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Communication

The formation of belite phase by using phosphogypsum and oil shale

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Abstract

This investigation aims at gaining in-depth knowledge for the cement clinker production by utilizing phosphogypsum (PG) and oil shale (OS) as raw materials. The raw mixtures (Raw Mix I and Raw Mix II) were burnt in a muffle furnace and then analyzed by X-ray diffraction (XRD) to observe the phases obtained. While fluorellestadite ($Ca_{10}(SiO_4)_3(SO_4)_3F_2$) and akermanite ($Ca_2MgSi_2O_7$) phases were observed with the Raw Mix I composed of 51.43% PG, 16.59% OS, 8.23% stone coal (SC) and 23.75% kaolinite clay (KC) in N_2 atmosphere at the temperature range of 1200–1300°C, the mineralogical phase belite (β-C_2S) of Portland cement (PC) was formed even at 1200°C by using the raw mixtures (Raw Mix II) composed of 35.84% PG, 11.56% OS, 5.73% SC, 16.55% C and 30.32% CaO. The intensity and the amount of belite peaks were increased with increasing burning temperature.

Keywords: Sulfate; Mineralizers; Clinker; Waste management; X-ray diffraction

1. Introduction

Alternatives for utilization of the massive amounts of a class of industrial by-product "gypsum," especially phosphogypsum (PG) have been sought worldwide due to growing environmental concerns [1]. Utilization of massive amounts of fossil fuels and carbonate containing raw material in conventional cement production caused serious environmental concerns worldwide to produce low-energy cement clinker with novel raw materials instead of carbonates and fluxing agents or mineralizers reducing clinkering temperature [2–7]. On the other hand, the production of cements in which alite (C_3S) is replaced by belite (β-C_2S) is another energy-saving idea, since the formation of C_2S is complete at a much lower clinkering temperature than the formation of C_3S [8–10]. Recently, some investigators [11,12] used PG-containing raw mixes to produce energy-saving cements. The available information in the area is somewhat controversial and is far from being sufficient for drawing conclusive results. Therefore, the authors of this study investigated also on one hand the formation of clinker phases with PG and oil shale (OS) in a muffle furnace [13], on the other hand the reductive decomposition of PG with OS to produce cement clinker at lower temperatures than that of a conventional one in a bench scale fluidized bed reactor [14].

In the present study, burning experiments at the temperatures of 1100 – 1300°C were carried out in a muffle furnace by using PG and OS as raw materials with the additives of stone coal (SC) and kaolinite clay (KC) to obtain clinker phases.

2. Experimental

2.1. Materials

PG was provided by TÜGSAS Samsun fertilizer plant, while OS samples were from Beypazar1 deposits. Besides these materials SC, KC, and CaO were added to the raw mixes prepared with PG and OS. SC was provided by the General Directorate of Mineral Research and Exploration (MTA) of Turkey in Ankara and KC was taken from the Turkish Cement Manufacturers Association (TCMA). The complete chemical analysis of materials and prepared raw mixtures (Raw Mixes I and II) are given in Table 1.

2.2. Method

The composition of Raw Mix I is given in Table 2 according to the exact values of silicate ratio (SR), alumi-

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Table 1
Chemical analysis of materials (w/w%)
Raw Mix I (w/w%): 16.59 OS + 51.43 PG + 8.23 SC + 23.75 KC. Raw Mix II (w/w%): 11.56 OS + 35.84 PG + 5.73 SC + 16.55 KC + 30.32 CaO.

	MgO	Al_2O_3	SiO_2	CaO	Fe_2O_3	SO_3	K_2O	Na_2O	F^-	P_2O_5	LOI
PG	0.07	0.36	1.17	32.68	0.07	42.28	0.02	0.04	1.79	0.49	21.82
OS	7.73	5.86	23.65	13.64	3.36	1.10	3.03	0.75	–	0.08	38.83
KC	0.35	13.92	51.74	12.81	3.77	0.16	2.62	0.17	–	–	13.87

Table 2
Values of SR, AR, and LSF of raw mixes

Materials	SR	AR	LSF (%)
Raw Mix I	2.44	3.98	37.46
Raw Mix II	2.44	3.98	95.63

Table 3
Experimental techniques and conditions used

Raw material	Apparatus	Medium	Temperature	Remarks
Raw Mix I	Muffle furnace	N_2	1100–1300°C	with ambient cooling of burnt raw mix to XRD (burning time: 1 h)
Raw Mix II	Muffle furnace	N_2	1100–1300°C	with ambient cooling of burnt raw mix to XRD (burning time: 1 h)

nate ratio (AR), and lime saturation factor (LSF) and was burned for 1 h at a temperature range of 1100–1300°C in N_2 atmosphere in a muffle furnace (Protherm, Alser, Ankara). The burnt product was taken to X-ray diffraction (XRD) Analyzers (Rikagu D-max 2200, Japan and Philips CuK_α, Netherlands) to determine the formation of the clinker phases in PC. The second raw mix containing a lesser amount of PG than the first one was burned at temperatures ranging from 1100°C to 1300°C in N_2 atmosphere and was mineralogically analyzed in XRD Analyzer. As the LSF value of the Raw Mix I was lower than that of PC, CaO was used to adjust the LSF value to that of PC as can be discerned from Table 2. The ranges of experimental conditions and the instruments used to determine clinker phases are given in Table 3 for the Raw Mix I and Raw Mix II.

3. Results and discussion

3.1. Results of experiments with the Raw Mix I

This raw mixture gave major amounts of oldhamite (CaS) and gehlenite ($Ca_2Al_2SiO_7$) and minor amounts of wollastonite ($CaSiO_3$) phases at 1100°C in N_2 atmosphere as shown in Fig. 1. When this raw mixture was burned at 1200°C in N_2 medium, akermanite ($Ca_2MgSi_2O_7$) and fluorellestadite ('Fell') [$Ca_{10}(SiO_4)_3(SO_4)_3F_2$] phases were observed as seen from Fig. 2. This quaternary compound was indicated in Refs. [5,6] as a characteristic phase of mineralized white cement. The authors [5,6] indicated that Fell can be formed from its oxides at temperatures as low as 750°C, and is stable up to 1240°C, at which temperature melts it incongruently to C_2S and liquid. Since the clinker phases, belite and alite, were not observed at these temperatures, burning temperature of the Raw Mix I in a muffle furnace was increased to 1300°C. As seen in Fig. 3, all peaks observed were entirely akermanite ($Ca_2MgSi_2O_7$).

3.2. Results of experiments with the Raw Mix II

This raw mixture was firstly burned at 1100°C in N_2 atmosphere in a muffle furnace. Since the anhydrite ($CaSO_4$) and CaO as major and calcium silicate sulphate ($Ca_5(SiO_4)_2SO_4$) as minor phases were observed at that temperature, burning of Raw Mix II was then carried out at 1200°C. Although major amounts of anhydrite were formed, minor amounts of belite structures could be formed even at 1200°C as shown in Fig. 4. In a previous study of the authors [13], belite could be obtained only at temperatures exceeding 1250°C with the raw materials containing 30%

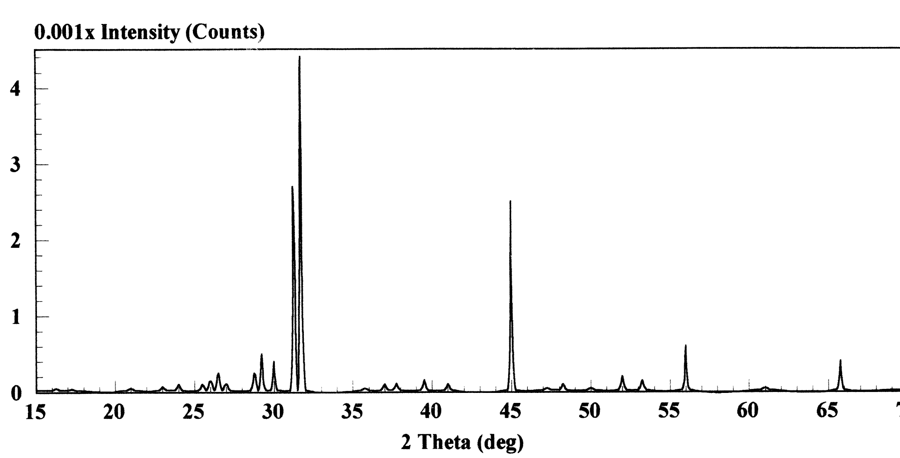

Fig. 1. The XRD of the burnt Raw Mix I at 1100°C in N_2 atmosphere. 2θ values of phases: gehlenite ($Ca_2Al_2SiO_7$) 2θ: 16.25, 17.25, 21, 24, 26, 29.25, 31.5, 35.75, 37, 37.75, 39.5, 41, 47.25, 50, 52, 53.25, 61; wollastonite ($CaSiO_3$) 2θ: 23, 25.75, 26.5, 28.75, 30, 48.25; oldhamite (CaS) 2θ: 27, 31.75, 45, 56, 65.75.

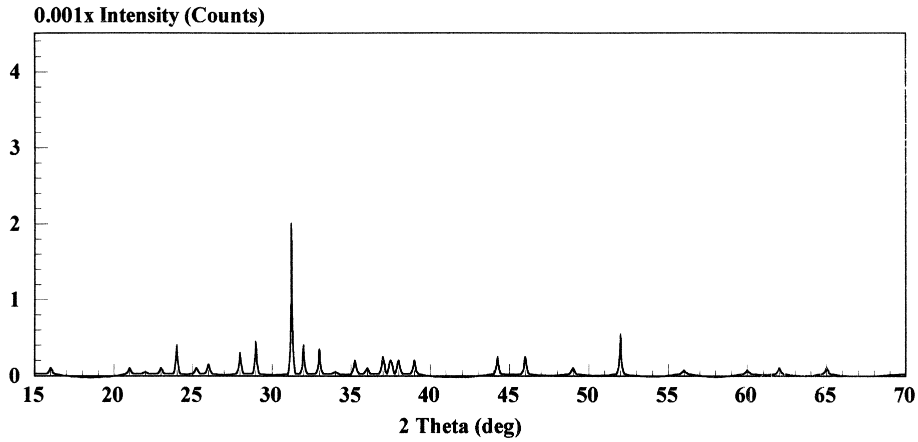

Fig. 2. The XRD of the burnt Raw Mix I at 1200°C in N_2 atmosphere. 2θ values of phases: akermanite ($Ca_2MgSi_2O_7$) 2θ: 16, 21, 23, 24, 25.25, 29, 31.25, 36, 37, 37.25, 38, 39, 44.25, 46, 49, 52, 62; fluorellestadite ($Ca_{10}(SiO_4)_3(SO_4)_3F_2$) 2θ: 22, 26, 28, 32, 33, 34, 35.25, 56, 60, 65.

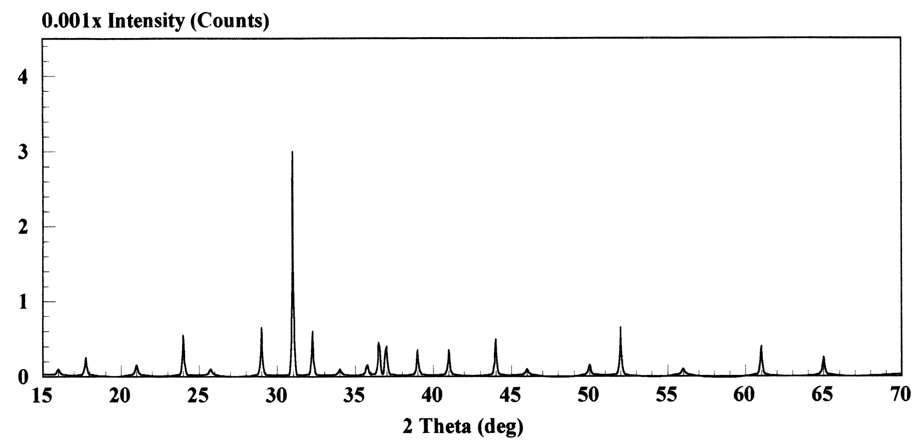

Fig. 3. The XRD of the burnt Raw Mix I at 1300°C in N_2 atmosphere. 2θ values of phases: akermanite ($Ca_2MgSi_2O_7$) 2θ: 16, 17.75, 21, 24, 25.75, 29, 31, 32.25, 34, 35.75, 36.5, 37, 39, 41, 44, 46, 50, 52, 56, 61, 65.

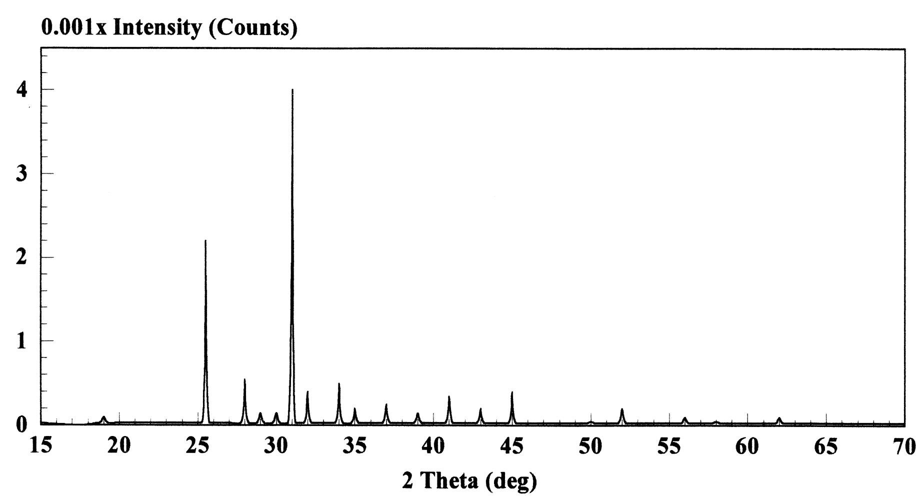

Fig. 4. The XRD of the burnt Raw Mix II at 1200°C in N_2 atmosphere. 2θ values of phases: belite (larnite, β-C_2S) 2θ: 19, 28, 29, 30, 32, 34, 35, 37, 39, 41, 45, 50, 58; anhydrite ($CaSO_4$) 2θ: 25.5, 31, 43, 52, 56, 62.

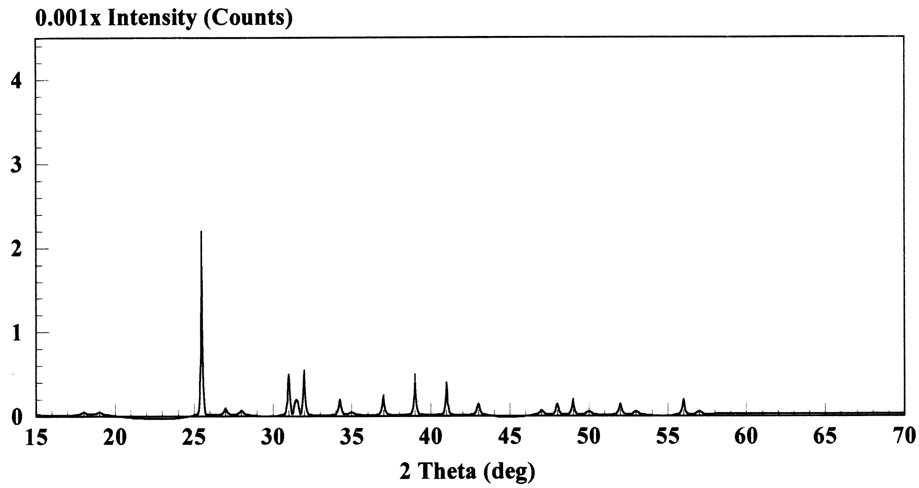

Fig. 5. The XRD of the burnt Raw Mix II at 1300°C in N_2 atmosphere. 2θ values of phases: belite (larnite, β-C_2S) 2θ: 18, 19, 27, 28, 31.5, 32, 34.25, 35, 37, 41, 43, 45, 48, 50, 52, 53, 57; anhydrite ($CaSO_4$) 2θ: 25.5, 31, 39, 47, 49, 56.

(w/w) OS and 70% (w/w) PG. When the raw mixture was burned at 1300°C in N_2 atmosphere, the intensity of belite peaks in Fig. 4 was increased as can be seen from Fig. 5.

4. Conclusion

When the raw mixture composed of 51.43% PG (Raw Mix I) was burned in the muffle furnace, any belite phase of PC was obtained. As the percentage of PG was decreased to 35.84% (Raw Mix II), belite phase was formed even at a burning temperature of 1200°C. The intensity of belite peaks was increased with increasing burning temperature. Any alite phase of PC was identified at the temperature range worked with these raw mixes. These findings were reported also for the mineralized cements [5,6]. Gimenez-Molina and Blanco-Varela [5] indicated that alite phase could be identified only as compatible in the solid state in the diagram zone poor in $CaSO_4$ and rich in CaF_2. Blanco-Varela et al. [6] reported that the raw mixes giving 'Fell' produced a melt phase rich in much alite (C_3S) with thermal treatment at temperatures of 1300–1400°C. Viswanathan et al. [10] developed a new inorganic cement named PORSAL consisting of 60% belite with no alite phase by burning of conventional raw materials with the mineralizer CaF_2 below 1350°C. On the other hand, Beretka et al. [11] used the raw mixes containing PG in a range of 32.75–37.35 (w/w%) with conventional limestone, fly-ash, and boxite. They obtained calcium sulpho aluminate (C_4A_3S) phase which gives higher mechanical strength at early ages due to rapid formation of non-expansive ettringite. Gadayev and Kodess [12] could obtain an insufficient quantity of alite (20–30% instead of 50–60%) only with the decreased content of the PG (10%) in raw mixes. It might be concluded from these findings that the PG and OS can be utilized as constituents of raw mixes to form clinker phases of PC by decreasing the percentage of PG in raw mixes.

Acknowledgments

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