

Environmental Implications of The Manufacture of Calcium Sulfoaluminate-Based Cements

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ABSTRACT

Interesting environmentally friendly features are associated with the manufacturing process of calcium sulfoaluminate (CSA) cements. Compared to Portland cements, a lower limestone requirement and synthesis temperature as well as a larger clinker dilution and waste utilization can be achieved.

In this work a CSA clinker was successfully synthesized in a laboratory electric oven by burning for two hours at 1250°C a raw mix composed by 58.5% anodization mud (a waste generated by the manufacturing process of anodized aluminium), 27.2 % limestone and 14.3% natural gypsum. In comparison with a Portland clinker, the synthesized CSA clinker enables a 70% reduction of limestone/clinker mass ratio as well as 42% and 59% savings of specific fuel consumption and CO₂ emission, respectively. The hydration properties of the related CSA cement were similar to those shown by industrial CSA cements. The investigation was carried out by means of X-ray diffraction analysis, differential thermal-thermogravimetric analysis and scanning electron microscopy.

INTRODUCTION

The quality of the environment is influenced to a significant extent by cement manufacture. On the one hand, considerable amounts of natural resources are consumed and large quantities of pollutants are generated, including also carbon dioxide responsible for the greenhouse effect and originating from both fossil fuel combustion and limestone thermal decomposition; on the other hand, the cement industry traditionally plays a leading role in the utilization of wastes coming from other industrial activities, so giving an important contribution to the protection of the environment.

Depending on their composition, industrial wastes and by-products can be employed as alternative fuels or sources of raw materials. As far as the latter use is concerned, the waste utilization can be performed in two ways for the manufacture of Portland and blended cements: (i) as a component of the kiln feed (in replacement of natural raw materials) and (ii) as a constituent (filler or active addition) of the final product. The active additions are often mixed in considerable amounts with Portland clinker and are able to improve important technical properties, also allowing a reduction of clinker concentration in the cement and a related decrease of kiln thermal requirement and emissions [Sivasundaram & Malhotra 1992; Wolsiefer et al. 1995; Bijen, 1996; Taylor, 1997; Bilodeau & Malhotra 2000; McCarthy & Dhir 2005].

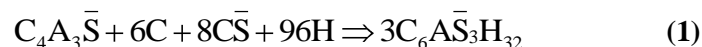
Special cements are obtained from non-Portland clinkers. In particular applications they behave better than Portland and blended cements but their peculiar composition can also be exploited to give a more pronounced environmentally friendly character to their manufacturing cycle [Kurdowski et al. 1986; Beretka et al. 1992; Chatterjee, 1992; Muzhen et al., 1992; Scrivener, 2003]. Compared to other hydraulic binders, special cements can utilize in their production processes a wider range of wastes and by-products generally difficult to reuse. Moreover, the related clinkers can require lower synthesis temperatures and reduced limestone concentrations in the raw mixes; hence, a decrease of both kiln thermal input (dependent to a considerable extent on limestone calcination) and CO₂ emission can be achieved.

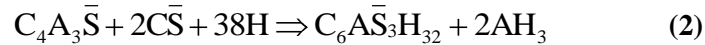
All the above-mentioned features are shown by calcium sulfoaluminate (CSA) cements derived from the addition of gypsum to CSA clinkers containing calcium sulfoaluminate ($C_4A_3\bar{S}$), dicalcium silicate (α - and/or β - C_2S) and anhydrite ($C\bar{S}$) as well as a variety of calcium silicates and aluminates, as minor constituents. Compared to Portland cements which contain only 3-5% of added gypsum, CSA cements enable higher reductions in clinker concentration and, correspondingly, greater environmental benefits.

The temperatures needed to obtain CSA clinkers (1200°-1300°C) are about 200°C lower than those necessary for the manufacture of Portland cement clinkers which require, furthermore, greater grinding energy being less porous due to the considerable amount of liquid phase formed at higher synthesis temperatures [Taylor, 1997].

The limestone amount necessary for the production of CSA cements is considerably lower than that required by Portland cement: the specific CaO requirement (referred to unit mass of compound) for $C_4A_3\bar{S}$ synthesis is 0.368, *i.e.* 50%, 56%, 59% and 80% of that necessary for the formation, respectively, of C_3S , C_2S , C_3A and C_4AF [Gartner, 2004].

The most important properties of CSA cements are related to their ability of generating ettringite ($C_6A\bar{S}_3H_{32}$) upon hydration of calcium sulfoaluminate ($C_4A_3\bar{S}$). $C_4A_3\bar{S}$ can react with water in two ways: *i*) together with lime and calcium sulfate to give only ettringite (reaction 1); *ii*) combined with calcium sulfate alone to give ettringite and aluminium hydroxide (reaction 2):





Ettringite produced in the reaction 1) shows an expansive behaviour which can be exploited by special binders like shrinkage-resistant and self-stressing cements [Mehta, 1973; Kurdowski et al. 1986; Muzhen et al. 1992]. Ettringite generated in the absence of lime (reaction 2) is not expansive and has the important property of giving high mechanical strength at early ages [Mehta, 1980; Mudbhatkal et al. 1986]. Other interesting features concerning these rapid-hardening CSA cements are high impermeability and chemical resistance as well as low dry-shrinkage and solution alkalinity [Wang Lan & Glasser 1996; Muzhen et al. 1997; Zhang & Glasser 1999; Glasser & Zhang 1999; Glasser, 2002, Bernardo et al. 2006; Bernardo et al. 2007; Marroccoli et al. 2007a].

Limestone, bauxite and gypsum are the main natural materials involved in the manufacture of CSA cements and can be usefully replaced by industrial wastes and by-products such as blast-furnace slag, coal combustion ash from both traditional combustors and fluidized bed reactors, waterworks slime, red mud, phosphogypsum and flue gas desulfurization gypsum [Belz et al. 1995; Arjunan et al. 1999; Beretka et al. 1996; Ikeda et al. 1997; Bernardo et al. 2003; Marroccoli et al. 2007b; Marroccoli et al. 2008; Marroccoli et al. 2009].

The substitution of an expensive natural resource like bauxite with Al_2O_3 rich by-products is particularly worthy of consideration. This paper is devoted to: a) investigate the synthesis and hydration properties of a CSA cement made from a clinker obtained by burning in a laboratory electric oven a raw mix composed by anodization mud (as main alumina source), limestone and natural gypsum; b) emphasize the role played by the CSA cement composition in reducing both kiln thermal requirement and CO_2 emission.

SYNTHESIS AND HYDRATION PROPERTIES OF A LABORATORY-MADE CSA CEMENT

Materials

The chemical composition of the raw materials used for the CSA clinker synthesis is indicated in Table 1.

Table 1. Chemical composition of anodization mud, limestone and gypsum, mass %

	anodization mud	limestone	Gypsum
CaO	6.54	53.16	8.69
CaSO ₄	21.61	0.14	62.27
Al ₂ O ₃	41.35	0.54	1.72
SiO ₂	2.57	2.16	1.74
MgO	1.20	1.16	1.64
SrO	-	-	-
P ₂ O ₅	0.14	-	-

TiO ₂	-	-	-
Fe ₂ O ₃	0.74	0.21	0.73
Mn ₃ O ₄	-	-	-
l.o.i. ^a	25.66	42.40	22.20
Total	99.81	99.77	98.99

^aloss on ignition at 950 °C

It can be noted that anodization mud is composed by significant amounts of Al₂O₃ and CaSO₄ required by the formation of a CSA clinker containing $C_4A_3\bar{S}$ and C_2S . In order to maximize the concentrations of $C_4A_3\bar{S}$ and C_2S in the burning product, limestone and gypsum are necessary.

The raw mix composition (Table 2) used for the CSA clinker synthesis was calculated assuming that Al₂O₃, on the one hand, and SiO₂, on the other, reacted to give only $C_4A_3\bar{S}$ and C_2S , respectively; furthermore, solid solution effects were neglected. The SO₃ content was twice the stoichiometric amount required by the formation of $C_4A_3\bar{S}$, in order to avoid considerable decreases of $C_4A_3\bar{S}$ concentration associated with SO₂ losses occurring at high burning temperatures. Table 2 also shows also the potential concentration values of $C_4A_3\bar{S}$, C_2S and $C\bar{S}$ in CSA clinker.

Table 2. Raw mix composition and potential concentration of $C_4A_3\bar{S}$, C_2S and $C\bar{S}$ in its burning product, mass %

Raw mix		CSA clinker	
anodization mud	58.50	$C_4A_3\bar{S}$	68.66
limestone	27.20	C_2S	10.92
gypsum	14.30	$C\bar{S}$	15.31

Testing procedures and investigation techniques

The raw mix was heated in a laboratory electric oven for 2 hours at 1250°C and then submitted to X-ray diffraction analysis (XRD) performed by a PHILIPS PW1710 apparatus operating between 5° and 60° 2θ (Cu Kα) in order to evaluate both conversion and selectivity of the reacting system. For the hydration tests, a CSA cement was prepared by grinding the clinker with 15% gypsum. The gypsum content was the stoichiometric amount required by the reaction (2).

Cement samples were paste hydrated (water/cement mass ratio equal to 0.50) and investigated by differential thermal-thermogravimetric analysis (DTA-TGA) and scanning electron microscopy (SEM). The pastes, shaped as cylindrical discs (15 mm high, 30 mm in diameter), were cured in a FALC WBMD24 thermostatic bath at 20 °C for times ranging from 3 h to 28 d. At the end of each aging period, the discs were broken for SEM observations or pulverized for DTA-TGA characterization after grinding under acetone (to stop hydration), followed by drying with diethyl ether and storing in a desiccator over silica gel-soda lime (to ensure protection against H₂O and CO₂).

DTA-TGA was carried out through a NETZSCH TASC 414/3 apparatus, operating between 20° and 1000 °C with a heating rate of 10 °C/min. For SEM observations a PHILIPS XL-30 ESEM instrument was used. Specimens were metallized with gold by means of an EMITECH K 950 apparatus.

RESULTS AND DISCUSSION

The XRD pattern of the CSA clinker synthesis is shown in Figure 1. No signals of reactants were found and the main peaks of $C_4A_3\bar{S}$, C_2S and $C\bar{S}$ together with weak peaks of C_3A , C_4AF and $C_5S_2\bar{S}$ (calcium sulfo-silicate) were detected.

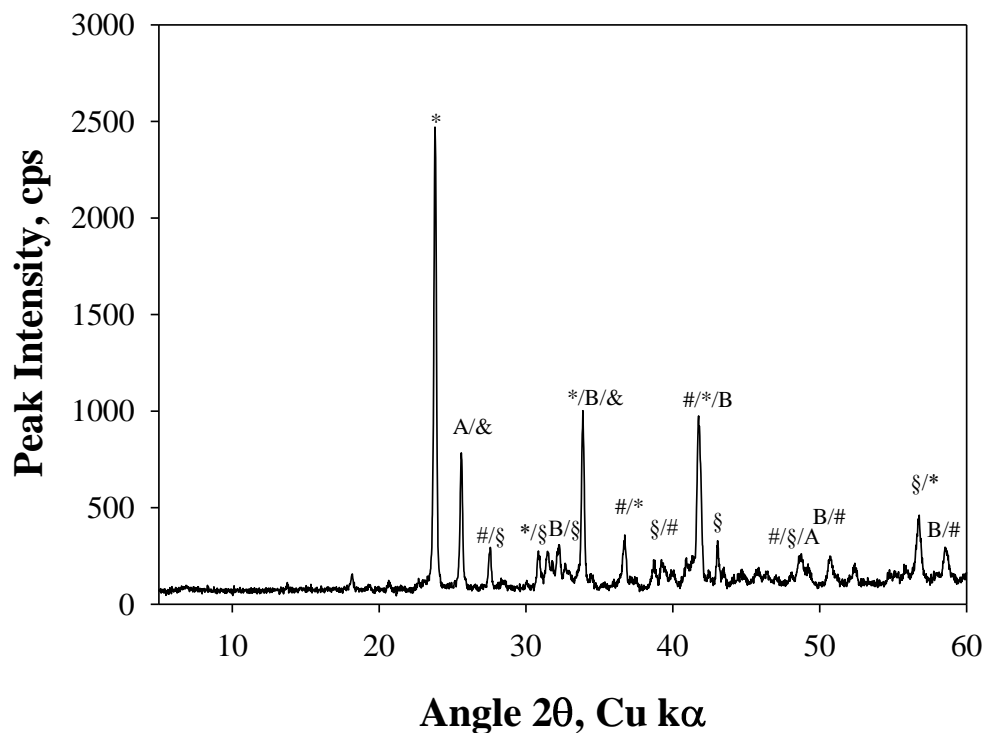


Fig. 1. XRD pattern of the mix raw burnt at 1250°C: * = $C_4A_3\bar{S}$, A = $C\bar{S}$, # = $C_5S_2\bar{S}$, § = C_2S , & = C_3A , B = C_4AF

The hydration behaviour is illustrated in Figures 2 and 3. Figure 2 shows the DTA-TGA thermograms for CSA cement pastes cured at 3 h, 8 h, 24 h, 7 d and 28 d. The products of the reaction (2), ettringite and aluminium hydroxide, were detected through their peculiar effects at about 200° and 300°C, respectively. It can be noted that the hydration is very rapid, particularly within the first 24 h.

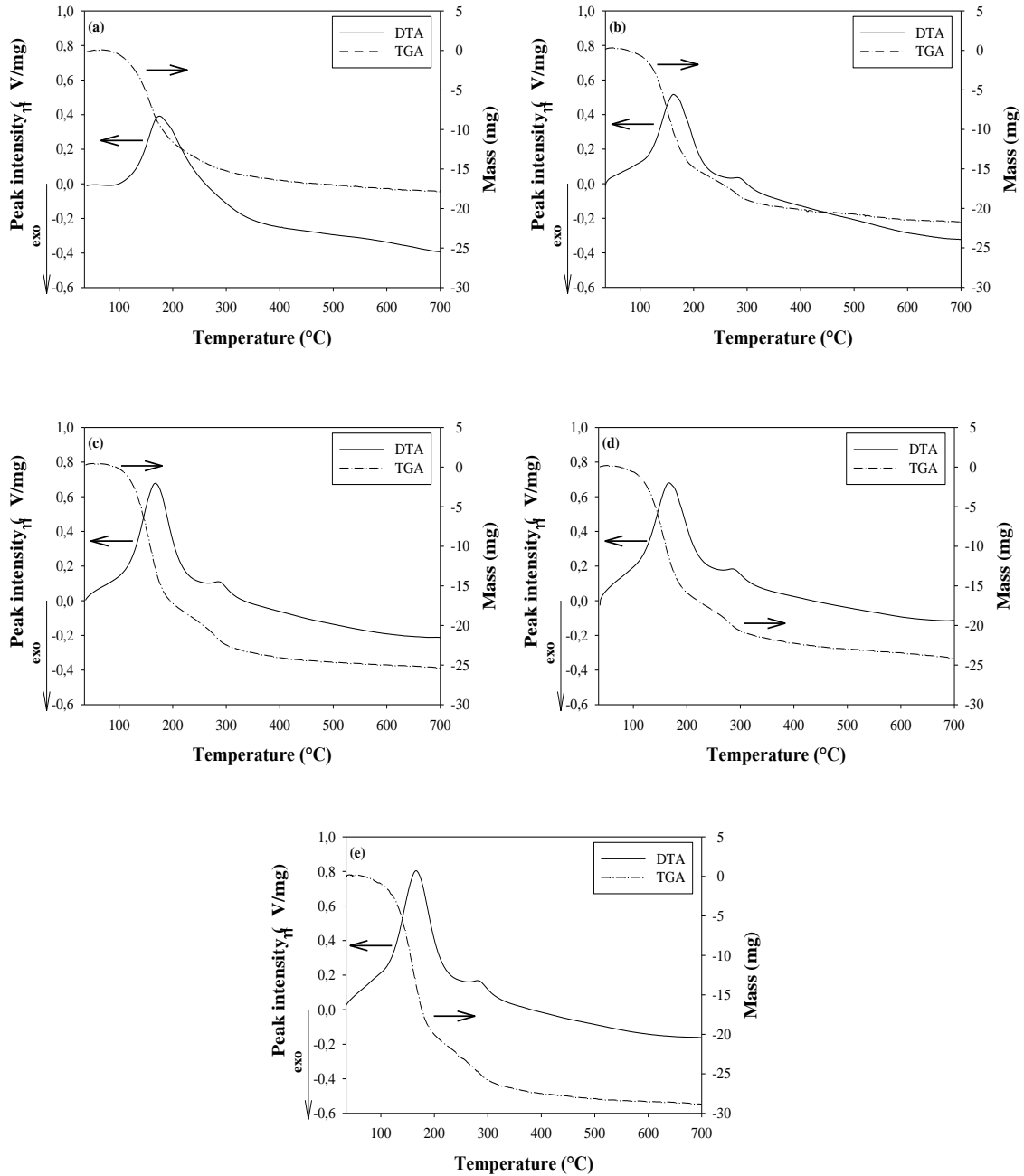
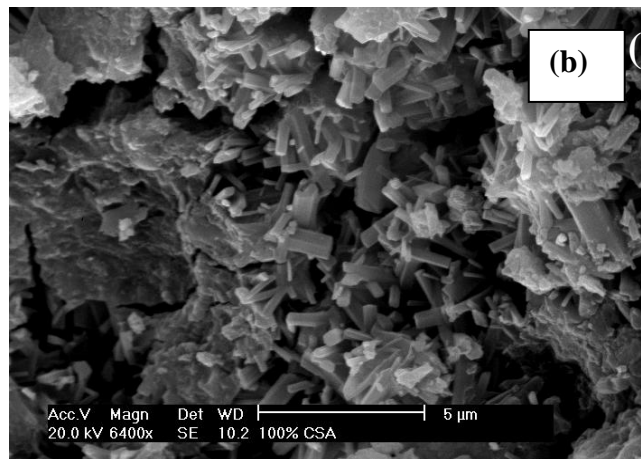
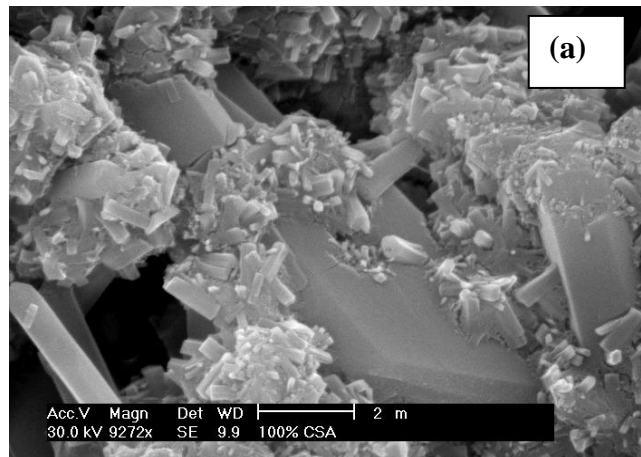


Fig. 2. DTA-TGA thermograms for CSA cement pastes cured at: (a) 3 h; (b) 8 h; (c) 24 h; (d) 7 d; (e) 28 d

Figure 3 shows micrographs of CSA cement pastes cured at 3 h, 24 h and 28 d. The fast rate of ettringite formation is confirmed. Its particles, easily recognizable as prismatic crystals with hexagonal cross section, already develop at 3 h and assemble at later ages in the form of large and close-packed clusters.

The hydration properties exhibited by the cement under investigation were similar to those shown by industrial CSA cements [Marroccoli et al. 2007a; Bernardo et al. 2007; Marroccoli et al. 2008].



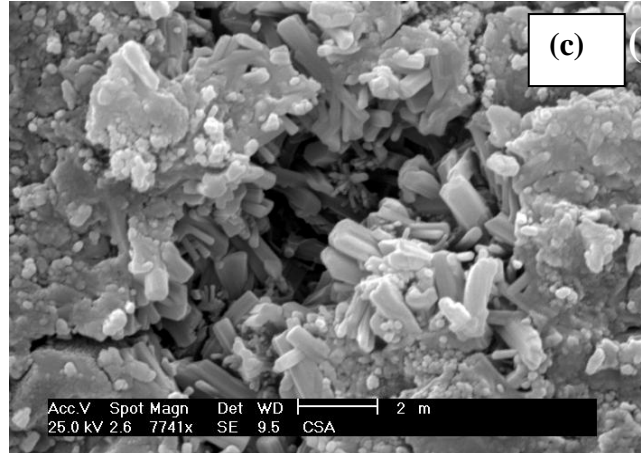


Fig. 3. SEM micrographs of CSA cement pastes cured at: (a) 3 h; (b) 24 h; (c) 28 d

KILN THERMAL REQUIREMENT AND CO₂ EMISSION IN THE MANUFACTURE OF PORTLAND AND CSA CEMENTS

A limestone/clinker mass ratio of 1.2-1.3 is typically encountered in the Portland cement manufacture. The limestone/clinker mass ratio for the CSA cement under investigation, calculated on the basis of the proportioning and the loss on ignition of the three components of its generating raw mix, is equal to 0.39. About 70% limestone saving can be therefore achieved.

The theoretical kiln thermal requirement for clinker manufacture is based on the assumption that the heat recoverable from cooling of both kiln gases and clinker is equal to that absorbed by heating raw mix to the clinkering temperature. It can be in practice ascribed to limestone calcination (Mehta, 1978), inasmuch as the heat absorbed during the burning of raw mix components different from limestone is offset by that generated during the synthesis of clinker compounds: if the thermal requirement for Portland clinker is 475 kcal per kg, that for CSA clinker is 30% of such value, namely 142 kcal per kg.

The global heat consumption is the sum of the theoretical heat requirement and the total heat losses. For a Portland clinker manufactured at 1400 °C it amounts to 800 kcal per kg (Mehta, 1978). For the CSA clinker it is 467 kcal per kg, assuming that the total heat losses are the same in both cases, namely 325 kcal per kg. These losses are overestimated for CSA clinker (made at a lower synthesis temperature) and therefore the related global heat consumption should actually be lower than 467 kcal per kg.

If a petroleum coke with a lower heating value of 8400 kcal/kg is used as kiln energy source, global heat consumptions of 800 and 467 kcal per kg imply specific fuel consumptions of 0.095 and 0.055 kg per kg of Portland and CSA clinker, respectively, with a 42% fuel saving for this latter.

The specific amounts of CO₂ generated by both limestone calcination and fuel combustion for the manufacture of Portland and CSA (clinkers and cements) are reported in Table 3.

Table 3. Calculated data for CO₂ emission in the Portland and CSA (clinkers and cements) manufacture

	CO ₂ from limestone ^a calcinations	CO ₂ from fuel ^b combustion	Total CO ₂ generated
Portland clinker [kg/(kg clinker)]	0.53	0.31	0.84
CSA clinker [kg/(kg clinker)]	0.16	0.18	0.34
Portland cement ^c [kg/(kg cement)]	0.50	0.29	0.79
CSA cement ^d [kg/(kg cement)]	0.14	0.15	0.29

^aWith a CaCO₃ concentration equal to 93% by mass

^bWith a carbon content oxidable to CO₂ equal to 88% by mass

^cComposed by 95% clinker + 5% gypsum

^dComposed by 85% clinker + 15% gypsum

For both CSA clinker and cement the same total reduced emission (0.50 kg/kg) is obtained, with CO₂ savings, compared to Portland clinker and cement, equal to 59% and 63%, respectively.

CONCLUSIONS

Calcium sulfoaluminate (CSA) cements are very interesting hydraulic binders which can be used in a variety of applications, due to the characteristics of ettringite, their main hydration product. The peculiar composition of CSA cements can also be exploited to give to their manufacturing cycle a reduced environmental impact if compared with that of traditional hydraulic binders. As a matter of fact, CSA cements contain larger amounts of additions and can utilize a wider range of wastes and by-products. Moreover, compared to Portland clinkers, CSA clinkers require lower synthesis temperatures and reduced limestone concentrations in the raw mixes; hence, a decrease of both kiln thermal input and CO₂ emission can be achieved.

It has been found that a laboratory-made CSA cement, based on a clinker obtained by burning a raw mix composed by anodization mud, limestone and natural gypsum, show hydration properties comparable with those of industrial CSA cements. The CSA clinker can be manufactured with considerable savings of specific fuel consumption and CO₂ emission.

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