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Synthesis, characterization and properties of calcium ferroaluminate belite cements produced with electric arc furnace steel slag as raw material

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ABSTRACT

This study investigated the use of 10 (M1), 17 (M2) and 27 wt.% (M3) electric arc furnace steel slag (EAFS) as a raw material in the production of calcium ferroaluminate belite cement clinker, after firing at 1320 °C. The thermal behavior of the raw meals was studied by TG/DSC and XRD whereas for the analysis of the clinkers, XRD/QXRD, SEM/EDS and EPMA were employed. The resulting clinker was co-grinded with 5 and 20 wt.% Flue Gas Desulfurization (FGD) gypsum and the properties were determined by a series of tests in accordance to EN standards. The evolution of hydration was investigated by SEM and the development of compressive strength. The results revealed that the formed phases in the clinkers were C_2S, C_4AF and $C_4A_3\hat{S}$. The main hydration products were ettringite, AFm and hydrogarnet. The leached Cr^{VI} was below 1 ppm in M3. Compressive strength in cements with 5 wt.% FGD gypsum was (in MPa): 18.3 for M1, 14.3 for M2 and 7.8 for M3 at 28 days, whereas for 20 wt.% FGD gypsum, the values were almost doubled.
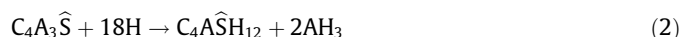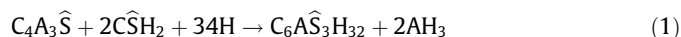
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1. Introduction

The transition towards resource efficient, low-carbon, closed-loop economies is an urgent necessity as our planet faces unprecedented environmental challenges. In the EU, in particular, the prospect of insufficient and often critical raw materials (metals and minerals) will hamper future economic development and actions are taken to prevent this [1]. With regard to industrial residues, the challenge lies in the development of integrated zero-waste flow sheets, which recover both (critical) metals and incorporate the various residues into building materials or other applications.

Worldwide more than 40% of steel production takes place in electric arc furnace (EAF) [2] and is associated with the generation of 20 Mt electric arc furnace steel slag (EAFS). In Europe, 37% of steel slags were used in cement production and 18.8% for road construction in 2010 [3]. In Greece, cement and steel production is about 6 Mt/y and 3.5 Mt/y respectively while EAFS production is 0.3–0.4 Mt/y; less than 1% is used in cement production and about 55% is used as coarse aggregates for road construction [4]. In general, the heavy metal content in slags (particularly V and Cr) is an issue of concern: Cr^{VI} content, for instance, is limited to 2 ppm in the final product according to the EU Directive 2003 [5].
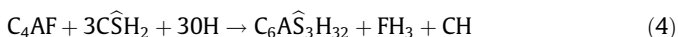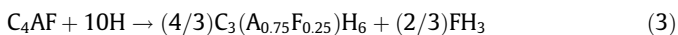
The past 30 years have seen the emergence of a number of alternative "greener" types of cement. However, in contrast to Portland cement, these new varieties have limited application in mainstream construction. Calcium ferroaluminate (CFAB), or sulfoaluminate belite cements (CSAB) are called "The Third Cement Series" [6,7] and find limited use in China. Ferroaluminate cements contain mainly C_4AF, C_2S, $C_4A_3\hat{S}$, and $C\hat{S}$. As a result, they are able to accommodate high quantities of iron and sulfur, being interground with 16–25 wt.% gypsum [8]. Compared to Ordinary Portland Cement (OPC) which has C_3S as its main compound, these cements require lower clinkering temperatures. Moreover, their clinkers are more friable due to their high porosity resulting also in energy reduction during grinding.

The hydration rate of $C_4A_3\hat{S}$ (Eq. (1)) is very fast, leading to the formation of trisulfoaluminate hydrate ($C_6A\hat{S}_3H_{32}$, AFt) [9]. In the absence of adequate gypsum, $C_4A_3\hat{S}$ reacts only with water (Eq. (2)) and forms monosulfoaluminate hydrate ($C_4A\hat{S}H_{12}$, AFm) [10]. In both cases crystalline $Al(OH)_3$ is also formed.

$$C_4A_3\hat{S} + 2C\hat{S}H_2 + 34H \rightarrow C_6A\hat{S}_3H_{32} + 2AH_3 \tag{1}$$

$$C_4A_3\hat{S} + 18H \rightarrow C_4A\hat{S}H_{12} + 2AH_3 \tag{2}$$

The ferrite phase, with a lack of anhydrite in the mixture, hydrates (Eq. (3)) to form hydrogarnet ($C_3(A_{0.75}F_{0.25})H_6$), whereas if sufficient gypsum is available, ettringite ($C_6A\hat{S}_3H_{32}$) and AFm are formed (Eqs. 4 and 5) [11].

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$$C_4AF + 10H \rightarrow (4/3)C_3(A_{0.75}F_{0.25})H_6 + (2/3)FH_3 \tag{3}$$

$$C_4AF + 3C\hat{S}H_2 + 30H \rightarrow C_6A\hat{S}_3H_{32} + FH_3 + CH \tag{4}$$

$$C_4AF + C\hat{S}H_2 + (n+2)H \rightarrow C_4A\hat{S}H_n + FH_3 + CH \tag{5}$$

During the hydration of the ferrite phase, the formation of other calcium aluminate phases is also possible, however these are metastable and the formation of hydrogarnet is favored [12]. Due to their low pH, low porosity and the ability of ettringite and AFm phases to bind heavy metals, CSAB–CFAB cements are of interest in hazardous waste encapsulation fields [13–15]. It has been suggested that hydrogarnet can host high quantities of Cr^{VI} [16]. Still, concerns do exist as well: the main hydrating phase, ettringite, is said to be prone to carbonation [17], thus posing a durability question, and they are sometimes expansive.

Recent studies conducted by various researchers show well developed results concerning the incorporation of different wastes as raw materials in CFAB–CSAB cement production. Wu et al. [18] have studied the use of municipal solid waste incineration (MSWI) fly ash in CSAB cements up to 30 wt.% and obtained a cement with high early compressive strength but lower strength gain in later ages. The results also showed that expansive properties are strongly dependent on gypsum content and that all the elements investigated for leaching in the hydrated paste are either well bounded in the clinker minerals or immobilized in the hydration products. Berger et al. [19] studied the potential of CSAB cements with 0 and 20 wt.% gypsum addition for $ZnCl_2$ stabilization/solidification. The use of 20 wt.% gypsum was beneficial in different ways, including improved compressive strength results. Arjunan et al. [20] have successfully prepared CSAB cements with satisfactory compressive strength, using bag house dust, low calcium fly ash and scrubber sludge. By using up to 30 wt.% phosphogypsum in the production of CSAB cements, Peysson et al. [21] concluded that the delayed ettringite precipitation led to a cement paste being damaged by high porosity and consequent cracking. Pelletier-Chaignat et al. [22] observed that at high CSAB/gypsum ratios, gypsum is consumed after 7 days. Luz et al. [23] produced blended cements by mixing 75 wt.% CSAB with 25 wt.% galvanic sludge that delivered acceptable compressive strength and good Cr retention. To the best of our knowledge, only Adolfsson et al. [24] used up to 25 wt.% EAFS as raw material in the production of CFAB type cements, but in combination with other steelmaking slags. This resulted in a cement with low mechanical strength in the later days of hydration.

The present work explores the production of calcium ferroaluminate belite cement clinker with 10 wt.%, 17 wt.% and 27 wt.% EAFS. The central aim was to understand the influence of EAFS on the clinkering process, on the microstructure of clinker and hydration products and on the main properties of the final cement mortars. The role of FGD gypsum co-grinded with the clinker in 5 wt.% and 20 wt.%, in order to control the hydrogarnet formation, was also briefly addressed through compressive strength measurements of hardened mortars.

2. Materials and methods

The raw materials used in the preparation of the raw meals were EAFS, limestone, bauxite and gypsum. EAFS was used as received from SOVEL S.A. industry, Greece. The chemical analysis (Table 1) was performed by XRF (Philips PW 2400). The crystalline phases (Fig. 1) were identified by XRD (SiemensD5000) using DIF-FRACplus EVA® software (Bruker-AXS) based on the ICDD Powder Diffraction File. The parameters used were 2θ range of 10–70°, Cu Kα radiation under 40 kV and 30 mA, 0.01° step size and step time of 1°/min. Quantitative determination was performed using

Table 1
Chemical composition of raw materials, wt.%.

Raw materials	EAFS	Limestone	Bauxite	Gypsum
CaO	32.50	48.90	3.62	31.80
FeO$_{total}$	26.30	1.00	23.00	0.04
SiO$_2$	18.10	9.00	14.30	1.76
Al$_2$O$_3$	13.30	1.36	49.20	0.18
MnO	3.94	n.d.	n.d.	n.d.
MgO	2.53	0.65	n.d.	1.85
Cr$_2$O$_3$	1.38	n.d.	n.d.	n.d.
P$_2$O$_5$	0.48	n.d.	n.d.	n.d.
TiO$_2$	0.47	n.d.	2.00	n.d.
SO$_3$	0.44	n.d.	0.23	41.54
BaO	0.14	n.d.	n.d.	n.d.
Na$_2$O	0.13	0.10	n.d.	n.d.
K$_2$O	n.d.	0.15	n.d.	n.d.
V$_2$O$_5$	0.06	n.d.	n.d.	n.d.
LOI	<0.50	38.00	10.00	23.14
Total	99.77	99.16	102.35	100.31

LOI: loss on ignition, n.d.: not determined.

the TOPAS® software (Bruker-AXS) based on the Rietveld method, normalized (Table 2). For the estimation of the mineralogical phases of the clinkers, modified Bogue equations were adapted to the thermodynamic system CaO–SiO$_2$–Al$_2$O$_3$–Fe$_2$O$_3$–SO$_3$ (CSAF$\hat{S}$) [25–27]. The phases expected to form were C$_4$AF, C$_2$S, C$_4$A$_3\hat{S}$ and C$\hat{S}$. Equations from 6 to 10 were used for the calculations (results are presented in Table 3).

$$\%C_4AF = 3.043(\%Fe_2O_3); \tag{6}$$

$$\%C_4A_3\hat{S} = 1.995(\%Al_2O_3) - 1.273(\%Fe_2O_3); \tag{7}$$

$$\%C_2S = 2.867(\%SiO_2); \tag{8}$$

$$\%C\hat{S} = 1.700(\%SO_3) - 0.445(\%Al_2O_3) + 0.284(\%Fe_2O_3); \tag{9}$$

$$\begin{aligned}\%C = &\, 1.000(\%CaO) - 1.867(\%SiO_2) - 1.054(\%Fe_2O_3) \\ &- 0.550(\%Al_2O_3) - 0.700(\%SO_3); \end{aligned} \tag{10}$$

The mineralogical phases of the clinkers were calculated also by the Rietveld method (QXRD) using the "Topas® Academic" software, besides the estimations derived from the Bogue equations (Table 3). The quality indexes, lime saturation factor (LSF), silica modulus (SM) and alumina modulus (AM) have been calculated based on established equations [7,28]. The results are presented in Table 3.

The synthesis of the raw meals was calculated by means of an MS Excel© worksheet, by regulating the content of limestone, bauxite and gypsum and by setting the desirable range of variation in the quality indexes LSF, AM and SM. Three types of clinker were prepared with 10 wt.% (M1), 17 wt.% (M2) and 27 wt.% (M3) EAFS content respectively. The content of the raw meals in limestone/bauxite/gypsum/EAFS (in wt.%) was: 62.0/20.0/8.0/10.0 for M1, 61.0/16.0/6.0/17.0 for M2 and 59.5/10.5/3.0/27.0 for M3. A small fluctuation in LSF, AM and SM is present.

For clinker production, all raw materials were individually milled in a Siebtechnik® planetary mill at a particle size <90 μm. After mixing and homogenization with a minimum water addition, pellets of 15–20 mm diameter were created. Dehydration took place in a muffle furnace at 110 °C for 24 h. For clinkering, the pellets were loaded in a magnesia–chrome refractory crucible covered with a lid in order to minimize gas emissions during firing. A Super Kanthal resistance furnace (Nabertherm®) was used. To stabilize the α'- and β-C$_2$S polymorphic forms, the clinker was cooled fast by the simultaneous application of blown air and crushing by means of a hammer.