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Red mud addition in the raw meal for the production of Portland cement clinker

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Abstract

The aim of the present research work was to investigate the possibility of adding red mud, an alkaline leaching waste, which is obtained from bauxite during the Bayer process for alumina production, in the raw meal for the production of 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 3.5% red mud ($(PC)_{R/M}$). The effect on the reactivity of the raw mix was evaluated on the basis of the unreacted lime content in samples sintered at 1350, 1400 and 1450 °C. Subsequently, the clinkers were produced by sintering the two raw meals at 1450 °C. The results of chemical and mineralogical analyses as well as the microscopic examination showed that the use of the red mud did not affect the mineralogical characteristics of the so produced Portland cement clinker. Furthermore, both clinkers were tested by determining the grindability, setting time, compressive strength and expansibility. 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 red mud did not negatively affect the quality of the produced cement.

Keywords: Red mud; Sintering; Cement; Hydration

1. Introduction

The general trend of today for the industrial wastes or by-products, which are produced in industrial countries, is to examine alternative ways for their exploitation in order to eliminate cost of disposal and avoid soil and water contamination. Many of these undesirable industrial materials contain significant amounts of inorganic ingredients, such as oxides of silicon, aluminum, calcium and iron, which, at suitable combinations, can be used in the production of Portland cement clinker.

Red mud is produced during the digestion of bauxite with sodium hydroxide. It generally exits the process stream as a highly alkaline slurry (pH 10–12.5) with 15–30% solids [1–4] and it is pumped away for appropriate disposal. It is a complex material whose chemical and mineralogical composition varies widely, depending upon the source of bauxite and the technological process parameters. It contains six major constituents, namely Fe_2O_3, $A1_2O_3$, SiO_2, TiO_2, Na_2O and CaO and small quantities of numerous minor/trace elements (as oxides) such as V, Ga, Cr, P, Mn, Cu, Cd, Ni, Zn, Pb, Mg, Zr, Hf, Nb, U, Th, K, Ba, Sr, rare earths, etc. Every red mud is composed of as many as 14–21 mineral phases [5–9]. Its brick red color is due to the iron oxides.

At all the world's 85 alumina plants, 1.0–1.6 tonnes of red mud is generated per tonne of alumina and it is estimated that over 66 million tonnes of this waste is impounded annually in the world. The disposal of such a large quantity of this alkaline waste sludge is expensive (up to 1–2% of the alumina price), as it requires a lot of land (approximately 1 km^2 per 5 years for a 1 Mtpy alumina plant) and causes a number of environmental problems [1].

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In Greece, the bauxitic red mud from the alumina processing plant is discharged, through a pipe line, at a rate of 500,000 tons/year into Antikyra Bay, on the northern shore line of the central Gulf of Corinth. At the outfall the red mud slurry has a concentration of 500 g/l and bulk density of 1.3 g/l [10–11]. The fine character of the metal-rich red mud, coupled with the shallow water at the dumping site, leads to great dispersion of the material and its transport over long distances. Thus, significant amounts of toxic metals, associated with the bauxitic red mud, are dispersed in the Gulf of Corinth.

It is well known that various industrial wastes, such as metallurgical slags, fly ash, glass, ceramics from the electronic industry, spent catalysts from refineries, sludge from waste water treatment and others, have been successfully used in clinker production [12–14]. These materials are added to the feedstock in such a proportion that the desirable mineralogical composition is achieved. However, the so far published literature has given little attention to the use of red mud in the production of Portland cement.

The aim of the present research work was to investigate the possibility of using red mud 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 3.5% red mud ($(PC)_{R/M}$). The produced clinkers were analyzed chemically and minerlogically by XRD and optical microscopy. The clinkers were then mixed with gypsum and the final cements samples were tested for grindability, setting times, compressive strengths and expansibility. The hydration products were determined by XRD analysis at the ages of 2, 7, 28 and 90 days.

2. Experimental

Uncausticised red mud from Aluminum de Grece was used as received and its mineralogical phases, which were determined by XRD analysis, are given in Fig. 1. The red mud was mixed with other raw materials, such as limestone, schist, Milos sand, ironferous sand and bauxite, in appropriate proportions in order to produce the raw meal to be tested for the production of Portland cement clinker ($(PC)_{R/M}$). A reference raw meal ($(PC)_{Ref}$), without red mud, was also

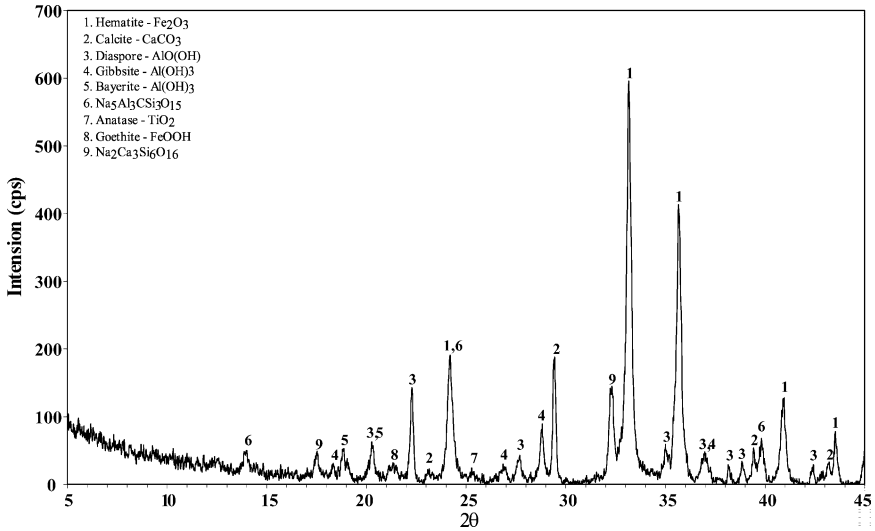

Fig. 1. Mineralogical phases of red mud.

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

Oxides	Content of raw materials (%)					
	Limestone	Schist	Bauxite	Milos sand	Iron sand	Red mud
SiO_2	0.25	52.62	17.58	93.66	1.88	6.80
Al_2O_3	0.08	8.10	42.52	1.64	3.44	19.95
Fe_2O_3	0.06	6.77	24.20	0.46	86.60	40.8
CaO	55.06	9.21	0.84	0.70	0.42	12.60
MgO	0.12	9.17	1.00	0.10	0.34	0.20
K_2O	0.02	0.78	0.76	0.19	0.20	0.14
Na_2O	0.01	0.98	0.15	0.10	0.19	2.70
LOI	43.37	11.10	10.99	3.07	2.29	10.54
SO_3	–	–	–	–	1.83	0.58
TiO_2	–	0.47	2.07	0.40	–	5.80

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

Raw meals	Raw meals composition (%)					
	Limestone (%)	Schist (%)	Bauxite (%)	Milos sand (%)	Iron sand (%)	Red mud (%)
$(PC)_{Ref}$	75.28	14.30	4.50	5.73	0.20	0.00
$(PC)_{R/M}$	74.80	11.40	3.00	7.30	0.00	3.50

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 effect on the burnability was evaluated on the basis of the unreacted lime content in samples sintered at 1200, 1350, 1400 and 1450 °C for 20 min in an electrical furnace and cooled rapidly in air. The unreacted lime (free lime) was determined according to the standard ethylene glycol method.

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. At the end of the sintering process, the samples were removed from the oven and left to cool inside a dryer in order to avoid the effects of air and moisture. The clinkers produced were analyzed by chemical analysis, X-ray diffraction and optical microscopy.

The clinkers were crushed and ground in a Bond ball mill to a specific surface area of about 3950 cm^2/g. Particle size distributions were measured by a laser scattering particle size distribution analyzer (Cilas: Model 1064). An amount of 0.1 g of sample powder was put in 100 ml of ethanol and underwent dispersion treatment by an ultrasonic dispersion unit for 60 s.

The soluble SO_3 content in the clinkers was measured and the ground clinkers were mixed with industrial $CaSO_4 \cdot 2H_2O$, so that the produced laboratory cements contained about 2.5% total soluble SO_3.

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 [15]. The normal consistency and setting times of cement pastes were determined using a Vicat apparatus according to the European Standard EN 196-3 [16]. Expansions of the cement pastes were determined the by Le Chatelier method.

For the study of the hydration products, the cement pastes were prepared by mixing 300 g of ground 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

The reactivity of the raw mixtures was evaluated on the basis of the unreacted lime (CaO_f) content after sintering at various temperatures. The CaO_f content in relation to the sintering temperature of the studied mixtures is given in Fig. 2. As it can be seen, the addition of the red mud in the raw mix led to a well-burnt clinker, with a free lime value of 1.94% at 1450 °C. The corresponding value for the reference sample was estimated at 2.27%.

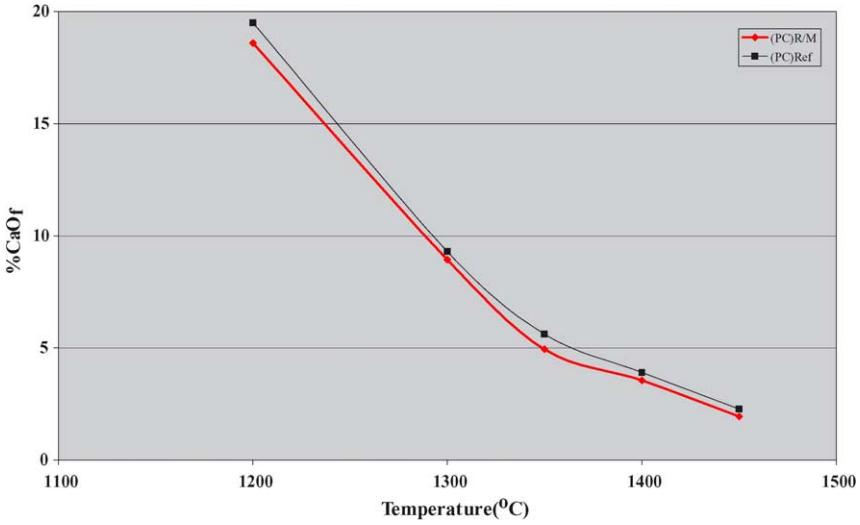

Fig. 2. Free lime at various temperatures for raw mixes with and without red mud.

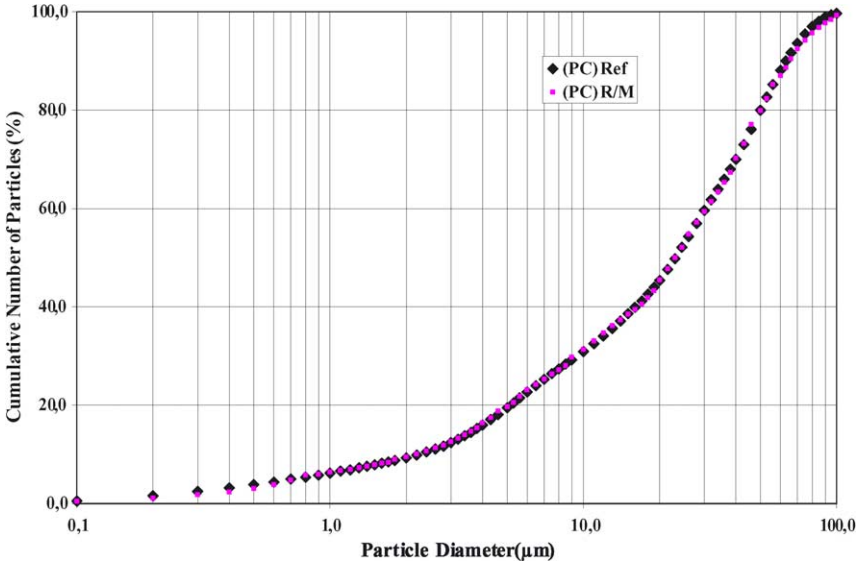

Fig. 3. Particle size distributions of cement samples by a laser scattering analyzer.

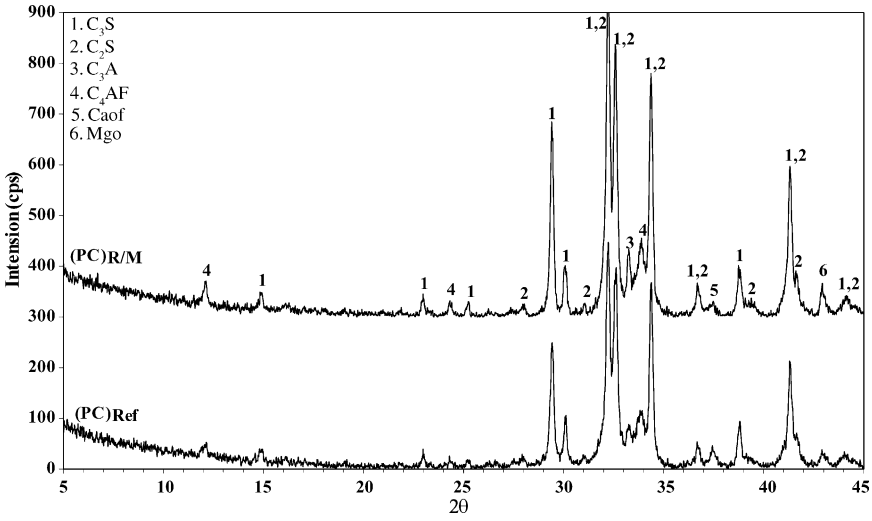

Fig. 4. X-ray diffraction of Portland cement clinkers with and without red mud residue.

The chemical analysis and the potential mineral composition of the Portland clinkers produced are given in Tables 3 and 4, respectively. As the tables show, the addition of the red mud residue by 3.5% did not seem to affect its mineralogical composition.

The clinkers were coground with 5% (w/w) gypsum in a ball mill of 1.5 kg capacity. The gypsum was of industrial origin (98%, w/w, $Ca_2SO_4{\cdot}2H_2O$, 46.7%, w/w, SO_3). 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. As can be seen, the addition of the 3.5 residue did not affect the mineralogical composition of the produced clinker. In both clinker types, the main mineralogical phases, C_3S, C_2S, C_3A and C_4AF, were well formed. The $(PC)_{R/M}$

Table 3
Chemical analysis of the Portland cement clinkers

Oxides	Content of the produced cement clinkers (%)	
	$(PC)_{Ref}$	$(PC)_{R/M}$
SiO_2	21.24	20.80
Al_2O_3	4.61	4.87
Fe_2O_3	3.23	3.87
CaO	66.52	65.78
MgO	2.27	2.40
K_2O	0.42	0.43
Na_2O	0.35	0.36
SO_3	0.30	0.35
TiO_2	0.28	0.54
CaO_f	2.30	1.95
LOI	0.22	0.23

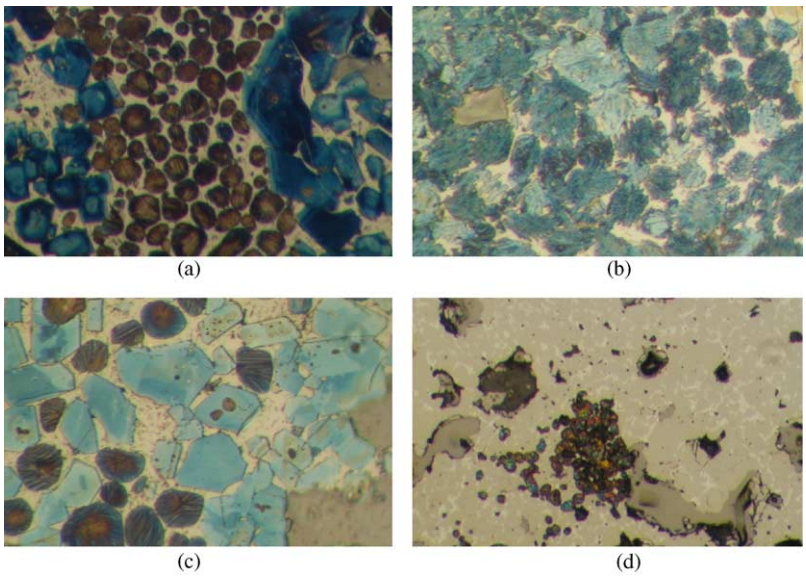

Fig. 5. Microstructure of Portland cement clinker without red mud residue: (a) large crystals C_3S, cluster C_2S (×500), (b) finger C_2S because of slow cooling (×500), (c) fine crystals of C_3A (×500), (d) small clusters of CaO_f (×200).

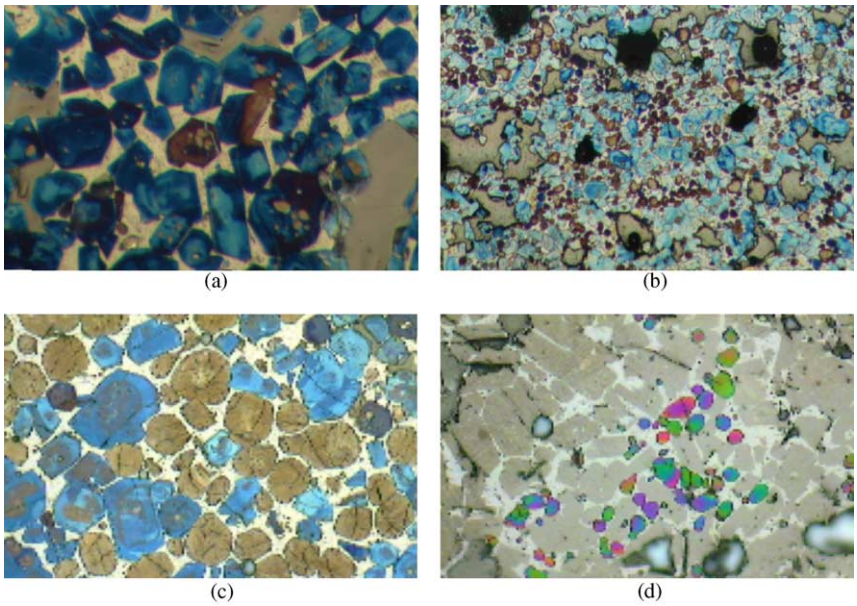

Fig. 6. Microstructure of Portland cement clinker with red mud residue: (a) well-formed alite crystals (×500), (b) crystals C_2S scattering among alite (×100), (c) high percentage of C_4AF (×500), (d) CaO_f scattering among alite (×500).

clinker contained more C_3A and less C_4AF than the $(PC)_{Ref}$ clinker. These differences were attributed to the partial replacement of schist and bauxite with red mud, which is higher in iron aluminum than the former. CaO_f was relatively higher in the reference synthesis, probably due to its higher content of CaO.

The microstructure of the Portland cement clinkers was examined by optical microscopy in polished sections. The addition of the red mud residue by 3.5% 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, especially in the $(PC)_{R/M}$ synthesis. Both clinkers contained more or less euhedral alite and they exhibited coalescence of alite crystals. In the case of $(PC)_{R/M}$, the alite crystals appeared well formed, with size 40 μm, whereas no decomposition of C_3S was observed. On the other hand, the size of C_3S, in the case of $(PC)_{Ref}$, was about 45 μm. In the optical microscope, belite was observed as bluish or brownish rounded crystals, rich in lamellas. No differences in the microstruc-

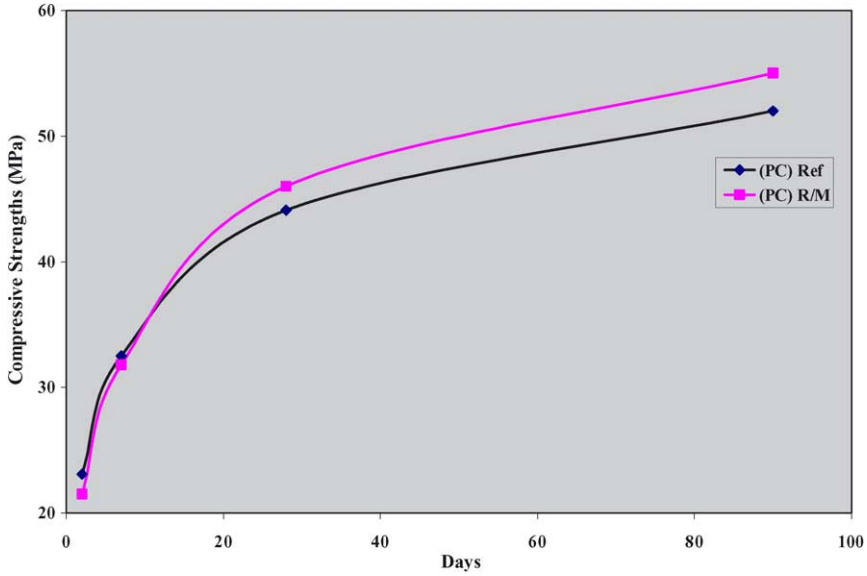

Fig. 7. Compressive strengths of the cements produced.

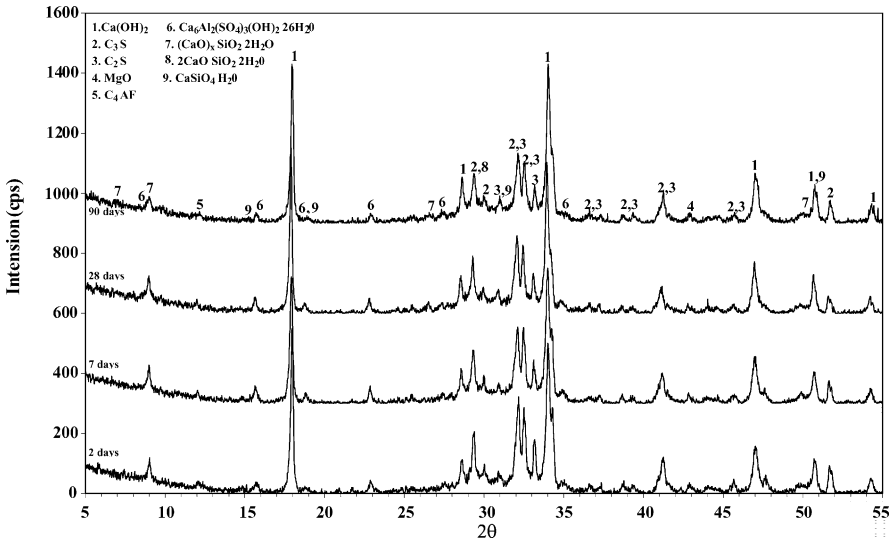

Fig. 8. X-ray diffraction of $(PC)_{Ref}$ pastes at 2, 7, 28 and 90 days.

ture of belite between $(PC)_{Ref}$ and $(PC)_{R/M}$ clinkers were detected, except that the $(PC)_{Ref}$ sample, occasionally, showed finger C_2S, apparently because of slow rate of cooling. In the reference clinker, the belite crystals existed mainly in nests and appeared as clusters. In the $(PC)_{R/M}$ clinker, belite crystals were few and 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 much more homogenous. Finally, in the $(PC)_{R/M}$ clinker, the liquid phase occurred as uniformly distributed fine crystals, whereas, in the case of $(PC)_{Ref}$, large crystals of C_3A were observed.

The water requirement and setting time, determined by Vicat probe and Vicat needle apparatus, as well as the results of expansion are reported in Table 6. The obtained values showed that the use of red mud 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, was well below the maximum accepted value of 10 mm (EN 197-3).

Table 4
Mineralogical composition of the produced Portland cement clinkers

Mineralogical phases	Cement clinkers composition (%)	
	$(PC)_{Ref}$	$(PC)_{R/M}$
C_3S	63.50	61.91
C_2S	13.08	13.02
C_3A	6.76	6.37
C_4AF	9.82	11.76

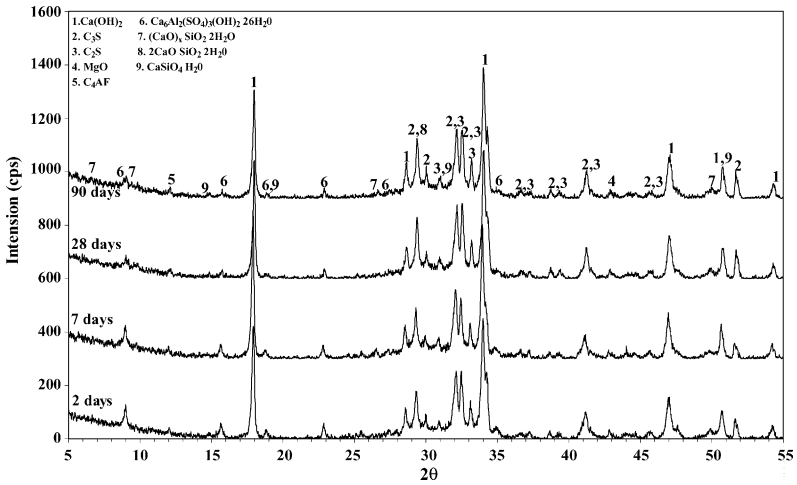

Fig. 9. X-ray diffraction of $(PC)_{R/M}$ pastes at 2, 7, 28 and 90 days.

Table 5
Results of grindability tests

Number of sample	$(PC)_{Ref}$	$(PC)_{R/M}$
Mill revolutions	4150	4100
Specific surface (Blaine, cm^2/gr)	3950	3960
Grindability index	0.95	0.97
Specific gravity (g/cm^2)	3.12	3.14
SO_3 (%)	2.45	2.40

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. The mortar, which contained the $(PC)_{R/M}$ clinker, showed relatively higher compressive strengths than the $(PC)_{Ref}$, especially at the ages of 28 and 90 days. This fact confirms the probability of the red mud utilization in the raw meal for cement production.

The XRD patterns of the $(PC)_{Ref}$ and $(PC)_{R/M}$ samples, hydrated at 2, 7, 28 and 90 days, are presented in Figs. 8 and 9, respectively. In both cases, the diffraction peaks of ettringite, CSH and $Ca(OH)_2$ appeared in all samples obtained during hydration. The peaks of the C_3S and C_2S phases diminish, especially at the age of 90 days. The higher peaks of $Ca(OH)_2$, in the case of $(PC)_{R/M}$, indicate a higher hydration rate than the $(PC)_{Ref}$ sample, at the ages of 2 and 7 days. Following the hydration progress, through peaks of $Ca(OH)_2$, at the ages of 28 and 90 days, it was possible to observe a higher intensity of these peaks in the case of $(PC)_{R/M}$.

Table 6
Results of setting time and expansibility

Sample	$(PC)_{Ref}$	$(PC)_{R/M}$
Initial time (min)	145	150
Final time (min)	225	215
Water of normal consistency (%)	23.3	24.1
Expansion (mm) (Le Chatelier)	1.5	2.0

4. Conclusions

The addition of red mud residue by 1% in the raw meal did not affect either the sintering or the hydration process during Portland cement production. More specifically, the sample with red mud presented the following characteristics:

1. The alite phase occurred as small well-formed crystals.
2. The belite crystals were few and 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.
3. The liquid phase occurred as fine crystals, uniformly distributed.
4. The values for setting times, water content for standard consistency and expansion were similar to those obtained with the reference ordinary Portland cement sample.
5. The compressive strengths were at least as high as those of the reference sample during hydration.

It is thus concluded that the red mud residue, produced during the digestion of bauxite with sodium hydroxide, 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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