

Utilization of steel slag for Portland cement clinker production

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Abstract

The aim of the present research work is to investigate the possibility of adding steel slag, a by-product of the conversion of iron to steel process, in the raw meal for the production of Portland cement clinker. Two samples of raw meals were prepared, one with ordinary raw materials, as a reference sample ((PC)_{Ref}), and another with 10.5% steel slag ((PC)_{S/S}). Both raw meals were sintered at 1450 °C. The results of chemical and mineralogical analyses as well as the microscopic examination showed that the use of the steel slag did not affect the mineralogical characteristics of the so produced Portland cement clinker. Furthermore, both clinkers were tested by determining the grindability, setting times, compressive strengths and soundness. The hydration products were examined by XRD analysis at 2, 7, 28 and 90 days. The results of the physico-mechanical tests showed that the addition of the steel slag did not negatively affect the quality of the produced cement.

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1. Introduction

Waste utilization is an attractive alternative to disposal in that disposal cost and potential pollution problems are reduced or even eliminated along with the achievement of resource conservation. Nevertheless, the utilization strategy must be coupled with environmental and energy considerations to use available materials most efficiently. The traditional way to utilize metallurgical slags in cementing materials is to partially replace Portland cement, which usually results in a lower early strength and longer setting times. Presence of activator(s) can accelerate the break-up of structure and hydration of slags [1].

Today, most metallurgical slags are used as aggregates for different applications, and only the ground granulated blast furnace slag is used for a partial Portland cement replacement. The partial replacement may decrease the early strength, but increase the later strength and improve microstructure and durability

of hardened Portland cement and concrete very significantly [2].

Steel slag is a by-product of the conversion of iron to steel process and it presents differences depending on the raw materials and process. Fifty million tons per year of steel slag are produced as a residue in the world [3]. In Europe every year nearly 12 million tons of steel slags are produced. Owing to the intensive research work during the last 30 years, today about 65% of the produced steel slags are used on qualified fields of application. But the remaining 35% of these slags are still dumped [4].

Because the chemical composition of steel slags is highly variable, the mineral composition of steel slag also varies. Olivine, merwinite, C₃S, C₂S, C₄AF, C₂F, RO phase (CaO–FeO–MnO–MgO solid solution) and free-CaO are common minerals in steel slag. Its chemical composition consists of CaO 45–60%, SiO₂ 10–15%, Al₂O₃ 1–5%, Fe₂O₃ 3–9%, FeO 7–20% and MgO 3–13% [5]. The presence of C₃S, C₂S, C₄AF and C₂F endorses steel slag cementitious properties. However, the C₃S content in steel slag is much lower than in Portland cement. Thus, the steel slag can be regarded as a weak Portland cement clinker.

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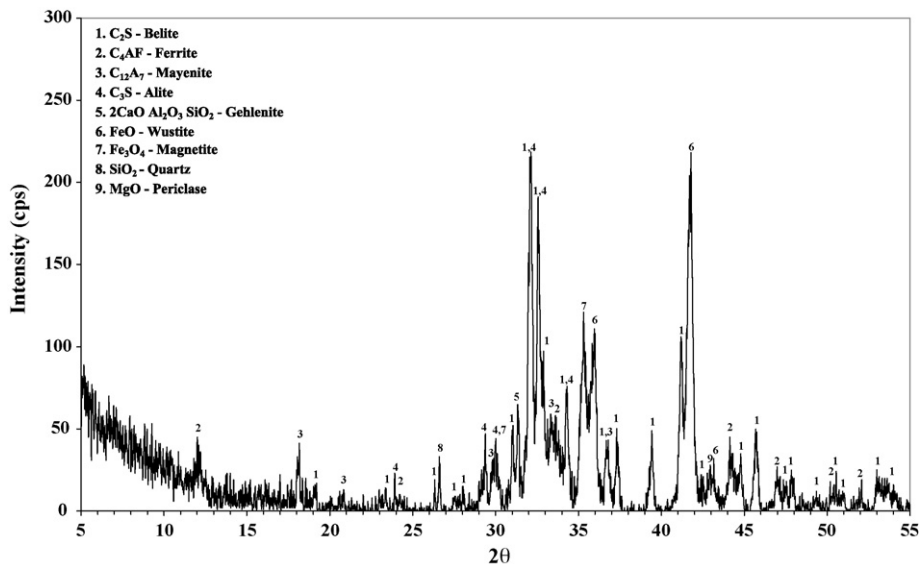


Fig. 1. X-ray diffraction of steel slag used.

The main problem with using steel slag in civil engineering is the possible presence of free lime, especially large-sized components of heated undissolved limestone, because when it hydrates, its volume increases and this swelling can lift the top layers [6].

However, a specialty steel slag cement, which is composed mainly of steel slag, blast furnace slag and Portland cement, has been commercially marketed in China for more than 20 years and uses approximately 40% of the total steel slag production [7]. This type of cement has the advantages of lower energy cost, higher abrasion resistance, lower hydration heat evolution and higher later strength development, but the disadvantage of longer setting time and lower early strength when compared with Portland cement.

Steel slag cement can be used for general construction use, especially suitable for mass concrete and pavement applications due to its special features. Furthermore, steel slag is used as asphalt concrete aggregate in some countries. The use of steel slag as aggregate for road construction and as armour stone for hydraulic structures has been reported [4]. However, high free-CaO content in steel slag may cause volume expansion problems [1].

The so far published literature has given little attention to the use of steel slag in the raw meal for the production of Portland cement. The aim of the present research work was to investigate the possibility of using steel slag as a raw material for the production of a typical Portland cement clinker. For that reason, two samples of raw meals were prepared, one with ordinary raw materials, as a reference sample ((PC)_{Ref}), and another with 10.5% steel slag ((PC)_{S/S}). The produced clinkers were analyzed chemically and mineralogically by XRD and optical microscopy. The clinkers were then mixed with gypsum and the final cement samples were tested for grindability, setting times, compressive strengths, and soundness. The hydration products were determined by XRD analysis at the ages of 2, 7, 28 and 90 days.

2. Experimental

Steel slag, coming from scrap smelting in electric arc furnaces, was supplied from Sidenor steel product manufacturing company of Greece. It was crushed in a jaw crusher and the fraction used in this study was the “0–5 mm”. Preliminary examination had shown that this fraction presented high content in calcium silicate phases and small amounts of metallic iron. Its mineralogical phases, which were determined by XRD analysis, using a Siemens D5000 diffractometer with nickel-filtered Cu K α_1 radiation (= 1.5405 Å, 40 kV and 30 mA), are given in Fig. 1. The steel slag microstructure was examined by optical microscopy. The microscopic observation of the polished impregnated samples was achieved using a Jenapol optical microscope in reflected light.

The steel slag was mixed with other raw materials, such as limestone, clay, sand, and bauxite, in appropriate proportions in order to produce the raw meal to be tested for the production of Portland cement clinker ((PC)_{S/S}). A reference raw meal

Table 1
Chemical analysis of raw materials for the production of Portland cement clinkers

Oxides	Content of raw materials (%)				
	Limestone	Sand	Clay	Bauxite	Steel slag
SiO ₂	0.25	81.03	60.53	3.11	17.53
Al ₂ O ₃	0.08	8.34	14.30	52.35	6.25
Fe ₂ O ₃	0.06	3.34	4.99	22.64	26.36
CaO	55.06	0.58	7.23	7.64	35.70
MgO	0.12	1.10	0.80	0.09	6.45
K ₂ O	0.02	1.63	0.78	0.76	0.26
Na ₂ O	0.01	0.14	1.18	0.15	0.2
TiO ₂	–	0.33	0.47	1.35	0.76
MnO	–	–	–	–	2.50
ZnO	–	–	–	–	0.85
LOI ₁₀₀₀	43.37	3.26	9.62	11.35	2.24

Table 2
Composition of the raw meals for the production of Portland cement clinkers

Raw meals	Raw meals composition (%)				
	Limestone	Sand	Clay	Bauxite	Steel slag
(PC) _{Ref}	78.00	14.40	3.70	3.90	–
(PC) _{S/S}	70.80	12.70	3.50	2.50	10.50

((PC)_{Ref}), without steel slag, was also synthesized for reasons of comparison. The chemical analyses of the raw materials used are given in Table 1. Based on those, and by using a computational software program, the syntheses of the two raw meals were derived and are presented in Table 2.

The sintering process applied was common for the production of both types of cement clinkers. The raw meals were shaped in small spheres, with a diameter of 2 cm, and dried at 110 °C. Then, they were placed inside an oven at 500 °C, the temperature was increased to 1000 °C, at which the samples remained for 30 min, and, finally, the temperature was further increased to 1450 °C, where the samples remained for 30 min [8]. At the end of the sintering process, the samples were rapidly cooled in order to avoid the formation of γ -C₂S. The clinkers produced were analyzed by chemical analysis, X-ray diffraction and optical microscopy.

The clinkers were crushed and grounded in a Bond ball mill to a specific surface area of about 3800 cm²/g (according to the Blaine air permeability method) [9]. Particle size distributions were measured by a laser scattering particle size distribution analyzer (Mastersizer/E—Malvern). An amount of 0.1 g of powdered sample was put in 100 ml of ethanol and underwent dispersion treatment by an ultrasonic dispersion unit for 60 s.

The soluble SO₃ content in the clinkers was measured and the ground clinkers were mixed with industrial CaSO₄·2H₂O, so that the produced laboratory cements contained about 2.5% total soluble SO₃. More specifically, the SO₃ content of samples (PC)_{S/S} and (PC)_{Ref} were measured 2.42% and 2.40%, respectively.

The standard consistency, the setting times and the soundness of the cement pastes were determined according to the European Standard EN 196-3 [10]. Compressive strength measurements were conducted at the ages of 2, 7, 28 and 90 days on mortar prisms (dimensions 40 mm × 40 mm × 160 mm), prepared and tested in accordance with European Standard EN 196-1 [11].

For the study of the hydration products, the cement pastes were prepared by mixing 300 g of grounded mixtures with 75 ml of water. They were then cured in tap water at a temperature 20 ± 2 °C. At the ages of 2, 7, 28 and 90 days, the hydration was stopped by means of acetone and ether extraction and the hydration products were determined by XRD analysis.

3. Results and discussion

3.1. Chemical and mineralogical characteristics of steel slag used

As shown in Table 1, the main components of steel slag fraction used are CaO, Fe₂O₃, SiO₂, MgO and Al₂O₃. Like most

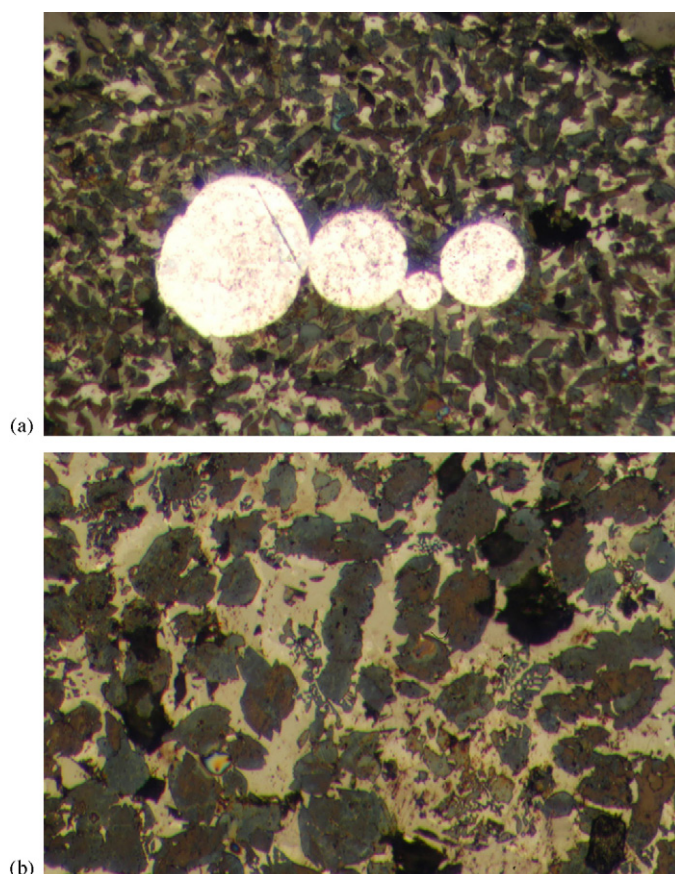


Fig. 2. Microstructure of steel slag used. (a) Entrapped metallic Fe and anhedral C₃S with decomposition (200×). (b) Finger C₂S and skeletal C₃S due to slow cooling (500×).

metallurgical slags, it has a chemical composition similar to that of Portland cement. The main difference in steel slag is the high iron oxide content, which exists in both the di- and trivalent states. Fig. 1 indicates that although crystalline calcium silicates are present in steel slag, the absence of a strong tricalcium silicates peaks at 29.2° 2 θ and 51.5° 2 θ suggests a deficiency in alite, which is the primary strength contributing phase during Portland cement hydration. Moreover, it should be noticed that wustite (FeO), which is the predominant mineral phase in steel

Table 3
Chemical analysis of the Portland cement clinkers

Oxides	Content of the produced cement clinkers (%)	
	(PC) _{Ref}	(PC) _{S/S}
SiO ₂	21.85	21.32
Al ₂ O ₃	5.82	5.28
Fe ₂ O ₃	2.78	3.85
CaO	67.85	66.35
MgO	0.53	1.37
K ₂ O	0.35	0.43
Na ₂ O	0.13	0.13
TiO ₂	0.18	0.17
SO ₃	0.20	0.13
CaO _f	1.15	1.05
LOI	0.22	0.24

Table 4
Mineralogical composition of the produced Portland cement clinkers

Mineralogical phases	Cement clinkers composition (Bogue) (%)	
	(PC) _{Ref}	(PC) _{S/S}
C ₃ S	61.75	62.24
C ₂ S	16.15	14.26
C ₃ A	10.72	7.49
C ₄ AF	8.45	11.70

slag, does not occur in ordinary Portland cement. This phase has no cementitious properties and does not combine to form hydraulic phases [12]. X-ray diffraction confirmed the absence of γ -C₂S. Dicalcium silicate was detected in the form of β -C₂S, which has been probably stabilized by the presence of impurity

Table 5
Results of grindability tests

Characteristics	(PC) _{Ref}	(PC) _{S/S}
Mill revolutions	4150	4100
Specific surface area (cm ² /g)	3850	3790
Grindability index	0.93	0.92

ions (Fe³⁺, Al³⁺) and relatively slow rate of cooling. This fact was attested and by the absence of amorphous glass between 26° 2 θ and 36° 2 θ . The detection of C₄AF, which is one of the major mineral phases found in Portland cement, indicates that the trivalent iron was able to combine with calcium and alumina to produce the ferrite phase upon cooling from the melt.

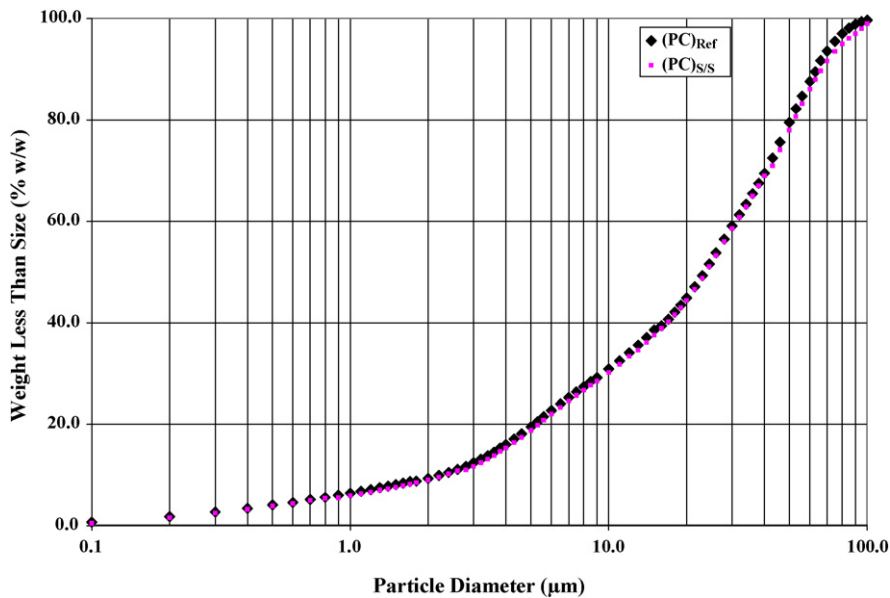


Fig. 3. Particle size distributions of cement samples by a laser scattering analyzer.

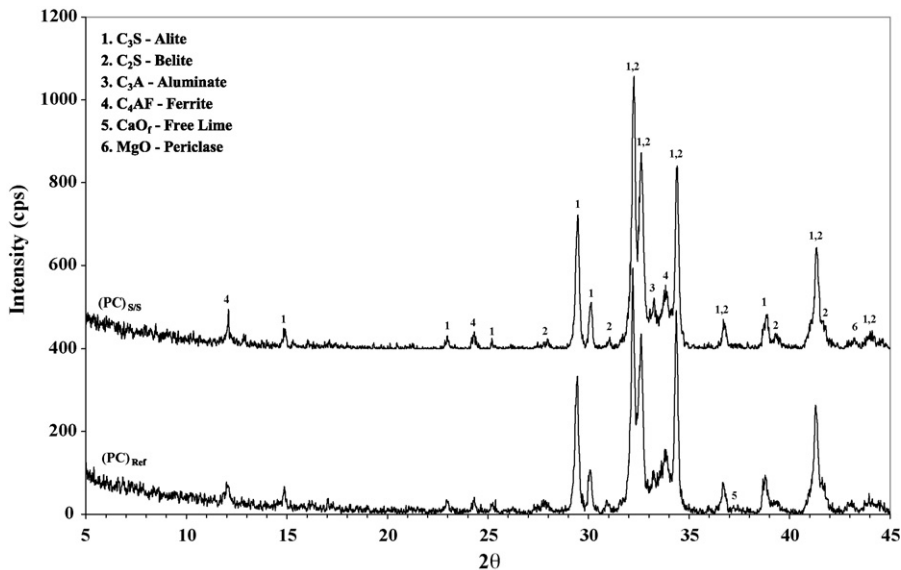


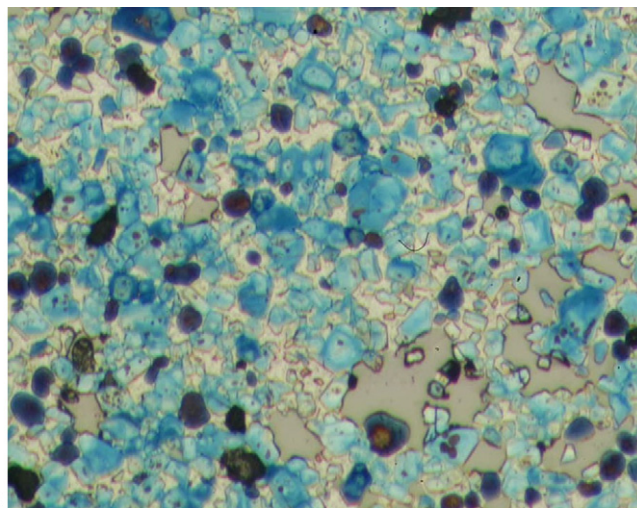
Fig. 4. X-ray diffraction of Portland cement clinkers with and without steel slag.

The above conclusions were also confirmed by optical microscopy observations (Fig. 2). Although the coarse alloy and metal particles have been separated and recovered, the steel slag still contains small amounts of metallic Fe. The presence of finger C₂S was attributed to the slow rate of cooling. The liquid phase solidified as uniformly distributed large crystals. The ferrite phase exhibits as dendritic, prismatic and massive.

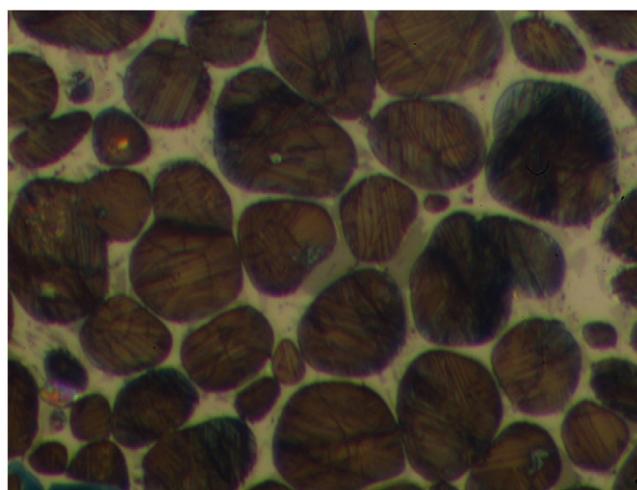
3.2. Chemical and mineralogical characteristics of clinkers produced

The chemical analysis and the potential mineral composition (according to Bogue) of the Portland clinkers produced are given in Tables 3 and 4, respectively. As the tables show, the addition of the steel making slag by 10.5% did not seem to affect its mineralogical composition.

The grinding of clinkers with the required quantity of gypsum was carried out in a ball mill of 1.5 kg capacity. The gypsum

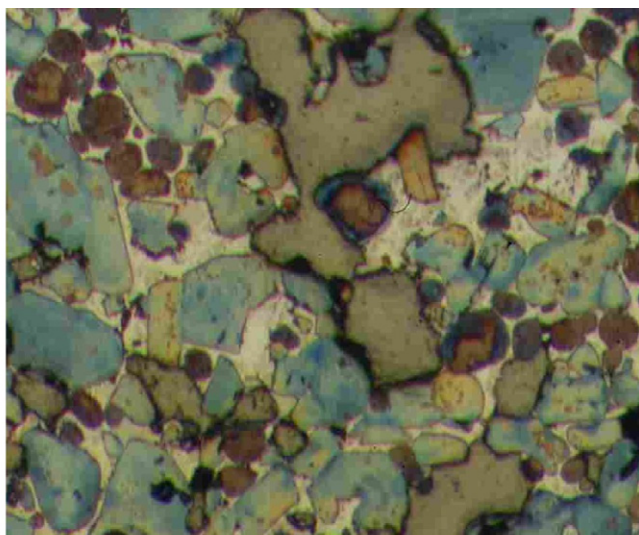


(a)

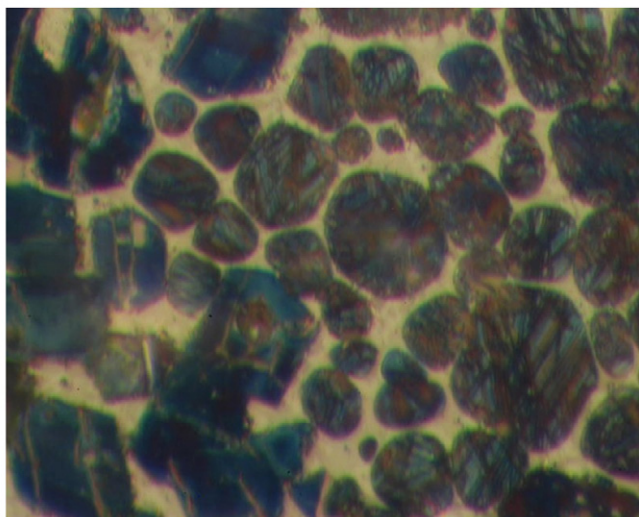


(b)

Fig. 6. Microstructure of Portland cement clinker with steel slag. (a) Well-formed alite crystals (100×). (b) Brownish rounded belite crystals (500×). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)



(a)



(b)

Fig. 5. Microstructure of Portland cement clinker without steel slag. (a) Large crystals C₃S (500×). (b) Bluish rounded belite crystals (500×). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

was of industrial origin (98% (w/w) CaSO₄·2H₂O, 47.3% (w/w) SO₃). The results of particle size distributions by a laser scattering analyzer are given in Fig. 3. The grindability index of each sample was determined and is presented in Table 5. Both cement samples gave similar results.

The XRD analyses of the produced Portland clinkers are given in Fig. 4. In both clinker types, the main mineralogical phases, C₃S, C₂S, C₃A and C₄AF, were well formed. The (PC)_{S/S} clinker contained more C₄AF, a difference that was attributed to the partial replacement of clay and sand with steel slag, which is higher in iron than the former. CaO_f was relatively low in both cases.

Table 6
Physical properties of the tested cements

Physical property	(PC) _{Ref}	(PC) _{S/S}
Initial time (min)	150	170
Final time (min)	180	205
Water of normal consistency (%)	26.8	26.1
Expansion (mm)	2.5	2.0

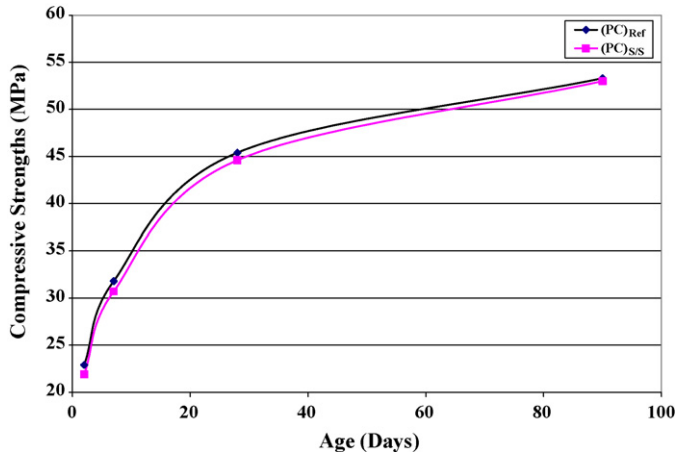


Fig. 7. Compressive strengths of the cements produced.

The microstructure of the Portland cement clinkers was examined by optical microscopy in polished sections. The addition of the steel slag by 10.5% did not seem to affect its microstructure and the formation of its characteristic mineralogical phases (Figs. 5 and 6). CaO_f was dispersed among other phases, in low percentages. Both clinkers contained more or less euhedral alite and they exhibited coalescence of alite crystals. The alite crystals appeared well formed, with average size $40\ \mu\text{m}$, whereas no decomposition of C_3S was observed. In the optical microscope, belite was observed as bluish or brownish rounded crystals, rich in lamellas. No differences in the microstructure of belite between $(\text{PC})_{\text{Ref}}$ and $(\text{PC})_{\text{S/S}}$ clinkers were detected. In both cases, the belite crystals were evenly distributed in relation to alite. Finally, the liquid phase solidified as uniformly distributed fine crystals.

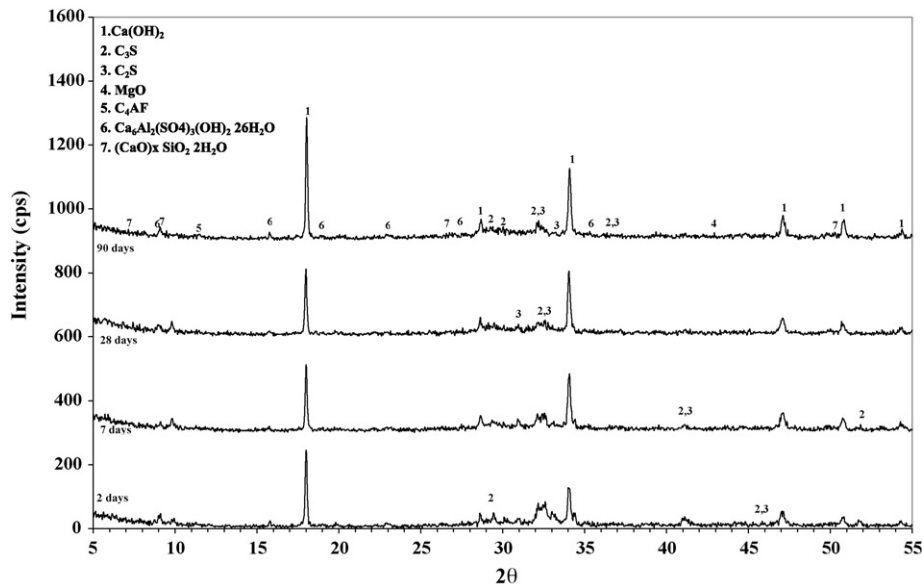


Fig. 8. X-ray diffraction of $(\text{PC})_{\text{Ref}}$ pastes at 2, 7, 28 and 90 days.

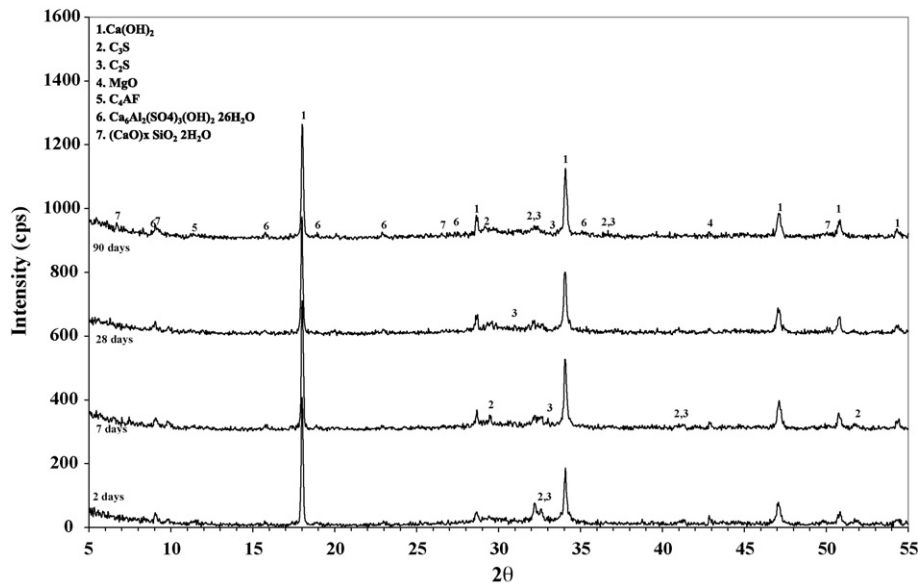


Fig. 9. X-ray diffraction of $(\text{PC})_{\text{S/S}}$ pastes at 2, 7, 28 and 90 days.

3.3. Physical, mechanical and mineralogical characteristics of Portland cements produced

Table 6 presents the cement water demand, the setting times and the expansion of the tested samples. The “water demand” is generally considered to be the quantity of water required for the preparation of a cement paste with standard consistency [10]. The obtained values showed that the use of steel slag in the raw meal only slightly affected the water content for standard consistency and the setting times. The expansion measured, according to the Le Chatelier process, varies from 2.0 to 2.5 mm while the limit according to EN 197-3 is 10 mm [10].

The mortars of the samples under investigation were tested for compressive strengths after 2, 7, 28 and 90 days of curing. The obtained results are shown in Fig. 7. Both mortars presented similar compressive strengths. This fact confirms the probability of the steel slag utilization in the raw meal for cement production.

The XRD patterns of the (PC)_{Ref} and (PC)_{S/S} samples, hydrated for 2, 7, 28 and 90 days, are presented in Figs. 8 and 9, respectively. In both cases, the diffraction peaks of ettringite (Ca₆Al₂(SO₄)₃·32H₂O), CSH, and Ca(OH)₂ appeared in all samples obtained during hydration. Following the hydration progress, the peaks of the C₃S and C₂S phases diminish, especially at the age of 90 days.

4. Conclusions

The addition of steel slag by 10.5% in the raw meal did not affect either the sintering or the hydration process during Portland cement production. More specifically, the sample with steel slag presented the following characteristics:

- The alite phase occurred as small well-formed crystals.
- The belite crystals were evenly distributed in relation to alite, indicating that the clinkering reaction had proceeded extensively in the direction of alite and that the raw mix was homogenous.

- The liquid phase occurred as fine crystals, uniformly distributed.
- The values for setting times, water demand and expansion were similar to those obtained with the reference ordinary Portland cement sample.
- The compressive strengths were at least as high as those of the reference sample during hydration.

It is thus concluded that the steel slag can be utilized as a raw material in cement production, at no cost to the producer, contributing, in this way, to reduction of the process cost.

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