

Synthesis and mechanical properties of a calcium sulphoaluminate cement made of industrial wastes

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ABSTRACT: Environmentally-friendly calcium sulphoaluminate clinkers were obtained from a mixture of aluminium dross, fluorgypsum, fly ash and CaCO₃ at temperatures within the range of 1100 to 1400 °C. After the heat treatments Ca₄Al₆O₁₂SO₄ was the main phase. Three different cements were prepared using the clinkers synthesized at 1250, 1350 and 1400 °C; the clinker powders were mixed with 20 wt% of hemihydrate. Cement pastes were prepared using a water/cement ratio (w/c), 0.4 followed by curing at 20 or 40 °C for periods of time ranging from 1 to 28 days. Most of the samples showed high compression strengths 40–47 MPa after 28 days, which were comparable to the strength of Portland cement. Ettringite was the main hydration product and its morphology consisted of acicular and hexagonal plates, which is typical of this phase.

KEYWORDS: Clinker; Calcium Sulpholuminate; Wastes; Ettringite

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RESUMEN: Síntesis y propiedades mecánicas de un cemento de sulfoaluminato de calcio hecho de residuos industriales. Se fabricaron clinkers de bajo impacto ambiental a base de sulfoaluminato de calcio calcinando mezclas de escoria de aluminio, fluoryeso, ceniza volante y CaCO₃ a diferentes temperaturas dentro de un rango de 1100 a 1400 °C. Se observó la formación de $Ca_4Al_6O_{12}SO_4$ como fase principal. Para obtener los cementos, los clinkers obtenidos a 1250, 1350 y 1400 °C se mezclaron con 20% en peso de hemihidrato. Se prepararon pastas usando una relación agua/cemento, de 0.4 y se curaron a 20 y 40 °C por diferentes periodos de tiempo desde 1 hasta 28 días. Los valores de resistencia a la compresión a los 28 días de curado de la mayoría de las muestras estuvieron entre 40–47 MPa, equiparables a los de referencia de pastas de cemento Portland. La etringita fue el principal producto de hidratación y su morfología consistió de placas hexagonales y aciculares, típicas de esta fase.

PALABRAS CLAVE: Clinker; Sulfoaluminato de calcio; Desechos; Etringita

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1. INTRODUCTION

Aluminum scrap recycling generates important amounts of dross, which forms on the surface of the aluminum liquid bath. There are several methods for the treatment of this byproduct and most of them focus on the recovering of metallic aluminum; its composition varies depending on the purification procedure, in general, it may contain Al_2O_3 , AlN, Al_4C_3 , SiO_2 , MgO, Al and minor quantities of Si, Fe and Mg. Many small aluminum recycling companies do not treat the generated aluminum dross

and it is usually confined in landscapes in incandescent state allowing the metallic aluminum to oxidize, therefore this kind of byproduct has a high alumina content (1). Aluminum dross has been used in several applications, such as reinforcing material in aluminum-dross composites (2) synthesis of spinel (3) by solid-state reaction with MgO, synthesis of SiAlON (4) and carbothermal reduction and nitridation process, as raw material for the preparation of refractory (5), manufacture of calcium aluminate cement (6) synthesis of Mg-Al, Ca-Al and Zn-Al type $LDH_{s}(7)$ using HCl and NaOH solutions. The high amount of alumina in the dross makes this waste a suitable material for the synthesis of several kinds of ceramics, in particular as a raw material for the synthesis of some cements.

Nowadays, the cementitious material most used worldwide is the Portland cement and its demand increases with the population growth. Nonetheless, its production involves the generation of great amount of CO₂ emissions, i.e, about 0.85-1.00 tons of CO_2 are produced for each ton of clinker (8, 9). In 2011 the global compsumption of Portland cement clinker was of 2.7 Gt which contributes to the generation of about 7% of total CO₂ emissions worldwide (10, 11). As the cement demand continues to grow, it is necessary to develop alternative low environmental impact binders able to attain mechanical properties similar or superior to those of Portland cement (12). One alternative is the calcium sulphoaluminate cements (Ye'elemite or $C_4A_3\overline{S}$), which is the core of this work.

A typical clinker of $C_4A_3\overline{S}$ contains 50–70 wt% of ve'elemite, 5–20 wt% of belite (C_2 S), 5–20 wt% of ferrite (C₄AF) and 3-10 wt% of mayenite (Ca₁₂Al₁₄O₃₃) (13). Ye'elemite and mayenite are responsible of the early setting of the cement, while belite shows a slow hydration contributing to the final strength to the cement (14). The ground clinker is usually mixed with 20–30 wt% of gypsum to prepare the cement. Calcium sulphoaluminate is usually obtained from mixtures of CaCO₃, Al₂O₃ and CaSO₄·2H₂O and the firing temperature leads to lower CO₂ generation compared to the Portland cement manufacture; the total energy required for its manufacture (1.337 kJ/kg) is also lower compared to Portland cement (1.756 kJ/kg) (15, 16). The ve'elemite clinker is also highly porous and this implies a reduction in production costs (17). C_4A_3S shows low alcalinity, suitable mechanical properties, appropriate stability in sea water (18, 19), can be used to for stabilizing dangerous wastes and fixation of heavy metals (20-22) and they are resistant to carbonation (23). The ye'elemite clinker has been also used as a partial or total substitute of CPO in order to reduce shrinkage and reduce setting time in special applications (24). The mechanical strength of mortars (containing commercial clinker, 20 wt% gypsum and cured at 20 °C) reached

42 MPa after one year (16). A study on mortars of C_4A_3S with 19 wt% of gypsum, reported the use of fillers of quartz and CaCO₃; the latter increased the hydration rate and decreased the setting time reaching compressive strength up to 34 MPa after 28 days of curing at 20 °C (25). Garcia-Mate et al. (26) found that mortars of $C_4A_3\overline{S}$ with an addition of 10 wt% of gypsum had 7 day strengths higher than a mortar containing 30 wt% gypsum; however, this situation inverted when a superplasticizer was added. Pastes containing alite-calcium sulphoaluminate (50 wt%)-slag(30 wt%)-limestone(20 wt%) developed a compressive strength of 90 MPa after 90 days of curing (27). One of the main characteristics of these cements is the formation of expansive ettringite, which is the result of the hydration process in presence of gypsum (28–31).

The source of the main components of several kinds of cements is mainly natural raw materials such as clays, alumina and CaCO₃ and can be synthetized at temperatures between 1300-1350 °C; however the formation of $C_4A_3\overline{S}$ has been reported from 1100-1325 °C (14), becoming stable from 1350-1400 °C (32). Several types of industrial wastes can be used as raw materials to obtain the Ca sulphoaluminte clinker. Wu et al. obtained a clinker of $C_4A_3\overline{S}$ from a mixture of Municipal Solid Incineration Wastes-Limestonebauxite-gypsum at 1250 °C, reaching more than 73.2 MPa after 28 days of curing (33). Li et al. (34) obtained a clinker by firing a mixture of fly ash, bauxite and calcium carbonate at 1300 °C. Li et al. (35) obtained the clinker at a temperature as low as 1150 °C using fly ash and sludge as raw materials. Singh et al. (36, 37) reported the formation of a ferric calcium sulphoaluminate from a mixture of CaO, red mud and bauxite at 1250 °C, as well as using waste from a fertilizer industry, bauxite and iron mineral ore at 1250 °C. In general, these works showed the feasibility to obtain a calcium sulphoalumninate clinker using several industrial wastes as raw materials. However, there is a great variety of industrial wastes that have the potential to be used as a source of the main components to fabricate this kind of cement. This work shows the feasibility of producing calcium sulphoaluminate clinkers from a mixture of aluminum dross, fluorgypsum and fly ash; the mechanical and microstructural characterization of the cements was carried out.

2. EXPERIMENTAL

The composition of raw materials used for the synthesis of all of the calcium sulphoaluminate clinkers was of 45.53 wt% of aluminum dross (AD), 12.82 wt% of fluorgypsum (FG), 0.64 wt% of fly ash (FA) and 41 wt% CaCO₃. The raw materials were ball milled until obtaining particle sizes smaller than 106 μ m (#140 ASTM mesh). Each raw material

was chemically analyzed by X-ray fluorescence specstroscopy (XRF, Table 1). Based on this chemical analysis a mixture was designed so as to obtain 80 wt% of calcium sulphoaluminate ($Ca_4Al_6O_{12}SO_4$) and 20 wt% of belite. Disk pellets of 4 cm in diameter were uniaxially pressed at 45 MPa. Samples were heat treated at different temperatures from 1100 to 1400 °C at intervals of 50 °C for 4 h at a heating rate of 10 °C/min. Soaking for 4 hours was selected in order to reach thermodynamic stability. The samples were then analyzed by X-ray diffraction (XRD).

The clinker samples obtained at 1250, 1350 and 1400 °C were selected based on the results obtained by XRD. In order to prepare the cements, samples were ball milled until obtaining a specific surface area of about 3800 cm²/g (Blaine, ASTM C-204) (38) and then mixed with 20 wt% of commercial hemihydrate $(CaSO_4 \cdot 1/2H_2O)$. The cement pastes were prepared by mixing the cements with water using water to cement ratio (w/c) of 0.4. Samples were cast in nylamid molds and cured at 20 and 40 °C for up to 28 days. A Portland cement paste was also prepared as reference and cured at 20°C; this reached 43.7 MPa after 28 days of curing at 20 °C. The setting time was determined using the procedure indicated in the ASTM-191 (39). The compressive strength was evaluated after 1, 3, 7, 14 and 28 days of curing, reporting the average of 4 samples. Fragments from the compressive essay were immersed in methanol in order to stop any further hydration. The fragments were then dried in a vacuum stove at 30 °C and then analyzed by X-ray Diffraction (XRD). The fracture surface of the samples was observed by scanning electron microscopy (SEM).

3. RESULTS AND DISCUSSION

The formation of $Ca_4Al_6O_{12}SO_4$ was detected by XRD analyses (Figure 1) in the samples treated at temperature as low as 1100 °C and it

TABLE 1. Chemical composition of raw materials

Oxides	Aluminum dross (wt%)	Fly ash (wt%)	Fluorgypsum (wt%)	CaCO ₃ (wt%)
Na ₂ O	2.496	_	_	_
MgO	5.043	1.377	—	0.03
Al_2O_3	63.19	24.81	_	0.03
SiO ₂	11.61	59.49	0.103	—
SO_3	0.833	_	56.33	_
Cl	4.636	_	_	_
K ₂ O	2.203	1.716	—	_
CaO	7.263	4.806	43.24	_
TiO ₂	0.983	1.663	_	-
MnO	0.503	_	_	_
Fe ₂ O ₃	1.203	6.126	_	0.029
CaCO ₃	_	-	-	97.07

was present even in the samples treated at 1400 °C in a lower quantity; the decreased intensity of the main reflection was attributed the thermodynamic instability of this compound at high temperatures. The formation of $Ca_4Al_6O_{12}SO_4$ is in agreement with previous reports that indicated the formation of ye'elemite at 1150 °C by using other industrial wastes (15). The formation of secondary phases depends on the sources of raw materials, in this case the other main phase detected was gehlenite ($Ca_2Al_2SiO_7$). The anhydrite was detected until 1200 °C, which indicated that the reaction to form $Ca_4Al_6O_{12}SO_4$ was still not complete at these low temperatures. Merwinite $(Ca_3Mg(SiO_4)_2)$ was detected at temperatures between 1100 and 1150 °C, which is an unstable phase that reacted with alumina at higher temperatures to form gehlenite (Ca₂Al₂SiO₇), which has been reported in this kind of commercial cements in as much as 15% (40). The spinel phase was present in the samples treated at all the temperatures, indicating its stability when aluminum dross is as a raw material. Above 1250 °C the peaks corresponding to calcium aluminate (CaAl₂O₄), mayenite (Ca₁₂A₁₄O₃₃), belite (Ca_2SiO_4) and pleochroite $(Ca_{20}Al_{26}Mg_3Si_3O_{68})$ were also detected. Calcium sulphoaluminate, belite, mayenite and calcium aluminate are considered cementitious phases, the latter forms from the decomposition of $C_4A_3\overline{S}$ which it becomes unstable above 1350 °C. On the other hand, phases such as gehlenite, spinel and pleochroite have poor hydraulic properties, however they may act as a reinforcing phases.

In Table 2 the setting times for each cement are reported. The system A1 showed the longest setting times compared to systems A2 and A3. The initial and final setting times decreased as the synthesis temperature increased, this occurred because at higher temperatures the samples contained lower amounts of the main cementive phase, $Ca_4Al_6O_{12}SO_4$. At 1350 and 1400 °C the quantity of the main cementive phase decreased and when taking into account that the amount of hemihydrate and the w/c ratio were the same for all the systems used, there were more water and gypsum available to form ettringite and therefore the hydration reactions occurred at higher velocities.

Figure 2 shows the compressive strength for the systems A1, A2 and A3 after 1, 3, 7, 14 and 28 days of curing at 20 or 40 $^{\circ}$ C.

The system A1 cured at 20 °C showed a strength loss of 3 MPa at 14 days due to the delayed ettringite formation, that involves a volume change and some crack formation. This was corroborated by XRD analysis which showed the presence of C_4A_3 after 1 day and its absence from 7 days onwards, together with more intense peaks of Ettringite. The strength of A1 increased to 41 MPa at 28 days since



FIGURE 1. XRD patterns of the heat treated mixture (1100 to 1400 °C).

Table 2.	Setting times	of the cements	obtained
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System	Synthesis temperature (°C)	Thermal treatment time (h)	Ratio w/c	Hemihydrate wt%	Initial setting time (min)	Final setting time (min)
A1	1250	4h	0.4	20	28	46
A2	1350	4h	0.4	20	23	37
A3	1400	4h	0.4	20	16	30

A1, A2, A3 have the same composition with 45.53 wt% of AD, 12.82 wt% of FY, 0.65 wt% of FA and 41 wt% of CaCO₃,

ettringite continued to grow in the cracks previously formed. The system A2 also showed a decrease in strength at 7 days caused by the delayed ettringite formation followed by an increase up to 43 MPa at 28 days. For the system A3, a continuos increase in strength from day 1 was observed, reaching 41 MPa at 28 days of curing, this indicates that the majority of the Ettringite formed during the first hours of setting. For the systems cured at 40 °C, sample A1 showed a decrease in strength of about 13 MPa at 7 days of curing, followed by an increase up to 43 MPa at 28 days, reaching 47 MPa. As the

curing temperature increased, a higher rate of ettringite growth was observed forming crystal of larger size, leading to the formation of cracks in the microstructure. The system A3 cured at 40 °C showed a slight strength loss of about 4 MPa at 14 days, then it reached 43 MPa at 28 days. The systems cured at 20 and 40 °C reached strengths above 40 MPa at 28 days of curing. These were lower than those of 59 MPa reported by Singh et al. (36) for a calcium sulphoaluminate cement obtained from waste materials and close to those reported by Xin et al. (41) of 47 MPa in pastes



FIGURE 2. Compressive strength of the systems A1 (1250 °C), A2 (1350 °C) and A3 (1400 °C) cured for 1, 3, 7, 14 and 28 days at 20 or 40 °C.

of calcium sulphoaluminate cement produced by using reagent grade chemicals.

Figure 3 shows the XRD patterns for the systems A1, A2 and A3 cured for 1, 7 and 28 days at 20 °C.

After 1 day, the main phase present in the system A1 was the calcium sulphoaluminate, which indicated that the reaction was not completed. The reflections corresponding to ettringite $(Ca_6Al_2(SO_4)_3(OH)_{12}26H_2O)$ indicated that it formed by a rapid dissolution of the calcium sulphoaluminate phase releasing Al³⁺, Ca²⁺ and SO₄²⁻ ions, which play an important role in the formation of the hydrate crystals. As the curing time increased the peaks corresponding to ettringite increased, the presence of gypsum at 7 days indicated that the reaction of ettringite formation was still not complete. Spinel was noted at all studied curing times since it is inert and do not form any hydrates. For the system A2



FIGURE 3. XRD patterns of the systems A1, A2 y A3 cured for 1, 7 y 28 days at 20 °C.

at 1 day of curing the main phase detected was $Ca_4Al_6O_{12}SO_4$ and, in minor amounts, $Ca_2Al_2SiO_7$, $Ca_{12}Al_{14}O_{33}$ and $Ca_6Al_2(SO_4)_3(OH)_{12}$ ·26H₂O. After 7 days the peaks corresponding to ettringite increased in intensity and no significant changes were evident after 28 days.

For system A3, the main phase detected from 1 day and at any other curing time was Ettringite, indicating its formation since the early stages. As discussed above, for A3 there were lower amounts of the main cementive phase, which means that more hemihydrate and water are available to form ettringite than in the case of the A1 and A2 systems. Under these conditions, sulphoaluminate reacts rapidly forming the hydrates. A fairly similar behavior was observed for the systems cured at 40 °C.

Figure 4 shows the microstructure images obtained by SEM for the systems A1, A2 and A3 cured for 1, 7 and 28 days at 20 °C. The systems A1 and A2 showed after 1 day of curing a compact morphology; as curing time advanced, the growing of ettringite needles and the formation of microcracks were observed. Since ettringite continued forming, the cracks were eventually filled by such phase and therefore the microstructure appeared compact after 28 days of curing, which was consistent with the increased compressive strength after 28 days. On the other hand, for sample A3 there were no evident microstructural changes during the studied times; the formation of ettringite since the early curing times resulted in a compact structure from as early as day 1.

Figure 5 shows the fracture SEM images corresponding to the A3 system cured for 1, 14 and 28 days at 20 or 40 °C. A strength loss was noted after 14 days of curing for 40 °C (A31440).) for this system. The ettringite crystals formed at 40°C were larger than those present after curing at 20 °C (A31420). The non-homogeneous growth of these crystals created voids and cracks leading to a decrease in strength.

Samples cured at 40 °C showed the formation of plackets leading to a less dense microstructure at 1 and 14 days in comparison with samples cured at 20 °C. In both samples cured at 20 and 40 °C ettringite continued growing filling the cracks previously formed, which in turn favored increased 28 days strengths.

4. CONCLUSIONS

- Environmentally friendly and high compressive strength calcium sulphoaluminate cements were developed (up to 47 MPa, similar to Portland cement).
- The formation of Ca₄Al₆O₁₂SO₄ was achieved at temperatures as low as 1100 °C. The amount of this phase increased at 1250 °C and then becomes unstable at temperatures above this temperature.
- Ettringite was the main hydration product. The systems synthesized at lower temperatures showed a decrease in strength at 7 days and/or 14 days of curing due to the delayed ettringite formation, which generates the formation of microcracks.



A1, A2, A3 have the same composition with 45.53 wt% of AD, 12.82 wt% of FY, 0.65 wt% of FA and 41.00 wt% of $CaCO_3$.

FIGURE 4. Fracture SEM images for samples A1, A2 and A3, cured for 1, 7 and 28 days at 20 °C. Identification example: A17 corresponds to the system A1 cured at 7 days.

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A3 has a composition de 45.53 wt% of AD, 12.82 wt% of FY, 0.65 wt% of FA and 41.00 wt% of CaCO₃,

Fracture SEM images of the system A3 cured for 1, 14 and 28 days at 20 or 40 °C. FIGURE 5. Identification example: A3120 corresponds to the system A3 cured for 1 day at 20 °C.

As the curing time was increased, ettringite filled the cracks showing a compact structure and increasing the compressive strength.

The system synthesized at high temperature and cured at 20 °C showed no decreasse in compressive strength at any curing time due to the early ettringite formation.

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