a solution of NaOH 85%, 12.5 M and sodium silicate 15%, using in the mixture commercial chemical additives based on lignosulphonate, melamine, and polycarboxylate. Results showed that additive worked in a different way in systems with Portland cement than with systems with fly ash and alkaline activation. It was concluded that alkaline activation has a positive effect over those materials rheology. Studies developed in India [9] experimented with low calcium fly ash geo-polymers, using NaOH solutions at different molarities and sodium silicate, concluding that compressive strength increases when solution morality increases; however, workability decreases. Some Spanish investigation incorporated sulfate to reactive systems —object of his study, to determine the effect as a possible promoter of crystallization of ash pasta prismatic test tubes zeolites [10]. The amount incorporated to the mixture was 2.5% by mass in respect to the ash content. In this research, it was concluded that soluble silica present in the active dissolution has a fundamental role in the initial development of mechanical strength. Surveys in Colombia studied the rice husk due to its high content of amorphous silica [11], which has made it a promising raw material, especially due to its possibility of becoming a cement supplement for concrete mixtures, mixing cement with complementary cementing materials such as fly ash, Rice husk ash and silica fume make the concrete more durable [12]. Korea and India have used fly ash in concrete and gypsum instead of sand and examined the impact of fly ash grain size on the thermal and mechanical performance of the composite [13].

The purpose of this research is to evaluate behavior of resistance to compression at different ages in systems containing cement and fly ash, 60%-40% respectively, using two activators: NaOH and a mixture of sodium sulfate and limestone. The results showed a positive effect of activators the mixture, which be verified comparing samples with activation in relation to the pattern without ash and with ash without activation.

II. Experiments

A. *Materials*

Below are the materials used in the experimental process, the percentages were calculated by weight:

Termopaipa Fly Ash. This fly ash is the by-product of Temopaipa Power plants I, II, and III in Boyacá, Colombia. Ash characterization results are shown below (Fig. 1).

Limestone. Limestone comes from Tolima state in Colombia. The result obtained by X Ray diffraction, showed that limestone contains calcite 94.5%, quartz 2.8%, biotite 0.3%, cristobalite 1.4%.

Sodium Sulfate (waste). The sodium sulfate used in this research is produced as an industrial waste. It is found as the nardite at 94.6% with 5.4% halite (NaCl).

Sodium Hydroxide. It is a waste from textile industrial, which was characterized by titration assay. Results showed NaOH with 3.4% concentration.

B. *Experimental Methods*

The experimental methods used: Fly ash characterization y Concrete Mixtures are described below.

C. *Fly ash characterization*

All Fly ash was characterized by X ray diffraction (XRD), X ray fluorescence, granulometry and scanning electronic microscopy, SEM, in order to determine its physical, chemical, and mineralogical characteristics. XRD was carried out using X Ray diffractometer Panalytical, Empyream model with pixcel detector 2X2 using cobalt tube (CoKα1 = 1.799), angular speed of 10degs-1, and 2 theta linearity over whole range.

The results were analyzed in Hi-Score Pluss software [19], following Rietveld semi-quantitative method with ICSD database. XRD results showed 67.3% amorphous material by weight, quartz 17.6%, and 1.3% magnetite (Fig. 1).

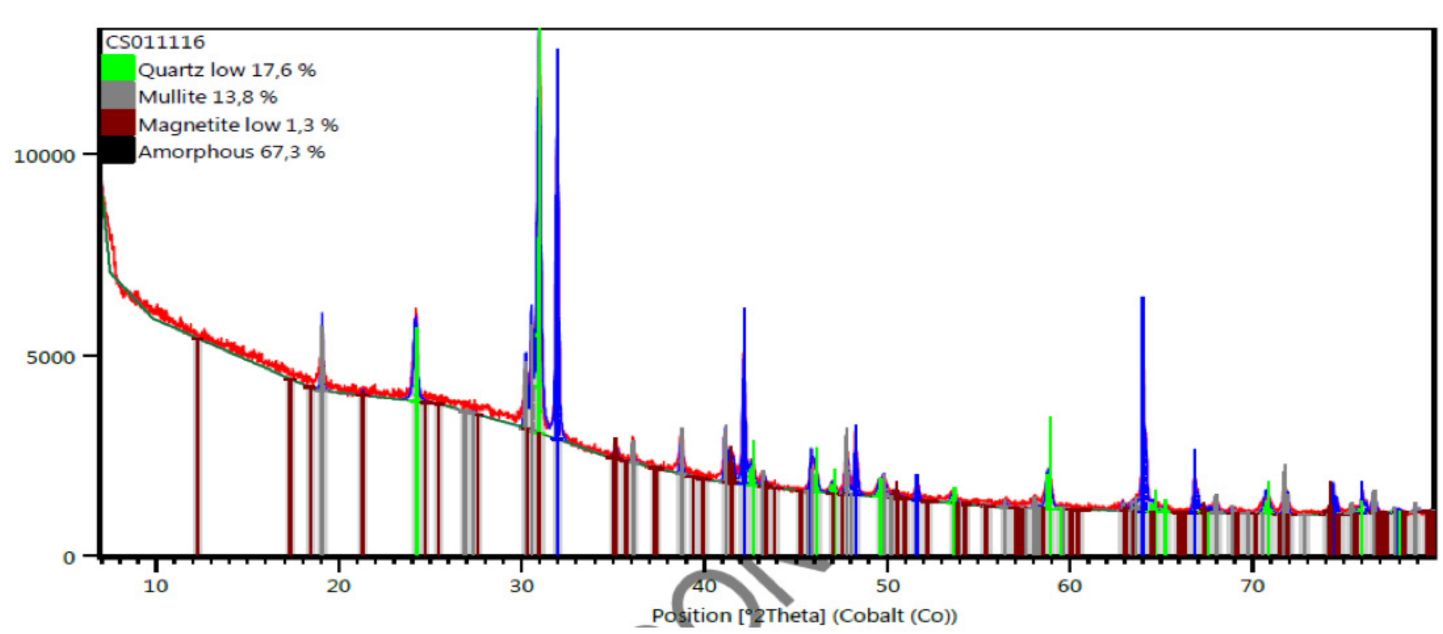

Fig. 1. Fly ash X ray diffraction results.
Source: Authors.

Analysis was carried out in JEOL JSM 6700F SEM equipment, with an accelerating voltage of 20 KV under high vacuum at 15 mm of distance approximately. Samples were prepared on a graphite tape and subsequently coated with graphite to create a conductive film on them. The images, Fig. 2, were taken with a backscattered electron detector (COMPO). The results showed mullite, quartz, magnetite, hematite and organic particles (high carbon content). Although mullite is mainly found in sphere shape in different sizes between 0.6 µm to 60 µm, mullite with irregular shape and porous aspect (sizes between 10 a 110 µm) were also observed.

In addition, spherical particles with high iron content were detected (lighter particles) with variations between 1 μm to 40 μm.

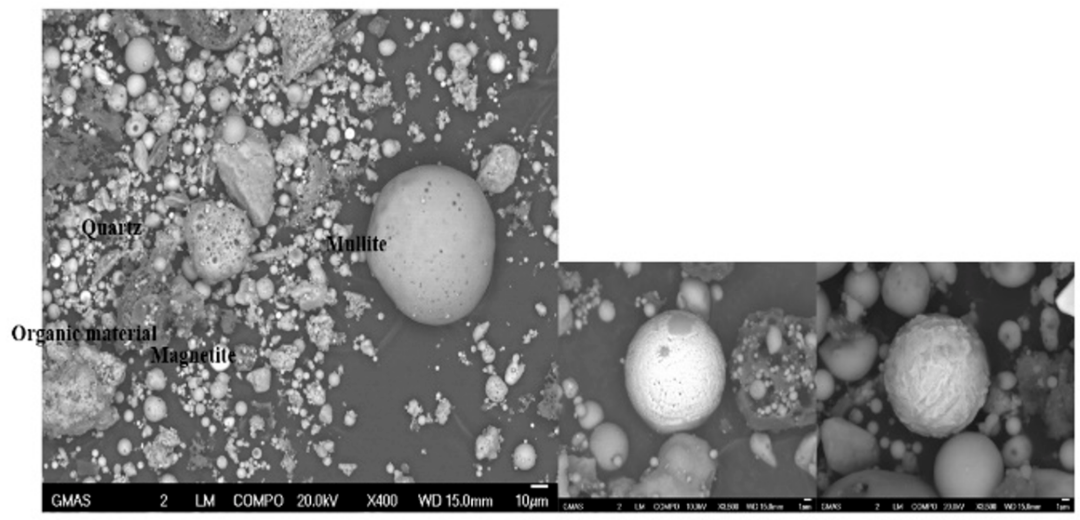

Fig. 2. Fly ash SEM images.
Source: The authors.

FRX results are presented in Table 1.

TABLE 1.
FLY ASH CHEMICAL COMPOSITION BY FRX.

Chemical compound	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	Mn_3O_4
%	64.4	1.18	24.4	5.41	0
Chemical compound	MgO	CaO	Na_2O	K_2O	ZnO
%	0.45	1.23	0.43	1.48	0
Chemical compound	P_2O_5	SO_3	V_2O_5	Cr_2O_3	SrO
%	0.66	NA	0.06	NA	0.11
Chemical compound	ZrO_2	BaO	NiO	CuO	
%	0.03	0.1	0	0	

Source: Authors.

This analysis was carried out using a Panalytical equipment Axios model of 4 kw [20], with a WDFRX-WROXY-LOI quantitative method. Retained percentages in sieve 200 (74 μm) and sieve 325 (44 μm) were calculated and the result was 10% and 24.4% correspondingly.

D. *Concrete Mixtures*

4 × 8 inch cylindrical concrete specimens were prepared in order to evaluate compression strength of concrete mixtures with replacement of 40% by fly ash, using activation with NaOH and sodium sulfate and limestone mix. A mixture to obtain a concrete with resistance to compression at 28 days of 210 kgf/cm² was designed. Results were compared with two reference patterns. One using 100% cement without either admixture activation or additives (RS1, and another one with a mixture of 60% cement and 40% fly ash, "cementous material", without either activation or admixture (RS2). The first mixtures were prepared using NaOH as activator, with dosage per gram of binder of 0.025, 0.05, 0.07 and 0.09, maintaining the other mixture elements constant. Then compression strength at 3, 14, 28, and 56 days was evaluated.

III. RESULTS

A. *NaOH Activation*

Table 1 and Fig. 3 show the results for compression strength of concrete samples at established ages as well as the relation water/Cementous material ratio, obtained of each mixture with NaOH activation.

Table 2.
Comparative of compression Compressive strength at 3, 14, 28, and 56 days of mixture of NaOH activation without ash.

MIXTURE	W/C	Compression Strength Kgf/cm²			
		3	14	28	56
RS1	0.797	91.6	145.1	166.5	221.1
0.025 % NaOH	0.638	70%	84%	104%	89%
0.05 % NaOH	0.643	61%	83%	93%	92%
0.07 % NaOH	0.68	66%	N.A	106%	102%
0.09 % NaOH	0.714	89%	N.A	113%	105%

Source: Aauthors.

In the Fig. 3 show in detail outcomes present in Table 2.

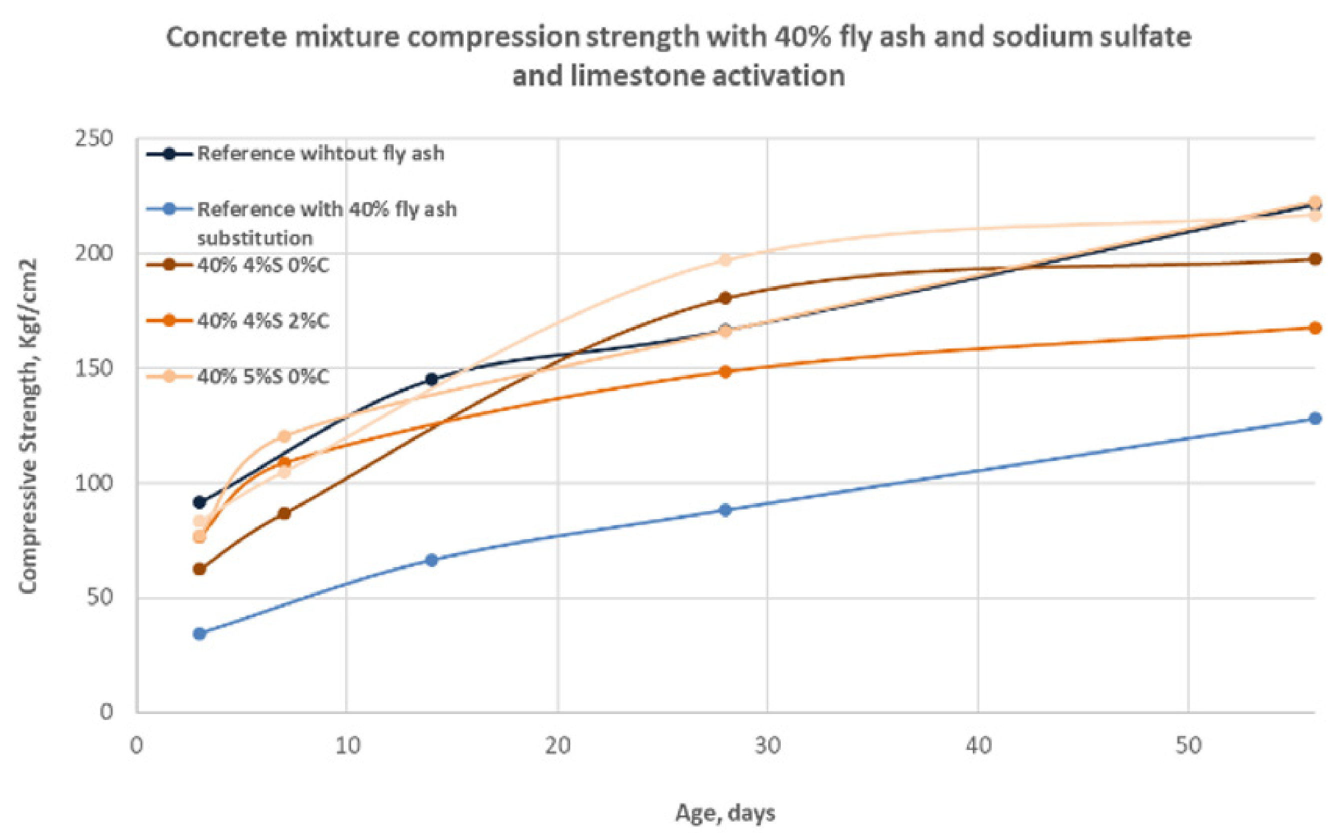

Fig. 3. Concrete mixture compression strength with 40% fly ash and NaOH activation
Source: Authors.

Results show that RS2 has low compression strength with respect to RS1 at different ages: 38% at 3 days, 53% at 28 days and 58% at 56 days. A significant increase of water consumption, which is reflected in the water-cementitious material ratio of 0.815 was observed; explained by the presence of unburned material in the fly ash.

Mixtures prepared with NaOH 0.09% showed compression strength near to RS1 at 3 and 14 days and improved at 28 and 56 days. The water-cementitious ratio, this mixture showed a relation of 0.714, which is lower than the one obtained with the patter without ash and without additives, but it is significantly high. Additionally, it is noted that all mixtures in which the activator was included had a significant improvement in compression strength compared to RS2.

Similar conclusions have been obtained in other laboratory studies, in which activation of ash with NaOH have been used as well as other alkaline substances showing a significant improvement in the development of mechanical strengths [14], [15], [16], [17].

B. *Sodium sulfate and Limeston activation*

Table 3 shows compression strength results respect to RS1 and water/Cementous material ratio of each one of the mixtures and Fig. 4 shows compression strength of each one of the mixtures at four different ages.

TABLE 3.
COMPRESSION STRENGTH AT 3, 14, 28 AND 56 DAYS WITH SODIUM SULFATE AND LIMESTONE ACTIVATION.

MIXTURE	W/C	Compressive Strength Kgf/cm²			
		3	14	28	56
RS1	0.797	91.6	145.1	166.5	221.2
40% 4%S 0%C	0.66	68%	60%	N.A	82%
40% 4%S 2%C	0.63	84%	75%	N.A	67%
40% 5%S 0%C	0.65	84%	83%	N.A	75%
40%5%S 2%C	0.68	91%	72%	N.A	89%

Source: Authors.

Following Fig. 4 shows in detail outcomes presented in Table 3.

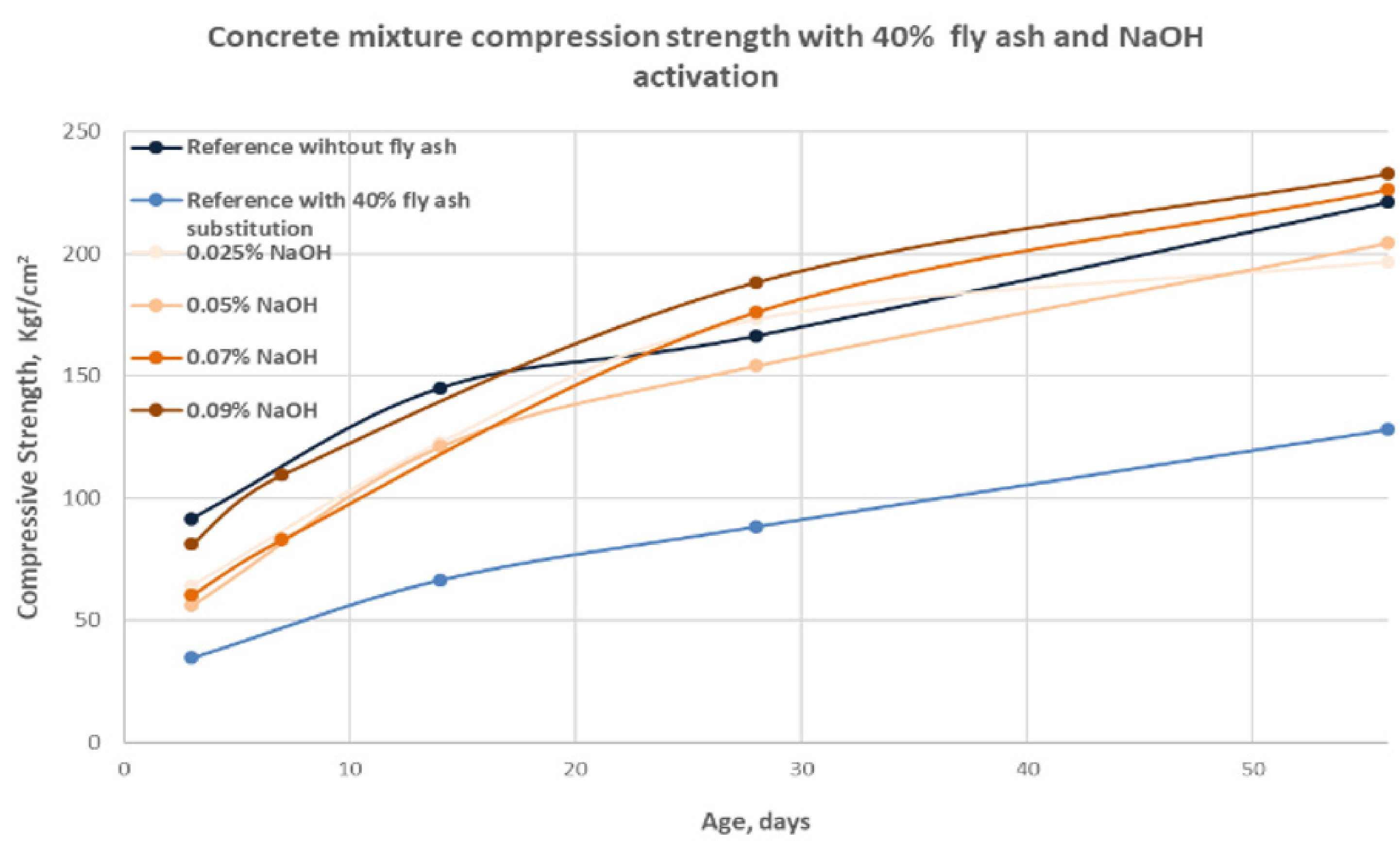

Fig. 4. Concrete mixture compression strength with 40% fly ash and sodium sulfate and limestone activation.
Source: Authors.

Results show that additions improve the behavior of compression strength, especially mixtures containing percentage of sodium sulfate and limestone (5. 0) and (5. 2). In the case of the combination (5.0), the curve coincides with the RS1 mixture at ages above 28 days, but it shows an unusual behavior especially at 7 days evaluation where the compression strength exceeds RS1, showing a behavior that is unusual when high percentages of fly ash replacement by cement are used. Although compression strength of the concrete mixtures with fly ash at early ages are less than compressive strength of RS1, these satisfactorily evolve at 28 days and exceed RS1. As in the case of NaOH activation, mixtures with activation increases its compression strength, some of these are close to RS1.

The above results are consistent with tests performed in mortar using activation with Na_2SO_4, lime and limestone ash with high percentages of unburned material, in which it is confirmed that activation improves compression strength, and it is comparable with standard samples with 100% cement [18].

IV. CONCLUSIONS

The research shows that concrete compression strength improves when NaOH or sodium sulfate and limestone mixture activation is used. Mixtures with activation have better performance respect to specimens with fly ash without activation.

Results allow concluding that not only NaOH but also sodium sulfate and limestone show a positive influence in the mixture mechanical properties, and that as NaOH or sodium sulfate and limestone increase, final compression strength overcome the ones of the pattern with ash. It is not possible to determine if one has a better performance than the other, for this reason the decision can be made bearing in mind the cost of activators.

The water-Cementous material ratio decreases when activators concentration increase, with both with NaOH and sodium sulfate and limestone mix, comparing them with the samples 100% cement, 40% ash, and 60% cement without activation.

Referencias

[1] A. M. Rashad, “A brief on high-volume Class F fly ash as cement replacement – A guide for Civil Engineer,” *Int J Sustain Built Environ*, vol. 4, no. 2, pp. 278–306, Dec. 2015. https://doi.org/10.1016/j.ijsbe.2015.10.002

[2] K. P. Keith, “Characterization of the Behavior of High Volume Fly Ash Concrete,” *Thesis Master*, Fac. Eng, Auburn, AU, Al, USA, 2011. Availabe: http://hdl.handle.net/10415/2784

[3] P. K. Mehta, “Effect of Fly Ash Composition on Sulfate Resistance of Cement,” *J Proc*, vol. 83, no. 6, pp. 994–1000. Nov. 1986. https://doi.org/10.14359/1892

[4] V. M. Malotra & P. K. Metha, *High-performance, high-volume fly ash concrete: materials, mixture proportioning, properties, construction practice, and case histories.* OT, CA: SCMSD, Inc., 2004. Available: http://worldcat.org/isbn/0965231070

[5] J. Z. W. Moon, Z. Wang, M. O. Kim & S.-C. Chun, “Strength enhancement of alkaline activated fly ash cured at ambient temperature by delayed activation of substituted OPC,” *Constr Build Mater*, vol. 122, pp. 659–666. Sep. 2016. https://doi.org/10.1016/j.conbuildmat.2016.06.111

[6] E. R. Nuñez, “Comportamiento Mecánico y durabilidad de morteros de cenizas volantes activadas alcalinamente,” *trabajo grado*, Dpto Ing, PUJ, BO, CO, 2013. Available: https://repository.javeriana.edu.co/bitstream/handle/10554/11159/RobayoNunezEstefania2013.pdf

[7] M. Criado, A. F. Jiménez & A. Palomo, “Effect of sodium sulfate on the alkali activation of fly ash,” *Cem Concr Compos*, vol. 32, no. 8, pp. 589–594. Sep. 2010. https://doi.org/10.1016/j.cemconcomp.2010.05.002

[8] M. Criado, A. Palomo, A. Fernández-Jiménez & P. F. G. Banfill, “Alkali activated fly ash: Effect of admixtures on paste rheology,” *Rheol Acta*, vol. 48, no. 4, pp. 447–455. Feb. 2009. https://doi.org/10.1007/s00397-008-0345-5

[9] B. S.-K. Reddy, J. Varaprasad & K. N.-K. Reddy, “Strength and workability of low lime fly-ash based geopolymer concrete,” *Indian J Sci Technol*, vol. 3, no. 12, pp. 1188–1189, Dec. 2010. Available: https://sciresol.s3.us-east-2.amazonaws.com/IJST/Articles/2010/Issue-12/Article13.pdf

[10] M. Criado, “Nuevos materiales cementantes basados en la activación alcalina de cenizas volantes. Carecterización de geles N-A-S-H en función del contenido de sílice soluble. Efecto del Na2 SO4,” *Ph.D. dissertation*, Depto Quim Inorg, CSIC, IETcc, MAD, ES, 2007. Disponible en http://hdl.handle.net/10486/1697

[11] D. Salazar-Carreño, R. G. García-Cáceres & O. O. Ortiz-Rodríguez, “Laboratory processing of Colombian rice husk for obtaining amorphous silica as concrete supplementary cementing material,” *Constr Build Mater*, vol. 96, no. 15, pp. 65–75. Oct. 2015. https://doi.org/10.1016/j.conbuildmat.2015.07.178

[12] A. Bicer, “Effect of fly ash particle size on thermal and mechanical properties of fly ash-cement composites,” *TSEP*, vol. 8, pp. 78–82, Dec. 2018. https://doi.org/10.1016/j.tsep.2018.07.014

[13] S. H. Jung, V. Saraswathy, S. Karthick, P. Kathirvel & S. J. Kwon, “Microstructure Characteristics of Fly Ash Concrete with Rice Husk Ash and Lime Stone Powder,” *Int J Concr Struct Mater*, vol. 12, no. 17, 1–9, Dec. 2018. https://doi.org/10.1186/s40069-018-0257-4

[14] A. Palomo, M. W. Grutzeck & M. T. Blanco, “Alkali-activated fly ashes: A cement for the future,” *Cem Concr Res*, vol. 29, no. 8, pp. 1323–1329, Aug. 1999. https://doi.org/10.1016/S0008-8846(98)00243-9

[15] G. Kovalchuk, A. Fernández-Jiménez & A. Palomo, “Alkali-activated fly ash. Relationship between mechanical strength gains and initial ash chemistry,” *Mater Const*, vol. 58, no. 291, pp. 35–52, Sep. 2008. https://doi.org/10.3989/mc.2008.v58.i291.101

[16] M. Criado, A. Palomo & A. Fernández-Jiménez, “Alkali activation of fly ashes. Part 1: Effect of curing conditions on the carbonation of the reaction products,” *Fuel*, vol. 84, no. 16, pp. 2048–2054, Nov. 2005. https://doi.org/10.1016/j.fuel.2005.03.030

[17] S. P. Singh, S. Chowdhury & P. N. Mishra, “An Experimental Investigation on Strength Characteristics of Alkali Activated Fly Ash,” *Procedia Earth Planet Sci*, vol. 11, pp. 402–409, 2015. https://doi.org/10.1016/j.proeps.2015.06.039

[18] D. Velandia-Manchego, C. Lynsdale, F. Ramirez, J. Provis, G. Hermida & A. Gómez, “Ultra optimum green concrete using high volume fly ash activated systems,” *MRS OPL Arch*, vol. 1612, no. 2, pp. 1689–1699, Dec. 2014. https://doi.org/10.1557/opl.2013.1118

[19] T. Degen, M. Sadki, E. Bron, U. König & G. Nénert, “The HighScore suite,” *Powder Diffraction*. vol. 29, Suppl S2, pp S13–S18, Dec. 2014. https://doi.org/10.1017/S0885715614000840

[20] *Axios FAST Simultaneous XRF Spectrometer.* (model 4 kw), Malvern Panalytical, Malvern, Reino Unido. Disponible en https://www.malvernpanalytical.com/es

Dimelsa Salazar-Carreño. Fundación Centro de Desarrollo Tecnológico-CENTREK (Bogotá, D.C., Colombia).

Rafael Guillermo García-Cáceres. Universidad Pedagógica y Tecnológica de Colombia-UPTC (Sogamoso, Colombia).

Alejandra Santa. Alienergy S.A.S. (Sogamoso, Colombia).