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The formation of alite phase by using phosphogypsum and oil shale

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Abstract

This study 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 Mixes I and II) were burnt in a muffle furnace and then analyzed by X-ray diffraction (XRD) to observe the phases obtained. While minor amounts of alite (C_3S) and major amounts of anhydrite phases were observed with the Raw Mix I containing 40.72% PG refined with water and lime wash by two and three times, respectively (PGR^{23}), in N_2 atmosphere at 1300 °C, minor amounts of alite (C_3S), free CaO and major amounts of anhydrite phases were formed in air atmosphere at 1300 °C with the Raw Mix II containing 40.72% PG refined with water and lime wash by three and four times, respectively (PGR^{34}). The change of burning medium and the increase in the number of wash with water and lime, respectively, resulted in any difference in terms of the formation of the alite peaks; however, the intensity and the amount of anhydrite peaks were decreased in N_2 atmosphere due to the more conversion of that to the oxide compared to that in air atmosphere.

Keywords: X-Ray diffraction; Clinker; Sulfate; Waste management

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]. Gimenez-Molina and Blanco-Varela [3] indicated that the 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 as mineralizer. Blanco-Varela et al. [4] 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. 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, because the formation of C_2S and calcium sulpho aluminate (C_4A_3S) is complete at a much lower clinkering temperature than the formation of C_3S [5]. Recently, Arjunan et al. [6] used three types of industrial waste materials, namely, bag house dust, class F fly ash and scrubber sludge and obtained calcium sulpho aluminate (C_4A_3S)-belite cement (SAB) which gives higher mechanical strength at early ages due to rapid formation of nonexpansive ettringite at approximately 1250 °C. Rodrigues [7] synthesized dicalcium silicate by using silica obtained from rice hull ash and analytical grade CaO or that obtained from thermal decomposition of $CaCO_3$ and analytical grade $BaCl_2.2H_2O$. Beretka et al. [8] 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 only the calcium sulpho aluminate (C_4A_3S) phase. Gadayev and Kodess [9] could obtain an insufficient quantity of alite (20–30%, instead of 50–60%) only with the decreased content of PG (10%) in raw mixes. The previous studies of the authors [10,11] revealed that the belite phase of the portland cement (PC) was formed even at temperatures of 1250–1350 °C from the original PG and oil shale (OS) materials containing F^-, P_2O_5 impurities and the intensity of those peaks was increased in N_2 atmosphere. The available information in the area is somewhat controversial and is far from being sufficient for drawing conclusive results.

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Table 1
Complete chemical analysis of materials (w/w%)

Raw Mix I (w/w%): 40.72 PGR^{23} + 6.79 sand + 6.79 OS + 13.57 SC + 32.13 CaO
Raw Mix II (w/w%): 40.72 PGR^{34} + 6.79 sand + 6.79 OS + 13.57 SC + 32.13 CaO
(SR = 2.82; AR = 4.61; LSF% = 108.7; HM = 2.56)

Material	MgO	Al_2O_3	SiO_2	CaO	Fe_2O_3	SO_3	K_2O	Na_2O	TiO_2	Mn_2O_3	P_2O_5[a]	L.O.I
PG	0.07	0.36	1.17	32.68	0.07	42.28	0.02	0.04	0.09	0.00	0.49	21.82
OS	7.73	5.86	23.65	13.64	3.36	1.10	3.03	0.75	0.31	0.08	0.08	38.83
SC	0.3	25.01	35.04	4.53	4.37	1.26	1.5	0.32	–	–	–	
KC	0.1	11.45	79.75	1.9	0.54	–	0.16	0.06	–	–	–	
Sand	0.1	0.2	99.1	0.2	0.1	–	0.2	0.1	–	–	–	

PGR^{23}: refinement of original PG with two times water and three times lime wash, respectively.

PGR^{34}: refinement of original PG with three times water and four times lime wash, respectively.

[a] Fluoride impurity of PG was determined as 1.79% (w/w) separately by using Ion Selective Electrode of ORION 960 Autochemistry System (Boston, USA).

In the present study, burning experiments at 1300 °C selected from the results of the previous studies of the authors [10,11] were carried out in a muffle furnace by using OS and differently refined PG (PGR^{23} and PG^{34}) as raw materials with the additives of stone coal (SC), kaolinite clay (KC) and CaO to obtain the alite phase of the PC in N_2 and air medium.

2. Experimental

2.1. Materials

PG was provided by TÜGSAŞ Samsun fertilizer plant, while OS samples were from Beypazarı deposits of Turkey. Besides these materials, SC, KC and CaO were added to the raw mixes prepared with OS and the refined/burnt PG. 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 (TÇMB). The complete chemical analysis of materials and prepared raw mixtures with the exact values of silicate ratio (SR), aluminate ratio (AR), lime saturation factor (LSF) and hydraulic module (HM) are given in Table 1. While the original PG was refined with water and lime wash by two and three times in the preparation of PGR^{23} for the Raw Mix I, PG of the Raw Mix II (PGR^{34}) was prepared by using three times water and four times lime wash as can also be discerned from Table 1.

Table 2
Experimental techniques and conditions used

Raw material	Apparatus	Medium	Temperature (°C)	Remarks
Raw mix I	Muffle furnace	N_2	1300	With ambient cooling of burnt raw mix to XRD (burning time: 1 h)
Raw mix II	Muffle furnace	Air	1300	With ambient cooling of burnt raw mix to XRD (burning time: 2 h)

2.2. Method

The ranges of experimental conditions and the instruments used to determine clinker phases are given in Table 2 for the Raw Mix I and Raw Mix II. The raw materials were burnt in a muffle furnace (Protherm/Alser, Ankara) for 1 h at 1300 °C in N_2 and air atmosphere for the Raw Mix I and Raw Mix II, respectively. The burnt products were taken to X-ray diffraction (XRD) analyzers (Rikagu D-max 2200, Japan) to determine the formation of the clinker phases in PC.

3. Results and discussion

3.1. Results of experiments with the Raw Mix I

This raw mixture gave major amounts of anhydrite ($CaSO_4$) and minor amounts of tricalcium silicate (C_3S,

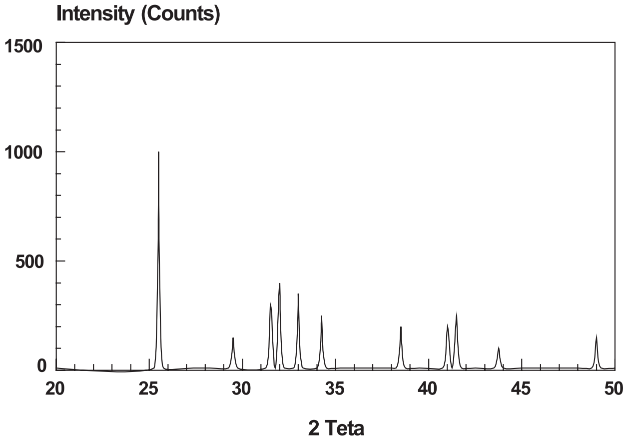

Fig. 1. The XRD of the burnt Raw Mix I at 1300 °C in N_2 atmosphere. 2θ values of phases: anhydrite: 25.5, 31.5, 38.5, 41, 43.75 and 49; alite: 29.5, 32, 33, 34.25 and 41.5.

alite) phases at 1300 °C in N_2 atmosphere as shown in Fig. 1. In the previous studies of the authors [10,11], the clinker phase obtained was only belite and the intensity of belite peaks could be increased only at temperatures exceeding 1250 °C with the raw materials containing more than 35% original PG. For the first time, alite peaks could be obtained at the conditions worked with the refinement of the original PG by using water and lime wash as indicated above.

3.2. Results of experiments with the Raw Mix II

Because the anhydrite ($CaSO_4$), as a major phase, and alite (C_3S), as a minor phase, were observed in N_2 medium with the Raw Mix I, the numbers of wash with water and lime, respectively, were increased in the refinement of the original PG for the Raw Mix II and that the mix was burnt in an air medium for 2 h at 1300 °C. This refinement procedure and the change of burning medium resulted in any difference in terms of the formation of the alite peaks but the intensity and the amount of anhydrite peaks were increased in air atmosphere as shown in Fig. 2 compared to that in N_2 atmosphere (Fig. 1).

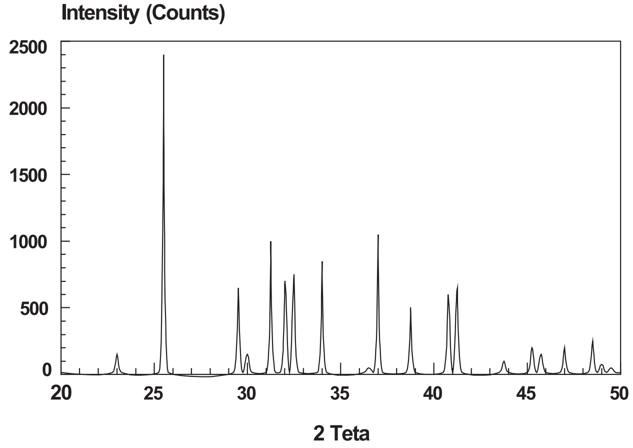

Fig. 2. The XRD of the burnt Raw Mix II at 1300 °C in air atmosphere. 2θ values of phases: alite: 23, 29.5, 30, 32, 32.5, 34, 41.25, 45.75 and 49.5; anhydrite: 25.5, 31.25, 36.5, 38.75, 40.75, 43.75, 45.25, 47, 48.5 and 49; CaO: 37.

3.3. Results of compressive strength experiments with the Raw Mix I and Raw Mix II

These experiments were made according to the Turkish Standards (TS-24) by preparing mortar mixtures as described in this standard method [12]. Consequently, the exhibited compressive strength values of the burnt products of the raw mixes used, which were much lower than that of the mortar cement and PC 32.5, were found as 2.3 and 5 N/mm^2 for 7 and 28 days, respectively. On the other hand, the comparable compressive strength values of the burnt products (9 and 22 N/mm^2 for 7 and 28 days, respectively) with that of the mortar cement could be obtained only by using both refined and precalcined PG as described in detail elsewhere [13,14]. As indicated by Ölmez and Yılmaz [15], all of the water-soluble impurities of PG can be removed by the simple washing treatment with water and lime as applied also in the present study, but P_2O_5 substituted in the crystal lattice of gypsum cannot be taken away from the cocrystalline form by that practice. The amount of P_2O_5 is affecting the early strength of the cement, as it interferes with the formation of C_3S [16].

4. Conclusion

When the raw mixture containing 40.72 % PGR^{23} (Raw Mix I) was burned in the muffle furnace in N_2 atmosphere for 1 h, minor amounts of the alite phase of PC was identified for the first time with the major amounts of anhydrite phase at 1300 °C. The change of burning atmosphere to air and the increase in the number of wash with water and lime, respectively, for the Raw Mix II, resulted in any difference in terms of the formation of the alite peaks but the intensity and the amount of anhydrite peaks were decreased in N_2 atmosphere compared to that in air atmosphere. The formation of the alite phase could be identified without decreasing the content of the PG or anhydrite ($CaSO_4$) at 1300 °C in the present study as a contrary to the findings for the mineralized cements [3,4] and the cements obtained from chemical gypsum and other industrial wastes [6–9]. 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 with the refinement of PG in a reducing (inert) medium without decreasing the percentage of PG in raw mixes, giving lower compressive strength values than that of mortar cement at early ages. As indicated also in the corresponding literatures [6–8], the mechanical strength of cements obtained from chemical gypsum and industrial wastes (calcium sulpho aluminate cements) can be retained or improved at 28 days or more, even if it is strongly reduced at early ages.

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