UTILIZATION OF EAF METALLURGICAL SLAG IN "GREEN" BELITE CEMENT

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În acest studiu, zgură de cuptor cu arc electric (EAFS) colectată de la Sovel S.A., Grecia şi calcar şi argilă, de la compania de ciment Titan S.A., Grecia, au fost utilizate pentru producerea şi caracterizarea cimenturilor tip belitice. Trei tipuri de clincher au fost preparate: belitic fara adaos de zgură folosit ca referinţă (BC), unul cu 5wt% EAFS (BC5) şi un altul cu 10wt% EAFS (BC10). Analiza clincherelor s-a făcut prin microscopie optică, SEM şi XRD. Cimenturile au fost testate în conformitate cu cerinţele standardului EN 196-1. Rezultatele au demonstrate că în toate cazurile, grăunţi belitici tip I au fost stabilizaţi în urma răcirii rapide. Ambele cimenturi cu zgură, au prezentat rezistenţă scăzută la compresiune în primele zile de hidratare comparativ cu cimentul de referinţă.

In this study, electric arc furnace steel slag (EAFS) collected from Sovel S.A., Greece and limestone and clay, from Titan Cement Company S.A., Greece, were used for the production and characterisation of belite type cements. Three types of clinkers were prepared: pure belite as reference, BC, one with 5wt% EAFS, BC5, and one with 10wt% EAFS, BC10. Analysis of the clinkers was done by optical microscopy, SEM and XRD. Cements were tested according to EN 196-1 standard. Results demonstrated that in all the cases type I belite grains were stabilised by fast cooling. Both types of slag cements had low early compressive strength compared with the reference one.

Keywords: electric arc furnace slag, belite cement, valorization

1. Introduction

Fifty million tons per year of steel slag are produced as a residue in the world [1]. In Europe every year nearly 12 million tons of steel slag's are produced [2]. Worldwide, the utilization of such slag's is of great environmental interest.

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Sovel S.A., Greece has a steel production of approximately 750.000t/y. The slag represents 13% of the steel production, approximately 97.500t/y slag. Steelmaking slag's (BOF, OBM, and EAF) are generated during refining operations. In Greece, from the total annually amount of EAFS processed, 55% are used in production of coarse aggregates for road construction because is financially viable for the producer and economically attractive to the customer [3]. For cement production, less than 1% is used, and the rest is stock-piled or used in other applications. The Greek cement industry is a vital sector of the economy with an annually cement production over 14.8 million tonnes. It is known that the cement industry produces a substantial amount of CO_2. Taking into account an average of 0.83 tonnes of CO_2/tone of cement, it results that the cement sector contributes 12.87 million tonnes of CO_2 annually. However, study cases have shown that a 9% reduction in CO_2 production is feasible in the case of wastes' utilization [4-6]. Belite type cement, also referred as "green", is reducing the CO_2 emissions by lower energy consumption due to lower firing temperature, in conjunction with a reduced content of limestone, compared to OPC (ordinary Portland cement). The energy demand is estimated at 15-20% less, for a LSF of 80-85%. The result is an increased content in belite mineral than alite [7-9]. The biggest disadvantage of belite (C_2S) rich cement is the slow rate of hydration. Cooling down to 900^{o}C at a rate in excess of 1000^{o}C/min [10, 11], is sufficient to give strength development comparable to OPC; this can be achieved by hammer crashing and forced air cooling. Fast cooling provides internal tensions in the core of the clinker assisting its grindability [12] and also stabilizes α'-, β - C_2S probably by limiting the exsolution of impurities that would occur during slow cooling [13]. On cooling, complex microstructure develops as a result of polymorphic transformations [14]. Lamellar structures form during α- α' transformation and twinning during α'-β, while the β- γ transformation is martensitic and hence strongly dependent on crystal size and matrix restraint [15].

In this study, utilization of EAF in the production of belite type cements, by using fast cooling by hammer crushing and forced air flow, was studied as a way to stabilize the hydraulic polymorphic phases.

2. Materials and methods

The materials used in this study are EAFS from Sovel S.A., Greece and limestone and clay from Titan Cement Company S.A., Greece. Slag was used as received. The chemical composition was measured by XRF and is presented in table 1.

Table 1

Chemical composition of the raw materials, wt. %

Oxides, %	EAFS	Limestone	Clay
CaO	32.5	48.90	5.55
Fe_2O_3	26.3	1.00	5.90
SiO_2	18.1	9.00	58.25
Al_2O_3	13.3	1.36	13.75
MnO	3.94	nd	nd
MgO	2.53	0.65	2.86
Cr_2O_3	1.38	nd	nd
P_2O_5	0.48	nd	nd
TiO_2	0.47	nd	nd
SO_3	0.44	nd	0.05
Cl	0.14	nd	nd
BaO	0.14	nd	nd
Na_2O	0.13	0.10	1.10
K_2O	nd	0.15	2.50
V_2O_5	0.06	nd	nd
LOI	1.56	38.00	9.80
LOI – loss of ignition, nd – not determined			

A modified Microsoft's Excel® spreadsheet was built for the estimation of the mineralogical phases formed according to Bogue equations, and the limits imposed by the indices, as lime saturation factor (LSF), silica modulus (SM) and aluminum modulus (AM). The goal was to achieve high belite hydraulic cements and for this reason LSF was kept in the range of 78-80%, specific to belite cements. Three clinkers were prepared: pure belite as reference clinker, BC, one with 5wt% EAFS called BC5 and finally a clinker with 10wt % EAFS named BC10. The mineralogical phases according to Bogue and specific limits of cement (LSF, AM, SM) are presented in table 2.

Table 2

Targeted compositions for the blends, wt.%

Target	C_3S	C_2S	C_3A	C_4AF	Total	LSF	AM	SM
BC	27.5	55	9	8.5	100	80	1.87	3.29
BC5	22.5	56	7.5	14	100	79	1.26	2.47
BC10	17.5	57.5	6	19	100	78	1.00	1.96

For the preparation of the clinkers, the raw materials were milled in a planetary mill at a particle size under 90µm. Mixing was done with a small amount of water and the paste was pelletized by hand as spheres of 10-20mm diameter. Drying of the pellets was performed for 24 h at 110ºC, followed by calcination at 1000ºC for 4 h. DTA tests for each raw meal were performed using a Nietzsche 404S with 10ºC heating rate till 1100ºC, in static air, in alumina crucible (figure 1). Preliminary experiments conducted to 1380ºC as the optimum clinkering temperature. For this cause, the pellets were loaded in a magnesia-chrome crucible and fired subsequently in a resistance furnace at 1380ºC with 40min soaking time. Cooling took place in air, with concurrent forced air blown and crushing by hammer, to increase the surface and thus the cooling rate. This was done in order to reach the polymorphic phases of α'– and β – C_2S and prevent the formation of γ – C_2S that has no hydraulic activity. After cooling, the evaluation of mineralogy was conducted by XRD, optical microscopy and SEM analysis. The XRD analyses were conducted on powder samples, with particle sizes lower than 125μm and parameters: angle 5-70º, increment 0.01 and scan speed 1 deg/min. For optical observation, clinkers were mounted in epoxy resin, and polished by SiC papers to 4000 grit by using alcohol in order to avoid the hydration. Resulted surface was etched with aqueous solution of Nital 1% for 30sec. For SEM analysis, the polished specimens were sputter-coated with a thin film of carbon. The specimens were preserved in desiccators with silica gel prior examinations to prevent hydration. Milling of the resulting clinkers took place in a planetary mill. Batches of 50g of clinker were milled in order to reach the finesses of particles between 4000 - 4100 cm^2/g. For the preparation of the cements the powders after milling were mixed with 5wt % of gypsum. The specific surface of the cements (Blaine) and the compressive strength were measured according to EN 196–6 and EN 196–1 respectively.

3. Results and discussions

Results from differential thermal analyses (DTA) are presented on figure1.

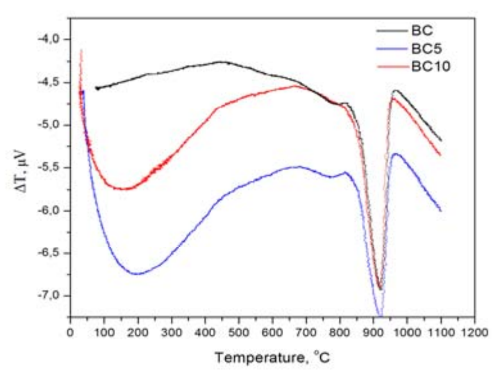

Fig. 1. Differential thermal analyses on the raw meals showing the mechanisms which take place in the kiln during preheating stage.

The endothermic peak in the temperature range of 100°C to 500°C in the case of BC5 and BC10 is attributed to the dehydroxylation of iron hydroxide followed by the transformation of FeO to α-Fe_2O_3. The dissociation of $CaCO_3$ starts from 850°C to approximately 950°C. In the case of cement types BC, BC5 and BC10, the main identified mineralogical phases are C_3S, C_2S, C_4AF and C_3A.

Alite is presented as monoclinic taking in the structure more MgO than Fe_2O_3 and Al_2O_3 caused by the ionic radius of Ca^{2+} which is closer to Mg^{2+} than to Fe^{3+} or Al^{3+} [16]. Belite mineral was stabilized by fast cooling as β polymorphic phase.

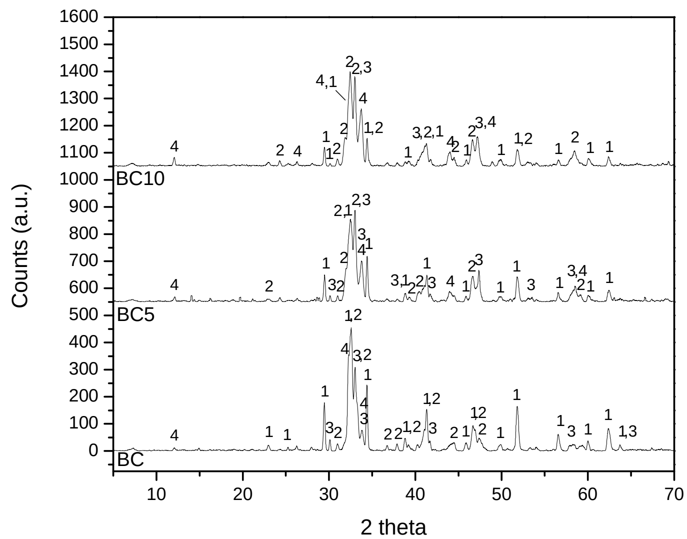

Fig. 2. XRD pattern of clinkers. Main minerals are presented as: 1-C_3S, 2-C_2S, 3-C_3A, 4-C_4AF

Textures were observed and recorded by reflected light microscope, presented in figure 3. Due to the fast cooling the belite polymorphism transitions are encouraged to occur successively, leading to the formation of complex microstructure due to twinning or exsolution within the crystals.

Belite is presented generally as round shape, blue color due to type of etching and crossed parallel striations.

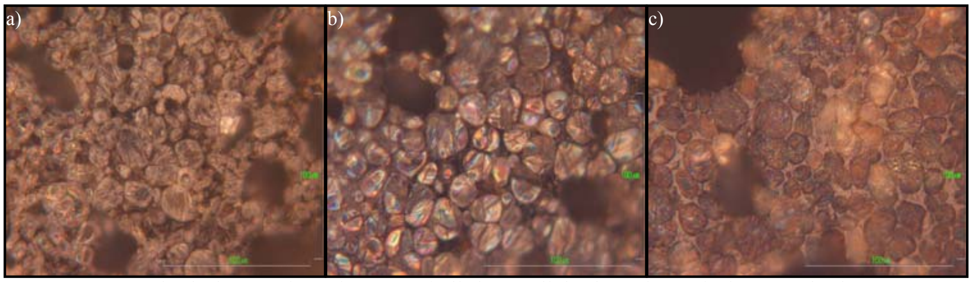

Fig. 3. Optical observation pictures of clinker polished section, nital 1% etched, 500X magnification: a) BC, b) BC5 and c) BC10 clinker

In all the cases regular round shapes are present. BC type clinker present type I belite (by Insley) with β – crossed lamellae due monoclinic to orthorhombic crossing [17], followed by BC5, with colourless belite with β twinning crossed parallel striation due to α' fired temperature held [18].

Some molten phases can be distinguished between belite round grains. In BC10, type I belite with twinning crossed parallel striations, specific to β polymorphic phase, smaller round shapes compared with BC and BC5, surrounded by molten phases probably C_4AF according with Bogue calculations [18].

SEM pictures of polished section are presented in figure 4.

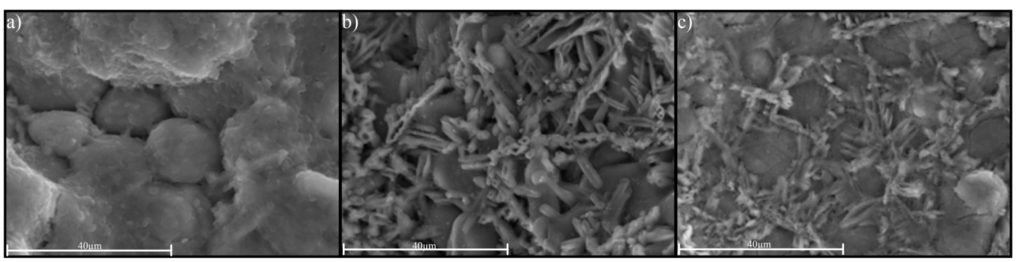

Fig. 4. SEM pictures of clinkers polished section: a) BC type clinker, present round shapes of belite grains growing up from molten phase, b) BC5 and c) BC10 type clinkers, present belite grains covered by a network of pipes-like ferrite crystals [18] which are broken or look like exploded probably due to the fast cooling. Some micro cracks are visible in type BC10, coming probably from the hammer action during cooling.

Compressive strength measurements revealed low early compressive strength development for BC5 and BC10. High content of molten phase and low basicity of the slag decrease the early days results compared with reference one. The compressive strength excided 35MPa for 28 days for all samples, due to the presence of belite mineral.

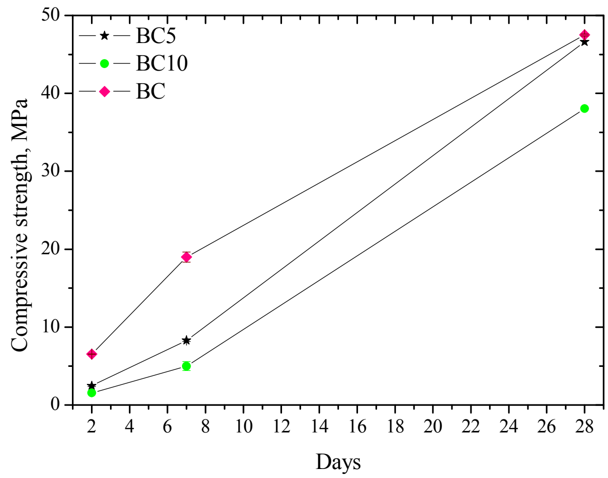

Fig. 9. Compressive strength results of the concrete

4. Conclusions

Belite cements with EAFS were produced successfully at lower temperature (1380ºC) compared to OPC (ordinary Portland cement) driving to less energy consumption. Utilisation of EAFS as a substituent of raw materials (clay and limestone) derived to low CO_2 emissions. In the formation of the minerals shape, BC5 and BC10 clinkers present well formed belite grains with high amount of molten phases compared with the reference one, as concluded by SEM pictures. Compressive strength results were diminished on early days by increasing of EAFS in compositions, due to the low basicity of slag, high ferric oxide content and low activity of the belite mineral in spite of fast cooling rate.

Utilisation of EAF steel slag’s can be performed without any inconvenient in the formation of the phases, but high amount of ferric oxide leading to high brownmillerite mineral came to decrease the early strength. Cement produced with EAFS in the composition can be used in specific field where no high early strength is requested.

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REFERENCES

[1] *I. Altun, I. Yilmaz*, "Study on steel furnace slags with high MgO as additive in Portland cement", in Cement and Concrete Research, **vol. 32**, no. 8, 2002, pp. 1247-1249

[2] EUROPEAN SLAG ASSOCIATION, Legal Status of Slag, 2006

[3] www.aeiforos.gr

[4] CEMBUREAU – Environmental Benefits of Using Alternative Fuels in Cement Production, A Life-Cycle Approach, 1998

[5] www.hcia.gr

[6] CEMBUREAU, Annual report, 2001

[7] *H. Uchikawa*, "Management strategy in cement technology for the next century: Part 3, World Cement, Nov. 1994, pp. 47

[8] *C. D. Lawrence*, "The production of Low-Energy Cements", in Lea's Chemistry of Cement an Concrete, Butterworth-Heinemann, Oxford, 2003

[9] *J.H. Sharp, C.D.Lawrence, R.Yang*, "Calcium sulfoaluminate cements-low energy cement special cement or what?", in Advance Cement Research, **vol. 11,** 1999, pp. 3-13

[10] J. Stark, A. Muller, I. Mielke, "On SO_3-containing belite clinker", in Silikattechnik, **vol. 38**, 1987, pp. 219-221

[11] *U. Ludwig, A. Wolter*, "Formation and stability of tricalcium silicate and alinite", in Zement-Kalk-Gips, **vol. 32**, 1979, pp. 455-459

[12] *B.W. Nicholas*, Understanding Cement, WHD Microanalysis Consultant Ltd, United Kingdom, 2010-07-05

[13] *F. Lamp, R. Seydel*, "On a new form of [beta]-belite", in Cement and Concrete Research, **vol. 19**, 1989, pp. 509-518

[14] *J.C. Chan, M.W. Kriven, J.F.Young,* "Physical stabilisation of the β-γ transformation in dicalcium silicate", in Journal of American Ceramic Society, **vol. 75**, 1992, pp. 1621-1627

[15] *B. Matkovic, V. Carin, T. Gaseca, I. Jelenic, F.J. Young*, "Influence of $BaSO_4$ on the formation and hydration properties of calcium silicate I. Doped calcium silicate", in Ceramic Bulletin, **vol. 60**, 1981, pp. 825-829

[16] *D. Stephan, S. Wistuba,*" Crystal structure refinement and hydration behaviour of doped tricalcium aluminate", in Cement and Concrete Research, **vol. 36**, 2006, pp. 2011-2020

[17] *K. Fukada, I. Maki,* "Orientation of [beta]-Ca_2SiO_4 solid solution lamellae formed in the host [alpha]-phase", in Cement and Concrete Research, **vol. 19,** 1989, pp. 913-918

[18] *D.H. Campbell,* Microscopical examination and interpretation of Portland cement and clinker, Portland Cement Association, United States of America, 1999.