

Synthesis of Calcium Sulfoaluminate Cements From Al₂O₃-Rich By-products from Aluminium Manufacture

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ABSTRACT

The relatively low environmental impact associated with the manufacturing process of calcium sulfoaluminate (CSA) cements can be further reduced through the utilization of industrial wastes as components of the clinker generating raw mix. The use of Al₂O₃ rich by-products like alumina powders, coming from the secondary aluminium manufacture, as partial or total substitutes for an expensive natural material like bauxite, is particularly worthy of consideration. Various raw mixtures containing 32-35% limestone, 27-34% natural gypsum, 0-38% bauxite and 0-34% alumina powders were heated in a laboratory electric oven for 2 hours in the temperature range 1200°-1350°C. The resulting CSA clinkers were submitted to X-ray diffraction analysis in order to assess the reactants conversion and selectivity towards the desired products. It has been found that, compared to bauxite, alumina powders enhance the formation rate of C₄A₃S̄, the main component of CSA cements, and shift the optimum temperature for its synthesis from 1350° to about 1250°C.

INTRODUCTION

Calcium sulfoaluminate (CSA) cements are interesting hydraulic binders from both technical and environmental point of view. They contain C₄A₃S̄ as main component together with calcium sulfates, dicalcium silicate (C₂S), tetracalcium iron aluminate (C₄AF), calcium sulfosilicate (C₅S₂S̄), calcium - aluminates (C₃A, CA, C₁₂A₇) and – silicoaluminates (C₂AS, CAS₂). Upon hydration, calcium sulfates, belonging or added to CSA clinker (under anhydrous and hydrated form, respectively), react with C₄A₃S̄ and generate ettringite (C₆A₃H₃₂) which, depending on the conditions of its formation [Mehta 1973; Mehta 1980; Kurdowski et al. 1986; Mudbhatkal et al. 1986; Muzhen et al. 1992; Wang Lan & Glasser 1996; Muzhen et al. 1997; Zhang & Glasser 1999; Glasser & Zhang 1999; Glasser 2000; Bernardo et al. 2006; Bernardo et al. 2007; Marroccoli et al. 2007a], regulates the technical properties of CSA cements (shrinkage compensation or self stressing behaviour or rapid-hardening associated with dimensional stability). C₂S can add strength and durability at medium and long ages, while C₄AF and calcium aluminates contribute to ettringite formation; on the other hand, C₅S₂S̄ and calcium-

silicoaluminates display a poor hydraulic activity. The distribution of the secondary components is mainly influenced by the synthesis temperature as well as the nature and proportioning of raw materials.

Compared to Portland cement production, the manufacturing process of CSA cements has a pronounced environmentally friendly character [Mehta 1980; Mudbhatkal et al. 1986; Beretka et al. 1992; Beretka et al. 1993; Majling et al. 1993; Belz et al. 1995; Beretka et al. 1996; Ikeda et al. 1997; Arjunan et al. 1999; Bernardo et al. 2003; Gartner 2004; Marroccoli et al. 2007b; Marroccoli et al. 2008; Marroccoli et al. 2009]. In this regard important features are: 1) synthesis temperatures 200°-300°C lower than those required by ordinary Portland cement clinkers; 2) clinkers easier to grind; 3) reduced amount of limestone in the kiln raw mix and, consequently, reduced thermal input and CO₂ generation; 4) greater usability of industrial wastes and by-products.

Several residues have been successfully experienced as substitutes for limestone, bauxite and gypsum, the main natural materials involved in the manufacture of CSA cements. Reactive silica and alumina can be given by pulverized coal fly ash and red mud [Marroccoli et al. 2007b] as well as blast-furnace slag [Belz et al. 1995] which is furthermore an important source of non-carbonated lime. Phosphogypsum [Beretka et al. 1996] and flue gas desulfurization gypsum [Marroccoli et al. 2008] can entirely replace natural gypsum. Fluidized bed combustion waste [Arjunan et al. 1999; Bernardo et al. 2003; Marroccoli et al. 2009], a mixture of coal ash and spent limestone sorbent generated during the combined process of coal combustion and “in situ” gas desulfurization within a fluidized bed reactor, is able to give the main oxides required by CSA cement manufacture (CaO, SO₃, SiO₂, Al₂O₃).

The replacement of an expensive natural resource like bauxite is of critical importance. The utilization of the so-called “alumina powders”, Al₂O₃ rich by-products of the secondary aluminium manufacture, as partial or total substitutes for bauxite in CSA clinker generating raw mixes, is explored in this paper. Mixtures containing limestone, natural gypsum, bauxite and/or alumina powders were heated in a laboratory electric oven at various temperatures. A mixture consisting only of natural raw materials was used as a reference term. All the burnt products were submitted to X-ray diffraction analysis in order to assess the reactants conversion and selectivity towards the desired hydraulic phases.

EXPERIMENTAL

Materials

The natural materials (limestone, bauxite, gypsum) and industrial by-products (alumina powders) used in this investigation came, respectively, from a cement factory and a secondary aluminium manufacturing plant, both operating in the Northern Italy. Their chemical composition is indicated in Table 1.

Table 1. Chemical composition of limestone, gypsum, bauxite and alumina powders, mass %

	limestone	gypsum	bauxite	alumina powders
CaO	53.16	8.69	2.73	1.33
CaSO ₄	0.14	62.27	-	0.40
Al ₂ O ₃	0.54	1.72	49.95	69.27
SiO ₂	2.16	1.74	12.14	5.86
MgO	1.16	1.64	0.30	7.50
SrO	-	-	-	0.06
P ₂ O ₅	-	-	-	0.05
TiO ₂	-	-	-	0.65
Fe ₂ O ₃	0.21	0.73	3.71	1.85
Mn ₃ O ₄	-	-	-	-
l.o.i. ^a	42.40	22.20	27.33	8.17
Total	99.77	98.99	96.16	95.14

^aloss on ignition at 950 °C

Testing procedures and investigation techniques

Four mixtures (M-0, M-1, M-2, M-3), having the composition shown in Table 2, were prepared.

Table 2. Composition of raw mixtures, mass %

	limestone	gypsum	bauxite	alumina powders
M-0	35.11	27.01	37.87	-
M-1	33.98	29.44	24.14	12.44
M-2	32.98	31.58	12.05	23.39
M-3	31.99	33.71	-	34.30

M-0 was the reference term consisting of only natural materials. M-1, M-2 and M-3 contained increasing amounts of alumina powders as substitutes for bauxite, with percentages of replacement equal to 32%, 65% and 100%, respectively. All the mixtures were heated in a laboratory electric oven for 2 hours at the temperatures of 1200°, 1250°, 1300° and 1350°C, then submitted to X-ray diffraction (XRD) analysis performed by a PHILIPS PW1710 apparatus operating between 5° and 60° 2θ, Cu Kα radiation.

The proportioning of all the raw mixtures was made by assuming that Al₂O₃ on the one hand, and SiO₂, on the other, reacted to give only C₄A₃S̄ and C₂S, respectively, and supposing also that solid solution effects were absent. 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 SO_2 losses occurring at high burning temperatures.

Table 3 shows the potential concentration values of $C_4A_3\bar{S}$, C_2S and $C\bar{S}$ in the burning products of the four mixtures.

Table 3. Potential concentration of $C_4A_3\bar{S}$, C_2S and $C\bar{S}$ in the burning products of mixtures M-0, M-1, M-2 and M-3, mass %

	$C_4A_3\bar{S}$	C_2S	$C\bar{S}$
M-0	54.86	20.76	12.23
M-1	57.71	16.16	12.87
M-2	60.04	12.39	13.39
M-3	62.23	8.86	13.87

RESULTS AND DISCUSSION

Figures 1-4 show the XRD patterns for M-0, M-1, M-2 and M-3 heated at 1250°C.

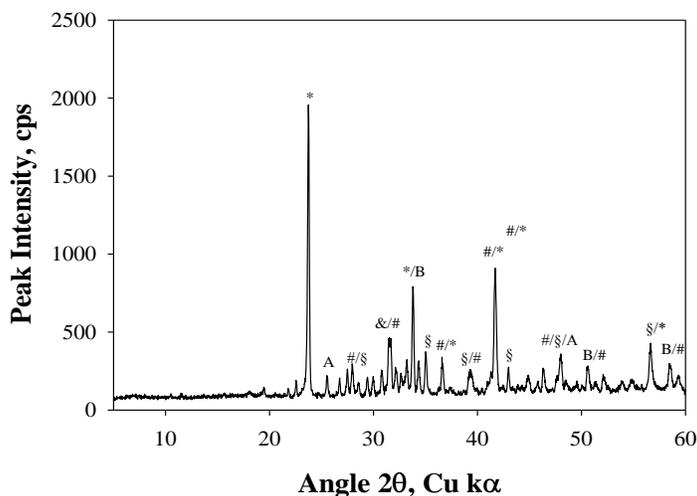


Fig. 1. XRD pattern of mixture M-0 burnt at 1250°C: *= $C_4A_3\bar{S}$, A= $C\bar{S}$, #= $C_5S_2\bar{S}$, §= C_2S , &= C_3A , B= C_4AF

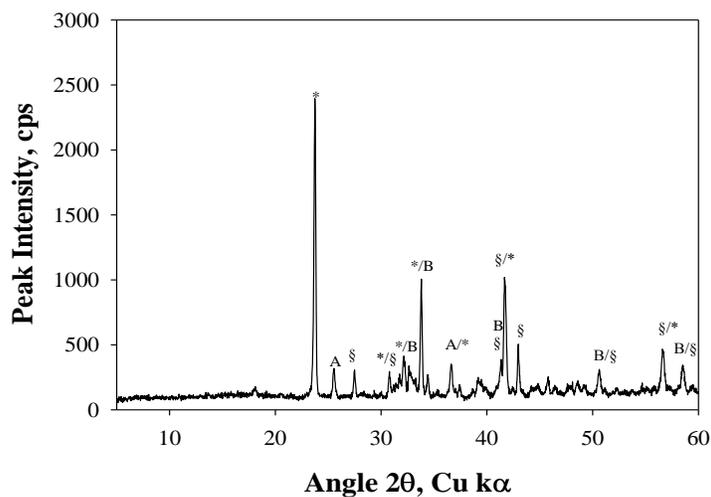


Fig. 2. XRD pattern of mixture M-1 burnt at 1250°C: $*=C_4A_3\bar{S}$, $A=C\bar{S}$, $\S=C_2S$, $B=C_4AF$

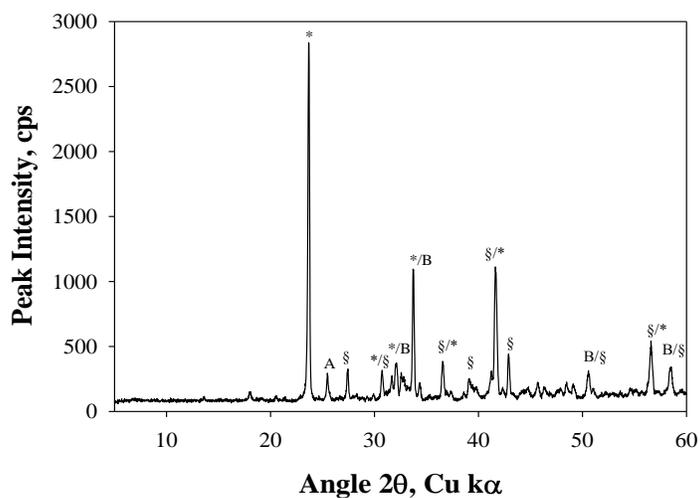


Fig. 3. XRD pattern of mixture M-2 burnt at 1250°C: $*=C_4A_3\bar{S}$, $A=C\bar{S}$, $\S=C_2S$, $B=C_4AF$

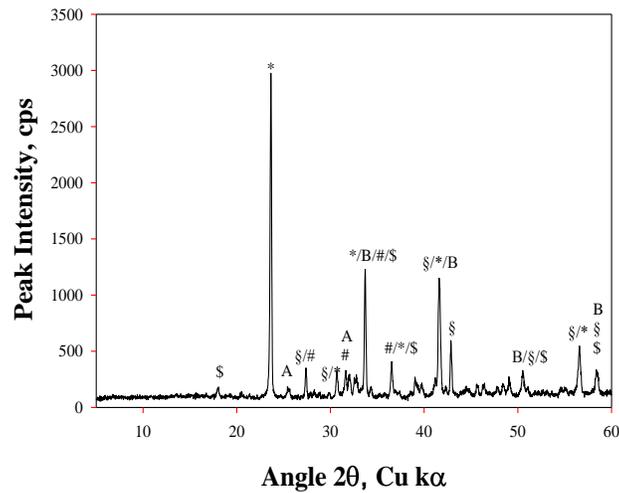


Fig. 4. XRD pattern of mixture M-3 burnt at 1250°C: $*$ = $C_4A_3\bar{S}$, $A=C\bar{S}$, $\# = C_5S_2\bar{S}$, $\$ = C_{12}A_7$, $\S = C_2S$, $B=C_4AF$

It can be noted the absence of reactants and the presence of $C_4A_3\bar{S}$, C_2S and $C\bar{S}$ as main constituents. Similar results were obtained at the other burning temperatures. As far as minor components are concerned, it has been observed the presence of: a) C_4AF in all the investigated mixtures; b) $C_5S_2\bar{S}$ in both mixtures M-0 and M-3; c) C_3A and $C_{12}A_7$ in the mixtures M-0 and M-3 respectively.

Figures 5 and 6 report the XRD intensity of the main peak of $C_4A_3\bar{S}$ and C_2S , respectively, as a function of the burning temperature.

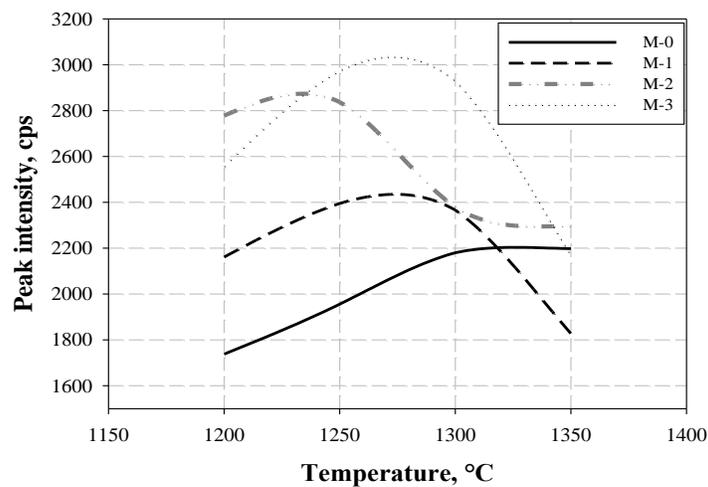


Fig. 5. XRD intensity of the $C_4A_3\bar{S}$ main peak for the burning products of mixtures M-0, M-1, M-2 and M-3

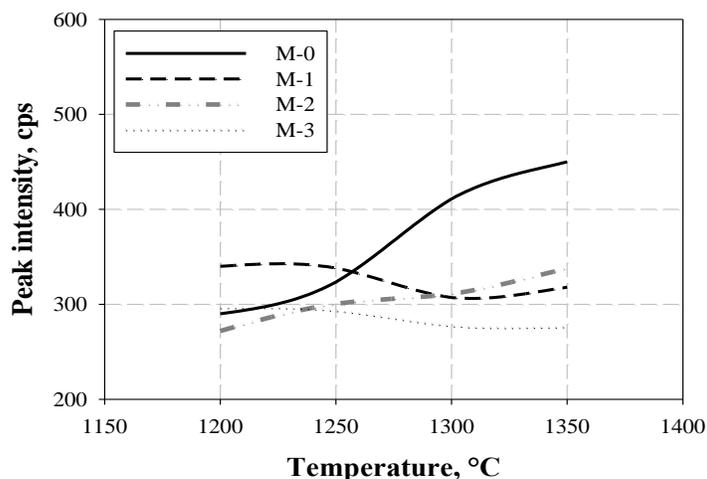


Fig. 6. XRD intensity of the C_2S main peak for the burning products of mixtures M-0, M-1, M-2 and M-3

As far as mixture M-0 is concerned, the burning temperature favourably influences the formation rate of C_2S and, to a lesser degree, $C_4A_3\bar{S}$. Regarding the waste-based mixtures, 1250°C was nearly the best temperature for $C_4A_3\bar{S}$ synthesis, whereas the C_2S formation rate was almost constant within the investigated temperature range. It can be also observed that an increase of the alumina powders concentration favour the $C_4A_3\bar{S}$ synthesis.

CONCLUSIONS

Compared to Portland cement production, the manufacturing process of calcium sulfoaluminate (CSA) cements shows several environmentally friendly features, among which the possibility of using various industrial wastes and by-products as sources of raw materials. Blast-furnace slag, coal combustion ash from both traditional combustors and fluidized bed reactors, waterworks slime, red mud and different chemical gypsums were successfully experienced in the past.

In this paper the utilization of alumina powders, the Al_2O_3 rich by-products of the secondary aluminium manufacture, in partial or total replacement of an expensive natural resource like bauxite, was investigated. Several CSA clinkers, obtained by heating in a laboratory electric oven, at temperatures ranging from 1200° to 1350°C, mixtures containing limestone, natural gypsum, bauxite and/or alumina powders were submitted to X-ray diffraction analysis.

In comparison with bauxite, alumina powders were able to increase the formation rate of $C_4A_3\bar{S}$, the key-component of CSA cements, and to reduce the best temperature for its synthesis to about 1250°C. The selectivity degree of the waste-based mixtures towards C_2S , the other main hydraulic phase, was almost constant within the investigated temperature range and lower than

that shown by the mixture without waste (at 1300° and 1350°C). In all the synthesized CSA clinkers reactants were absent. Furthermore, together with anhydrite, a few secondary products were detected such as C_4AF and $C_5S_2\bar{S}$, C_3A or $C_{12}A_7$.

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