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Mechanical and chemical behavior of calcium sulfoaluminate cements obtained from industrial waste

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ABSTRACT

A calcium sulfoaluminate clinker was synthesized calcining a mixture of fly ash, fluorogypsum, aluminum slag, and calcium carbonate at 1250 ℃. The clinker was mixed with 15, 20, or 25% e.p. of $CaSO4·\frac{1}{2}H_2O$. The pastes were prepared with a water/cement ratio of 0.5. Compression resistance of cements cured in potable water and corrosive mediums at 40 ℃ was evaluated. The cements cured in potable water developed compressive strengths of 38-39 MPa; those immersed in corrosive mediums showed a decrease in this property after the chemical attack. Ettringite was the main product of hydration. The degradation of the cements by chemical attack was due to a decalcification and dealumination of the pastes.
Keywords: calcium sulfoaluminate; ettringite; compressive strength; chemical attack.

RESUMEN

Se sintetizó un clínker de sulfoaluminato de calcio calcinando una mezcla de ceniza volante, fluoryeso, escoria de aluminio y carbonato de calcio a 1250 °C. El clinker fue mezclado con 15, 20 o 25 % e.p. de $CaSO_4·\frac{1}{2}H_2O$. Las pastas se prepararon con relaciones agua/cemento de 0.5. Se evaluó la resistencia a la compresión de cementos curados en agua potable y en medios corrosivos a 40 °C. Los cementos curados en agua potable desarrollaron resistencias a la compresión de 38-39 MPa, los inmersos en medios corrosivos presentaron una disminución en esta propiedad después del ataque químico. La etringita fue el principal producto de hidratación. La degradación de los cementos por ataque químico es debida a una descalcificación y dealuminación de las pastas.
Palabras clave: sulfoaluminato de calcio; etringita; resistencia a la compresión; ataque químico

RESUMO

Foi produzido um clínquer de sulfoaluminato de cálcio a partir da calcinação a 1250°C de uma mistura de cinza volante, escória de alumínio, carbonato de cálcio e gesso de flúor. Esse clínquer foi misturado com 15%, 20% e 25% e.p. de $CaSO_4·\frac{1}{2}H_2O$. As pastas foram preparadas com relação água/cimento igual a 0,5. Foi avaliada a resistência à compressão das pastas curadas em água potável e em meios corrosivos a 40°C. As pastas curadas em água alcançaram resistências à compressão de 38-39 MPa, enquanto as pastas imersas em meios corrosivos apresentaram uma redução da resistência frente ao ataque químico. A etringita foi o principal produto da hidratação desses cimentos. A degradação dessas pastas de cimento por ataque químico ocorreu devido a uma descalcificação e dealuminização dos produtos hidratados.
Palabras-clave: sulfoaluminato de cálcio; etringita; resistência à compressão; ataque químico.

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1. INTRODUCTION

Cement is a material utilized in the construction of cities and houses, with a growing demand dependent upon demographic growth. The use of concretes constituted with appropriate materials, conveniently provided and well-consolidated, ensures the durability of the constructions. The most frequently used binding material in construction is Portland cement; however, in its production processes large quantities of fossil fuels and, in a parallel manner in its decarbonation process of raw materials large quantities of CO_2, are emitted into the atmosphere, contributing around 7% of the global CO_2 emissions (Roy et al., 1999; Gartner et al., 2004). There are a variety of alternative and viable materials (industrial wastes) that can be used for the substitution of Portland cement. Their use is based on the importance of minimizing CO_2 emissions, as well as increasing interest in the production of cementive materials that develop good mechanical properties and good stability in corrosive environments.

An alternative to partially or completely substitute the use of Portland cement is the manufacture of calcium sulfoaluminate (CSA) cement which presents a crystalline structure that consists of a tridimentional arrangement of AlO_4 tetrahedrons interlinked with Ca^{+2} and SO_4^{-2} ions located in the existent intervals (Sharp J.H. et al., 1999). This type of cement has low CO_2 emissions, forming at a temperature of approximately 1250 ºC, in addition to developing good mechanical properties (compression resistance) (Older, 2005; Zhou et al., 2006; Garcia-Maté et al., 2015; Hargis et al., 2014). On the other hand, there is a large quantity of wastes such as slag, gypsum, and fly ash among others, that show considerable quantities of Al_2O_3, CaO, and $CaSO_4$ in their chemical composition, these being the main components for the production of CSA clinkers. An important advantage derived from the manufacture of this clinker from industrial waste is the decrease in air, soil, and visual contaminations that these create (stored outdoors) and the decrease in CO_2 emissions to the environment. Li et al. reported the synthesis of CSA utilizing high alumina fly ash, bauxite, and limestone as the starting materials (Li et al., 2007), where the main stages of synthesis were CSA and tricalcium silicate (C_3S). A sulfoaluminate-belita was synthesized at 1150 ºC from fly ash, powders, and muds collected from industrial processes. As a product of synthesis, the clinker obtained showed stages such as gehlenite (formed by the decomposition of belita at temperatures higher than 1100 ºC), CSA, and belita (Li et al., 2001). During the synthesis of CSA utilizing industrial wastes, the formation of gehlenite is obtained as a secundary product of synthesis, this stage being responsible for the decreased formation of CSA (Arjunan et al., 1999). The synthesis of a sulfoaluminate-ferrite through the use of lime, gypsum, red mud, and bauxite at 1250 ºC showed stages such as $C_4(A_3F)_3\bar{S}$, C_4AF, and C_2F. The density of this increased with the rise in the quanity of red mud; finally, the hydration products formed were ettringite and $C_3(AF)H_6$ (Singh et al., 1997). The use of waste from fertilizer, bauxite, and mineral iron processing facilities as raw material for the synthesis of CSA at 1230 ºC generated stages such as CSA, C_4AF, C_2AF, $2C_2S \cdot C\bar{S}$ and a small quantity of free lime. A larger quantity of mineral iron increased the quantity of C_4AF and decreased the quantity of CSA (Singh et al., 2008). CSA has been synthesized from a mixture of jarosite-alunite and waste from a hydrometallurgic process (developed to economically treat ores from low-grade nickel oxides) at 1300 ºC (Katsioti et al., 2005). In general, the pastes prepared with the clinkers obtained from the mentioned industrial wastes or byproducts showed good mechanical properties. Ettringite is the main product of hydration in a CSA cement, occuring as a natural process of the combination of this cement, water, and calcium sulfate (Mehta, 1967). The characteristic morphology of ettringite is comprised of crystals that exhibit hexagonal prisms or plaques (Moore et al., 1968). The formation of ettringite in the first stages of hydration contributes to the development of the mechanical properties. However, the development or

formation of this phase in later stages (delayed ettringite formation, DEF) can be detrimental. The DEF in hardened cementive materials generates micro-cracks deteriorating the mechanical properties, this is due to it being considered expansive. In many cases, DEF is attributed to an excessive quantity of sulfates present in the cement (Taylor, 2001; Gallardo M. et al., 2014). The development of the physical and chemical properties of new construction materials in environments similar to those in which Portland cement is exposed to on a daily basis has given rise to interest in this area of research. Studies have been performed on the durability or chemical stability of various types of cements, whose purpose is the study of the behavior of the reactions that occur on these construction materials varying the conditions to which they are exposed on a daily basis. For example, research on the chemical attack on Portland, pozzolanic, and slag concretes was carried out simulating acid rain with a H_2SO_4 and HNO_3 solution with a pH of 3.5. The results indicated that calcium hydroxide is the compound in which the attack of the solutions begins; therefore, it could act as a barrier against the attack of hydrated silicates. The pozzolanic concretes showed a greater attack than those prepared with slag. The diffusion increased at high water/cement ratios due to the high permeability (R. Sersele et al., 1997). Studies were performed on the chemical durability of an API cement class B (utilized in oil wells) in order to determine the effects resulting from SO_4^{-2}, Mg^{+2}, and Cl^- ion attacks that were carried out using Na_2SO_4, $NaCl$, and $MgCl_2$ aqueous solutions as the curing medium. The formation of tobermorite, portlandite ettringite, and monocloroaluminate was detected as the result of the transformation of the anhydrous stages of the cement. Portlandite increased in quantity with the passage of time. The interaction between the SO_4^{-2} ions and the cement generated partially soluble gypsum, which subsequently reacted with C_3A facilitating the formation of ettringite. The Cl^- ions were chemically bound to the hydrated calcium aluminates resulting in the formation of Friedel salt. The Mg^{2+} ions contributed to the decalcification of the cement and in turn reacted with hydroxyl, giving rise to the formation of brucite (Martin J.J. et al., 2008). The study of the chemical durability of a geopolymer prepared with metakaolin exposed to an HCl solution for 10 days with a concentration of 0.5 N at 60 ℃ resulted in a degradation of the pastes due to the destruction of the geopolymeric structure and the release of Na, Al, and Si towards the acidic solution. An exchange of ionic species was evidenced between H_3O^+ and Na^+. The chemical attack was more intense on pastes with a higher $SiO_2/Al_2O_3=3$ and $Na_2O/Al_2O_3=0.55$ ratio, with a 33.1% loss of their initial resistance. Pastes with a lesser $SiO_2/Al_2O_3=2.6$ and $Na_2O/Al_2O_3=0.55$ ratio only lost 2% of their initial resistance. The mechanism involved in the deterioration was the ionic exchange of the HCl dissociation on Cl^- and H_3O^+ ions, where Cl^- ions neutralized charges with Na^+ ions giving rise to a NaCl precipitation (Burciaga-Diaz O. et al., 2007). The objective of this paper is the development assessment of the compressive strength and chemical stability of calcium sulfoaluminate cements synthesized from a mixture of fly ash, aluminum slag, and fluorogypsum at 1250 ℃.

2. EXPERIMENTAL PROCEDURE

The materials utilized were fly ash (fa), aluminum slag (as), and fluorogypsum (fg). The latter two were subject to a grinding process until a particle size less than 106 μm (#140 ASTM mesh) was obtained. Subsequently, the chemical composition of each material was analyzed through X-ray fluorescence (XRF), the results of which are shown in Table 1.

Table 1. Chemical composition in oxides of the raw material.

Oxides	Aluminum Slag as (e.p. %)	Fly Ash fa (e.p.%)	Fluorogypsum fg (e.p.%)
Na_2O	2.496	-	-
MgO	5.000	1.377	-
Al_2O_3	63.19	24.81	-
SiO_2	11.69	59.49	0.103
SO_3	0.833	-	56.33
Cl_2	4.636	-	-
K_2O	2.203	1.716	-
CaO	7.263	4.806	43.24
TiO_2	0.983	1.663	-
MnO	0.503	-	-
Fe_2O_3	1.203	6.126	-

Based on the chemical composition, the wastes were mixed in the required proportions in order to obtain CSA in accordance with the following reaction: as + fa + fg + $CaCO_3$ = CSA (80% e.p.) + Ca_2SiO_4 (20% e.p.). The proportions of each starting material were adjusted with $CaCO_3$ (97% purity). The starting materials were homogenized in plastic containers with acetone and alumina balls for 4 hours; they were subsequently dried at 80 ºC for 12 hours. Pills 2 cm in diameter were made through uniaxial pressing at 45 MPa, which were then subject to thermal treatment at 1250 ºC for 4 hours. The formation of the CSA was corraborated through X-ray diffraction. The clinker obtained was grounded until obtaining a specific superficial area of approximately 3800 cm^2/g (ASTM C-204), and was subsequently mixed with 15, 20, or 25% e.p. calcium sulfate ($CaSO_4·½H2O$) in order to prepare the CSA cement. The pastes were prepared with a water/cement ration of 0.5 in accordance with the procedure indicated in the Mexican standard NMX-C-085-ONNCC-2002 (NMX-C-085). The nomenclature of the systems was the following: 515, 520, and 525, where the first number indicates the water/cement ration and the latter two indicate the calcium sulfate content. The mixtures were emptied into Nyalcero molds and vibrated for 60 seconds in order to eliminate porosity. The already filled molds were covered with plastic and placed in isothermic chambers at 40 ºC for 24 hours. Subsequently, the cubes were removed from the molds and placed in containers with water (potable water) in order to begin humid curing at the aforementioned temperature for 1, 3, 7, 14, or 28 days; after each curing period, the compressive strength was evaluated. For the effect of comparison, Ordinary Portland cement (OPC commercial) samples were elaborated as control references. These samples were elaborated and cured under the same conditions as the CSA-based cements.

For chemical durability tests, samples were cured for 7 days in potable water which were subsequently submerged in corrosive mediums for 14, 28, or 42 days for the chemical resistance evaluating by means of measuring their compressive strength. The samples were submerged in 2 liters of H_2SO_4 0.5 N, $MgCl_2$ 06 N, and Na_2SO_4 0.04 N solution (elaborated with deionized water) at 40 ºC in order to simulate aggressive conditions. The compressive strength measurements were done in an automated hydraulic press (Controls model 50-C7024) with a 250 kN capacity, using a loading speed of 350 N/s. The tests were done in accordance with the procedure described in the standard ASTM C109/C109-M95 (ASTM-C109). In order to identify the stages present resulting from the hydration reactions and the chemical attack, samples with 28 (potable water) and 42 (corrosive medium) days of immersion were analyized through X-ray diffraction (XRD).

Fragments were selected, preferably from the surface of each one of the cubes tested in a chemical attack, and were submerged in methanol and dried for 48 hours in an oven at 40 ℃. Samples were analyzed before and after the chemical attack through Scanning Electron Microscopy (SEM).

3. RESULTS

Figure 1 shows the diffraction pattern of the synthesized clinker at a temperature of 1250 ℃. The reflections corresponding to the CSA were primarily observed. Secondary stages such as gehlenite ($Ca_4Al_2SiO_7$), calcium aluminate ($CaAl_2O_4$), mayenite ($Ca_{12}Al_{14}O_{33}$), and pleochroite ($Ca_{20}Al_{26}Mg_3Si_3O_{68}$) were formed. Belite ($Ca_2SiO_4$) was obtained in a lesser percentage than what was intended due to the thermodynamic stability of secondary stages formed at 1250 ℃. On the other hand, gehlenite and spinel are considered non-cementing stages due to their small or lack of reactivity in the presence of water, but these could act as reinforcement stages.
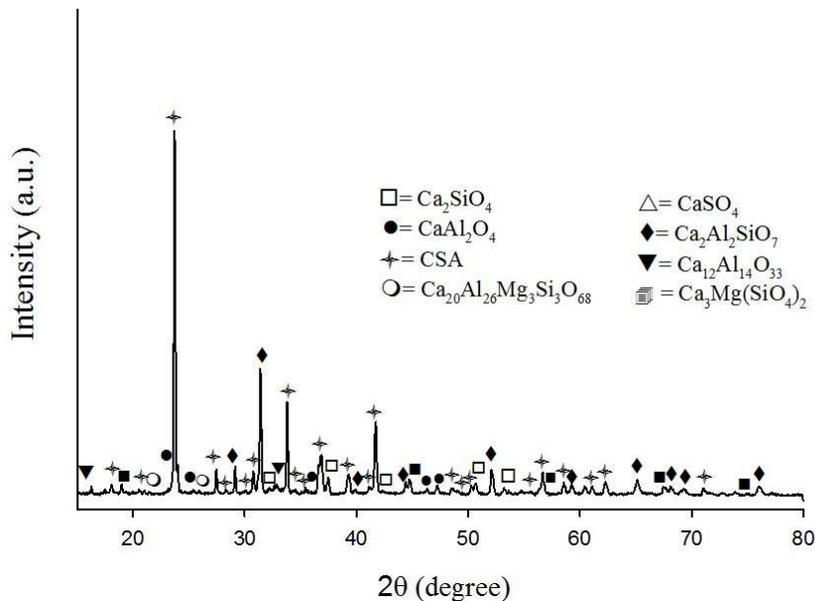

Figue 1. XRD pattern of the synthesized at 1250 ℃.

Figure 2 shows the compressive strength results of systems 515, 520, and 525 cured from 1 to 28 days at 40 ℃. In system 515, a gradual development of the compressive strength was observed from day one and up to 14 days; at 28 days the compressive strength decreased, favored by the delayed ettringite formation. System 520 showed a decrease in compressive strength at 7 days with a slight increase at 14 and 28 days; however, a low strength developed ending with 24.25 MPa. In system 525, an increase in the compressive strength was observed in function with time (from 1 to 14 days); at subsequent times it remained at the same strength of 38.9 MPa at 28 days. It is possible that ettringite formed almost in full during the first days of curing, and the subsequent increase is due to the growth of this stage within the pores weak zones (micro-cracks). The presence of gypsum and CSA residue in the days following the start of the curing process indicates that the hydration reactions shall continue with the passage of time. This system showed the best compressive strength values. Based on the aforementioned, a greater quantity of gypsum increases the mechanical resistance due to the formation of the largest quantity of ettringite from the first days of curing. The compressive strength results obtained were found within the value established in the

standard NMX-C061-ONNCCE-2001 (20-40 MPa at 28 days of curing). The experimentally obtained value for the OPC cement was 38 MPa.
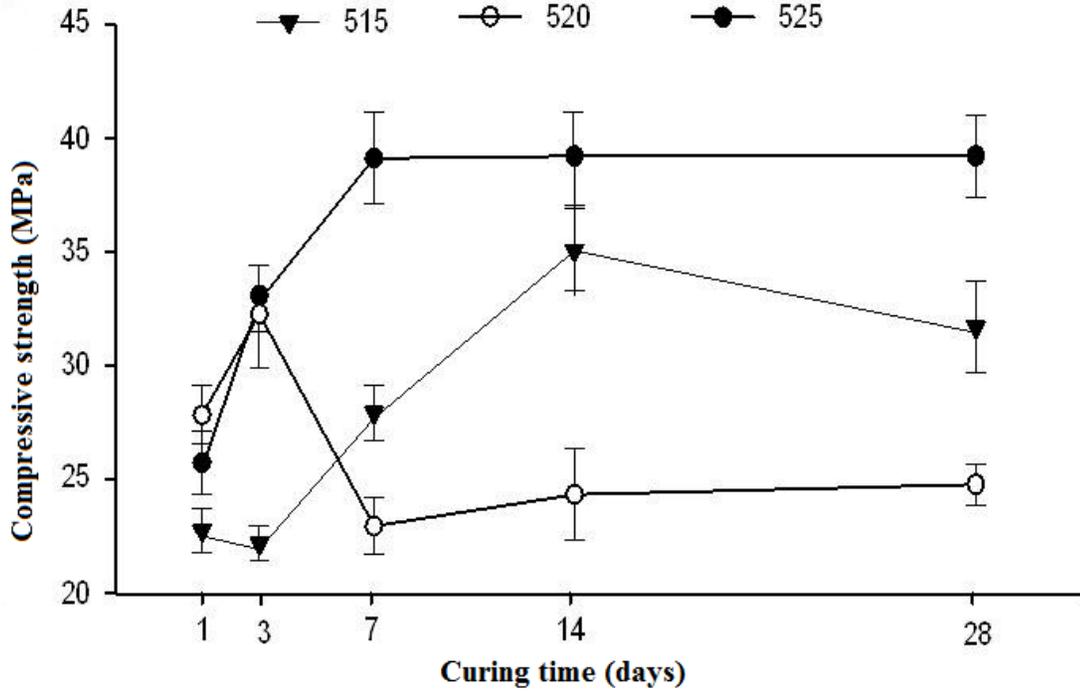

Figure 2. Compressive strength of systems 515, 520, and 525 cured at 40 ºC.

Figures 3 and 4 show the XRD patterns of systems 515 and 525 at 1, 14, and 28 days of curing at 40 ºC. In system 515 (Figure 3), during the first day reflections were observed corresponding to ettringite and these reflections increased in intensity at 14 and 28 days of curing. In system 525 (Figure 4), during the first day reflections were observed corresponding to the CSA and gypsum, these latter reflections were observed up to 14 days later. The reflections corresponding to ettringite were visible from day one and increased in intensity at 14 and 28 days. The gradual increase in intensity of the reflections of the hydration products indicated the delayed ettringite formation. This was not enough to affect the mechanical properties given that the increase of this stage possibly took place within the present pores. For both systems, reflections corresponding to the spinel and gehlenite were observed without apparent changes in the intensity of the reflections in function to the time of curing, due to these two stages being inert in the presence of water.

Figure 3. XRD patterns of system 515 at 1, 14, and 28 days of curing at 40 ℃.

Figure 4. XRD patterns of system 525 at 1, 14, and 28 days of curing at 40 ℃

Figure 5 shows the micrographs of fracture surfaces of systems 515 and 525 at 1, 14, and 28 days of curing at 40 ℃. In system 515 during the first day, a dense microstructure is seen with the presence of some cracks distributed in the matrix. At 14 days, a microstructure is observed with a denser and more compact matrix where the cracks decreased in quantity explaining the increase in

compressive strength that was presented in the curing time. At 28 days of curing, some weak zones were observed generated by the growth of hydrates giving rise to a decrease in the compressive strength of the material.
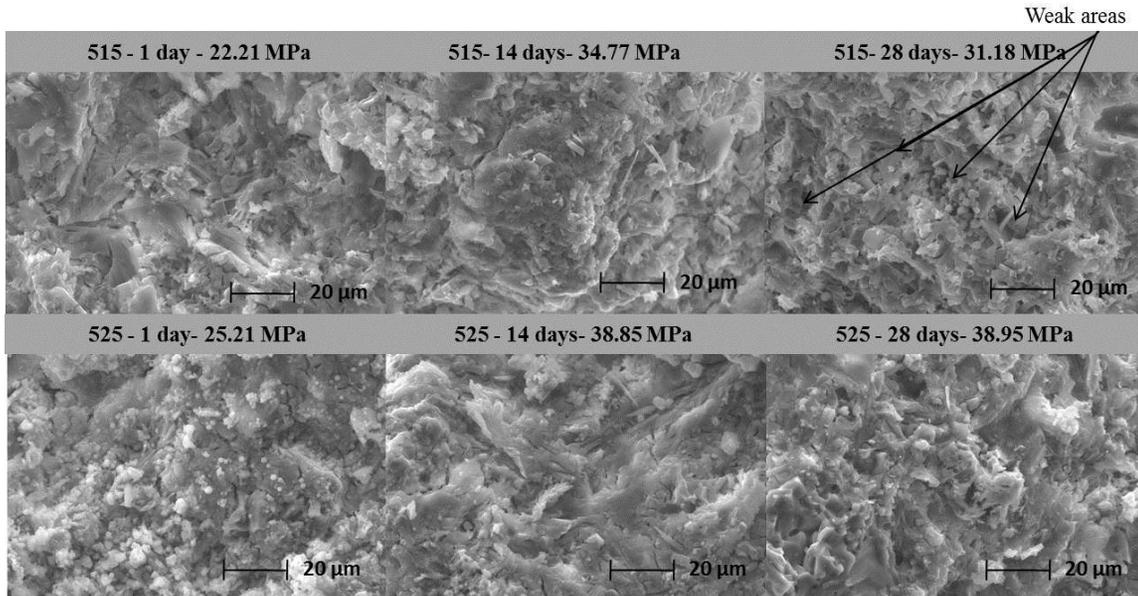

Figure 5. Micrographs of fracture surfaces of samples of systems 515 and 525 at 1, 14, and 28 days of curing at 40 ℃.

In the surface microstructures of system 525 on day one, white nodes were observed immersed in a dense ettringite matrix. These white nodes are associated with the formation of gypsum. At 14 days of curing, greater densification of the matrix was presented similar to the microstructure observed at 28 days, corroborating the similarity in mechanical properties at 14 and 28 days of curing. System 525 developed the best compressive strength, showing greater stability in function to time by not showing decreases in resistance. Due to the aforementioned, the stability of this system was evaluated immersed in aggressive solutions. Samples of this cement were cured for 7 days in potable water (38.95) and subsequently immersed in corrosive solutions.

Figure 6 shows the compressive strength results obtained from the samples after being immersed in corrosive mediums for 7, 14, 28, and 42 days at 40 ℃. The samples immersed in a solution of $NaSO_4$ 0.04 N developed the greatest compressive strength at 42 days of curing (34.63 MPa). The samples immersed in solutions of H_2SO_4 and $MgCl_2$ developed similar compressive strength at 42 days with values of 28.10 and 29.2 MPa, respectively. A decrease in compressive strength of 28.6 and 25.83% was observed in samples immersed in H_2SO_4 and $MgCl_2$ solutions, respectively. These variations could be attributed to the interaction of the samples with the Cl^-, Mg^{+2}, SO_4^{-2}, and Na^+ ions present in the corrosive solutions. The samples immersed in potable water did not show a decrease in compressive strength at any time during the curing (1-28 days).
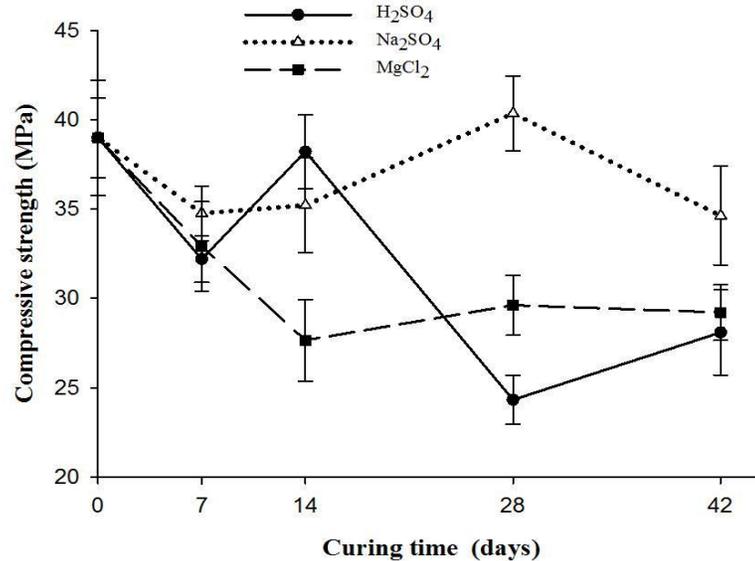
Figure 6. Compressive strength of system 525 cured in aggressive solutions at 40 °C.

The results obtained from the XRD characterization of the samples immersed in aggressive solutions at 42 days of curing are shown in Figure 7. High intensity reflections were observed corresponding to gypsum in samples immersed in a H_2SO_4 solution, indicating a degradation of the ettringite caused by the diffusion of SO_4^{-2} ions inside of the microstructure, causing a dissolution of the material. For samples immersed in $MgCl_2$ and Na_2SO_4, a pattern was observed similar to the one described above, except that the reflections corresponding to gypsum had low intensity indicating a moderate attack on the material.

Some damage could be seen during a visual analysis, where a softening of the surface was observed which was greater in the samples immersed in the acid solution, indicating a greater aggressiveness by this solution.
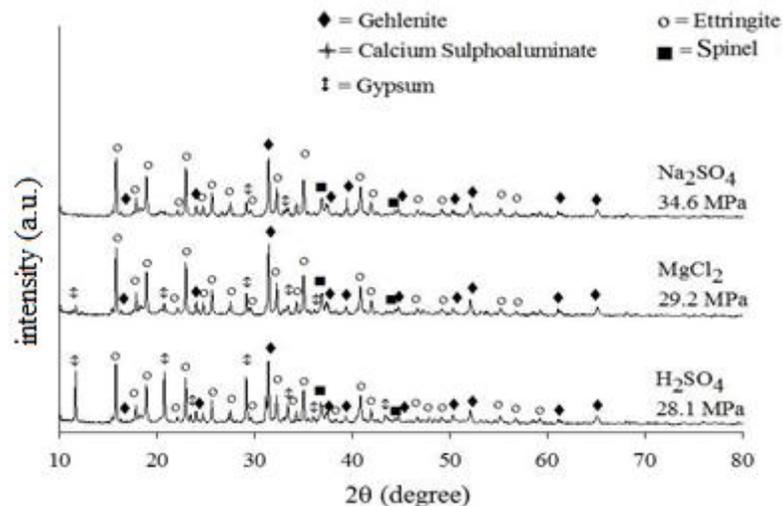

Figure 7. XRD patterns of system 525 immersed in aggressive solutions for 42 days at 40 °C.

Figure 8 shows a micrograph of a sample immersed in a H2SO4 0.5 N solution at 40 ºC. The region of chemical attack was observed from the surface with a depth of approximately 129 µm, visually observing a grayer shade than the rest of the sample. The EDS analysis indicated a migration of Al^{+3} ions caused by the attack of the acid solution. A 22 µm thick crack formed due to a change in volume, caused by the migration of calcium ions and sulfates to the exterior, increasing the attack given that the new surfaces were exposed to the corrosive solution. Under the crack a dense and compact matrix was observed, suggesting that it is a zone where the corrosive medium did not penetrate.
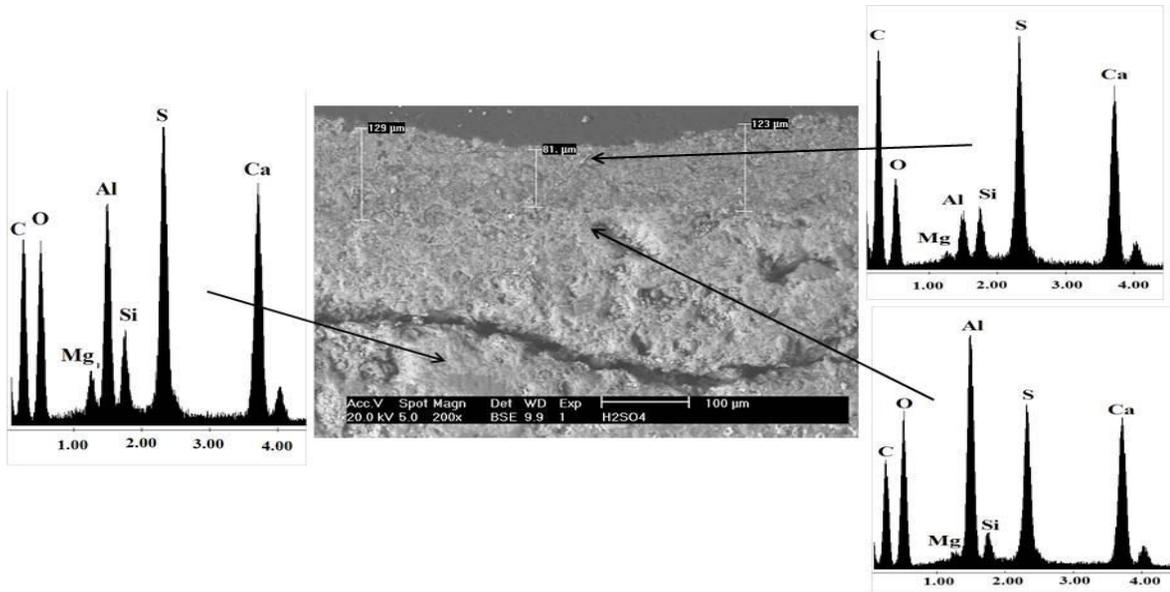

Figure 8. Micrograph of the cement after 42 days immersed in a H_2SO_4 0.5 N solution.

Figure 9 shows the microstructure of a sample immersed in a $MgCl_2$ 0.6 N solution for 42 days at 40 ºC. The depth of the chemical attack was approximately 380 µm, being greater than the one observed in the cement attack with a H_2SO_4 solution. In the area above the crack, an interface with a high Mg content was observed due to a slow diffusion of Mg^{+2} ions in the sample, indicating an ionic exchange with calcium ions. The non-corroded area showed a compact microstructure.
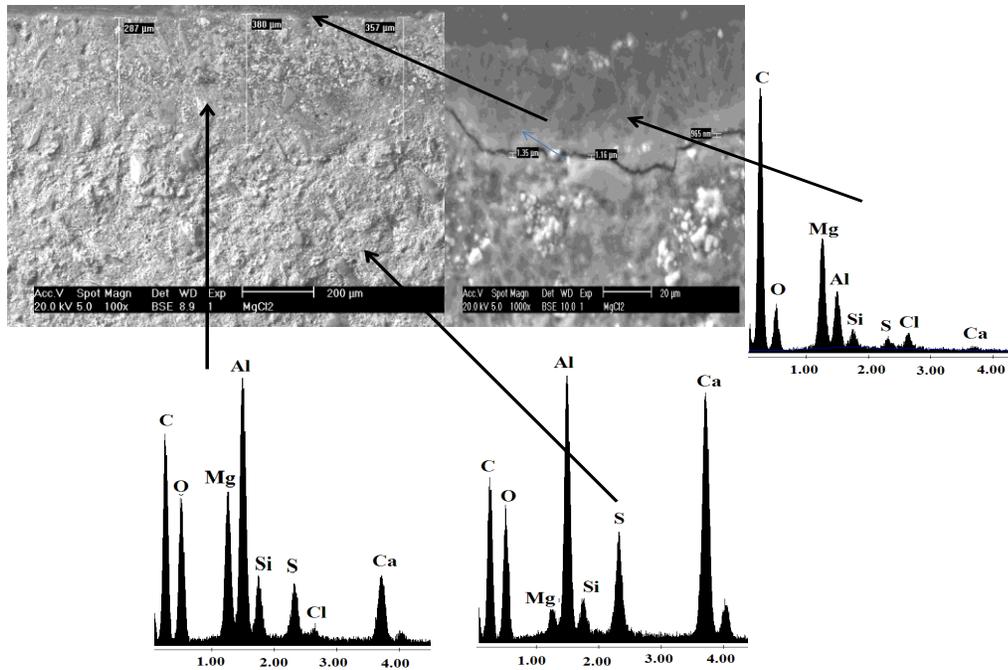
Figure 9. Micrograph of the cement after being immersed for 42 days in a MgCl2 0.6 N solution.

Figure 10 shows the microstructure of a sample immersed in a Na2SO4 0.04 N solution for 42 days at 40 ºC. An attack depth of 46.7 µm with a granular appearance was observed; these are possibly gypsum nodes, the product of a decalcification of the material. Alumina particles inside the matrix were observed, indicating a migration towards the exterior of calcium and sulfate ions. The cement immersed in this solution showed a greater resistance to the attack and its compressive strength was 34.63 MPa at 42 days of immersion; this is possibly due to the Na^+ ions having displaced the Ca^{+2} ions, forming part of the crystalline network.
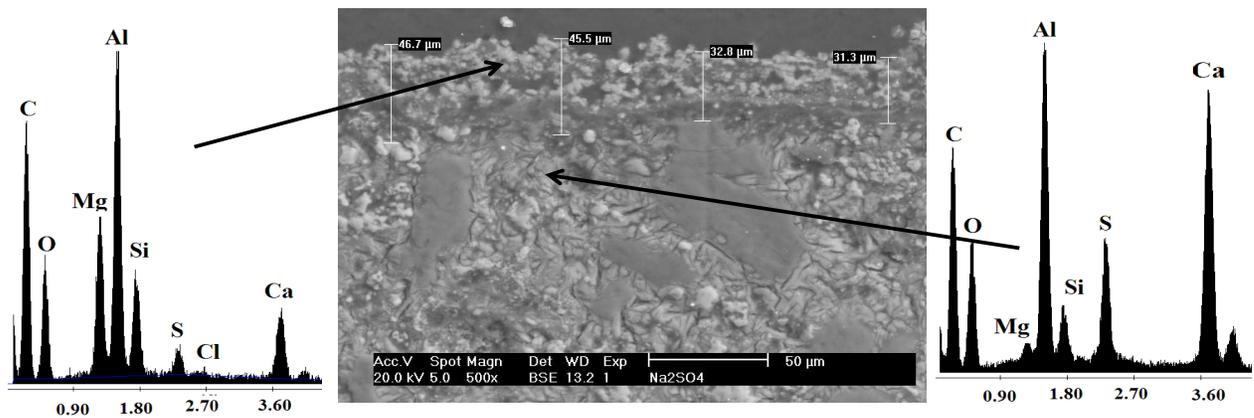

Figure 10. Micrograph of the cement after 42 days of immersion in a $NaSO_4$ 0.6 N solution.

4. CONCLUSIONS

A calcium sulfoaluminate clinker was obtained from the synthesis of a mixture of aluminum slag, fly ash, and fluorogypsum. The clinker showed in its composition stages such as calcium sulfoaluminate, gehlenite, calcium aluminate, mayenite, and belite.

The cements elaborated with calcium sulfoaluminate synthesized from industrial wastes developed compressive strengths of 38.95 MPa, similar to those developed by the Ordinary Portland pastes cured under the same conditions.

The pastes immersed in a (Na_2SO_4) solution showed a high resistance to attack by sulfates, developing a compressive strength of 34.63 MPa after 42 days of immersion.

The degradation of pastes by the attack of H_2SO_4 and $MgCl_2$ occurs by dealumination and decalcification processes. The samples immersed in H_2SO_4 and $MgCl_2$ developed a compressive strength of 28.10 and 29.2 MPa, respectively, after 42 days .of curing.

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