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Thermal analysis of borogypsum and its effects on the physical properties of Portland cement

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Abstract

Borogypsum, which consists mainly of gypsum crystals, B_2O_3 and some impurities, is formed during the production of boric acid from colemanite, which is an important borate ore. In this study, the effect of borogypsum and calcined borogypsum on the physical properties of ordinary Portland cement (OPC) has been investigated. The calcination temperature and transformations in the structures of borogypsum and natural gypsum were determined by differential thermal analysis (DTA), thermogravimetric analysis (TGA) and X-ray diffraction (XRD) techniques. Thermal experiments were carried out between ambient temperature and 500 °C in an air atmosphere at a heating rate of 10 °C min^{-1}. After calculation of enthalpy and determination of conversion temperatures, borogypsum (5% and 7%), hemihydrate borogypsum (5%) and natural gypsum (5%) were added separately to Portland cement clinker and cements were ground in the laboratory. The final products were tested for chemical analysis, compressive strength, setting time, Le Chatelier expansion and fineness properties according to the European Standard (EN 196). The results show that increasing the borogypsum level in Portland cement from 5% to 7% caused an increase in setting time and a decrease in soundness expansion and compressive strength. The cement prepared with borogypsum (5%) was found to have similar strength properties to those obtained with natural gypsum, whereas a mixture containing 5% of hemihydrate borogypsum was found to develop 25% higher compressive strength than the OPC control mixtures at 28 days. For this reason, utilization of calcined borogypsum in cement applications is expected to give better results than untreated borogypsum. It is concluded that hemihydrate borogypsum could be used as a retarder for Portland cement as an industrial side. This would play an important role in reducing environmental pollution.

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Keywords: Portland cement; Thermal analysis; X-ray diffraction; Physical properties; Mechanical properties; Borogypsum

1. Introduction

Over 120 million tons of borogypsum is produced as an industrial by-product of boric acid production at the factories of the Bandırma Etibank Foundation in Turkey. The material consists mainly of gypsum, B_2O_3 and some impurities and causes various environmental and storage problems. Borogypsum is a valuable raw material on account of its boron content, but B_2O_3 causes water and soil pollution [1–3]. Some useful processes have been applied to borogypsum to lower the undesired B_2O_3 content by reaction with water and carbonate solutions (Na_2CO_3 and $NaHCO_3$) [4,5]. The usage of borogypsum in the cement industry as an alternative to gypsum has been investigated [6–9]. In these studies, borogypsum with different B_2O_3 ratios was mixed with clinker in order to observe its effects on the physical and chemical properties of the cement.

In the present study, the conversion temperatures of borogypsum to hemihydrate and soluble anhydrite structures are determined and compared to those of natural gypsum. In addition, the physical and mechanical properties of cements prepared using borogypsum and hemihydrate borogypsum as cement additives in cement are investigated.

2. Materials and methods

2.1. Raw materials

The chemical compositions of materials used in the experiments are presented in Table 1. The borogypsum samples were collected from boric acid plants in Bandırma. Colemanite is treated with sulfuric acid solutions during the production of boric acid. In the process, press-filtration

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Table 1
Chemical composition of materials

Constituents (%)	Borogypsum	Natural gypsum	Hemihydrate borogypsum (at 190 °C)	Cement clinker
SiO_2	7.740	5.800	8.940	22.030
Al_2O_3	1.370	0.620	2.290	5.900
Fe_2O_3	0.740	0.310	0.680	3.610
CaO	25.240	28.790	28.640	65.100
MgO	0.880	0.200	3.360	1.210
Na_2O	0.100	–	0.060	0.230
K_2O	0.790	–	0.780	0.950
SO_3	35.620	43.200	37.340	0.240
Cl^-	0.004	–	0.013	0.004
Loss on ignition	20.910	20.830	9.020	0.130
B_2O_3	7.000	–	8.800	–
Free CaO	–	–	–	1.460

treatment is applied in order to separate the undesired solid compounds prior to boric acid crystallization. Some of the boric acid solution remains in the cake while the filtration is over. At this stage, borogypsum is obtained as a filtration cake. The reaction is given below.

$$Ca_2[B_3O_4(OH)_3]_2 \cdot 2H_2O + 2H_2SO_4 + 4H_2O$$
$$\rightarrow 6H_3BO_3 + 2[CaSO_4 \cdot 2H_2O]$$

2.2. Determination of conversion temperatures, heat flow and structure by DTA–TGA, XRD

The conversion temperature of borogypsum to hemihydrate structure was monitored by differential thermal analysis (DTA) and thermogravimetric analysis (TGA). DTA–TGA curves for natural gypsum and borogypsum samples were obtained by using closed alumina crucibles in an air atmosphere at a heating rate of 10 °C min^{-1}. The particle size of the borogypsum was found to lie in the range 0.140–0.071 mm. Hemihydrate and soluble anhydrite borogypsum samples were produced at 190 and 220 °C, respectively, and their conversion patterns were confirmed by X-ray diffraction (XRD) studies. The apparatus used for the DTA–TGA analysis was manufactured by Setaram. The furnace used was equipped with a computer programmer, which permits variation of temperatures up to maximum 1600 °C. DTA permits the determination of the temperature and the nature of the different transformations (dehydration and allotropic transformations) [10,11].

2.3. Preparation and testing methods of cements

Portland cements were produced by intergrinding the Portland cement clinker with borogypsum (5% and 7%), hemihydrate borogypsum (5%) and natural gypsum (5%) by grinding mill. The cements were tested for compressive strength, chemical analysis, setting time, Le Chatelier expansion and fineness properties as per the European Standards, EN 196-1, EN 196-2, EN 196-3, EN196-6 [12–15]. All of these experiments were carried out in the Akçansa Cement Factory in İstanbul, Turkey under real industrial conditions.

3. Results and discussions

3.1. Characterization of natural gypsum by thermal analysis

DTA–TGA curves for gypsum determined at a 10 °C min^{-1} heating rate are presented in Fig. 1. There were two

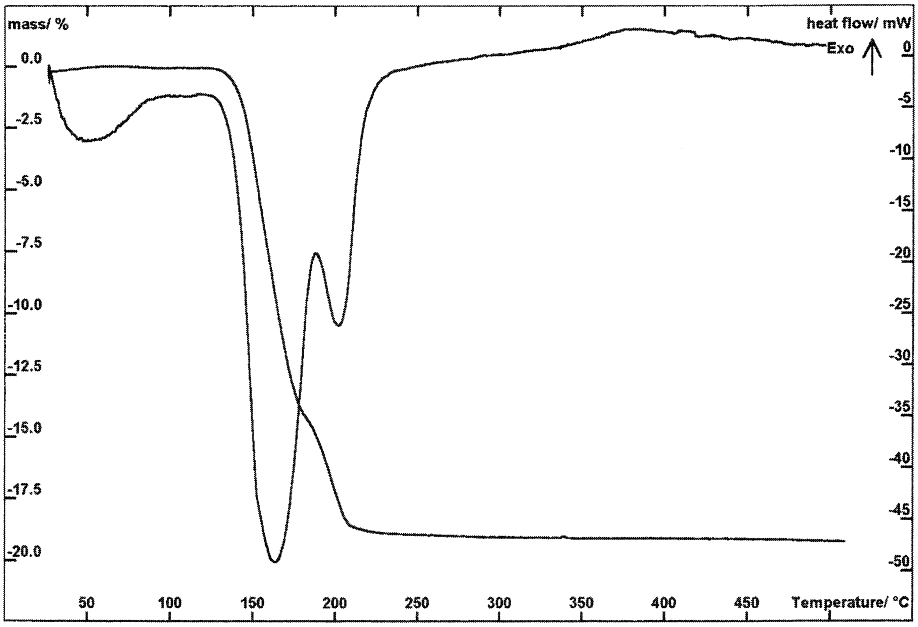

Fig. 1. DTA–TGA curves of the natural gypsum.

basic endothermic peaks, which appeared at 128 and 235 °C as observed in the DTA curve of gypsum. It is obvious that a certain weight loss is seen as two fields. The first one is observed in the range from 128 to 188 °C, with a peak at 164 °C that corresponds to the loss of 14.5% of the initial mass. This loss corresponds to the elimination of the hydrated water, which has 222.24 J/g enthalpy produced after the endothermic reaction. A second endothermic peak is observed in the range from 188 to 235 °C, with a peak at 200 °C that corresponds to the loss of 4.5% of the initial mass. At this stage, the heat of reaction is calculated as 37.16 J/g. As a result, $CaSO_4$ (soluble anhydrite) was obtained at 235 °C with total 19% mass loss. In fact, the transformation of gypsum into the hemihydrate structure, then into soluble anhydrite, is completed sequentially after two endothermic reactions given below:

$$CaSO_4 \cdot 2H_2O_{(s)} \rightarrow CaSO_4 \cdot 1/2H_2O_{(s)} + 3/2H_2O_{(g)} \text{ first stage}$$

$$CaSO_4 \cdot 1/2H_2O_{(s)} \rightarrow CaSO_{4(s)} + 1/2H_2O_{(g)} \text{ second stage}$$

Different dehydration temperatures have been obtained in previous DTA–TGA studies of natural gypsum. Strydom and Potgieter [16], who studied the dehydration of natural gypsum, obtained a curve, which reveals a 19.6% total decrease of the sample mass showing the total elimination of the crystallization water, that is to say the water molecules of $CaSO_4{\cdot}2H_2O$. The two peaks obtained by Guoxi and Yueming [17], are determined at 162 and 174 °C for natural gypsum. These peaks can be interpreted as modifications of the crystalline structure. In general, all $CaSO_4{\cdot}2H_2O$ dehydration studies through DTA show the presence of the two endothermic peaks. However, the corresponding temperatures have been quite varied according to the experimental conditions such as heating rate, nitrogen or air atmosphere and impurities of the sample [19].

Table 2
Temperature and nature of each thermal transformation of natural gypsum and borogypsum

Peak	Temperature (°C)	Reaction	Nature
Gypsum			
1	164 (peak max.)	$CaSO_4{\cdot}2H_2O_{(s)} \rightarrow CaSO_4{\cdot}1/2H_2O_{(s)} + 3/2H_2O_{(g)}$	Endothermic
2	200 (peak max.)	$CaSO_4{\cdot}1/2H_2O_{(s)} \rightarrow CaSO_{4(s)} + 1/2H_2O_{(g)}$	Endothermic
Borogypsum			
1	170 (peak max.)	$CaSO_4{\cdot}2H_2O_{(s)} \rightarrow CaSO_4{\cdot}1/2H_2O_{(s)} + 3/2H_2O_{(g)}$	Endothermic
2	200 (peak max.)	$CaSO_4{\cdot}1/2H_2O_{(s)} \rightarrow CaSO_{4(s)} + 1/2H_2O_{(g)}$	Endothermic

3.2. Characterization of borogypsum by thermal analysis

DTA–TGA curves of borogypsum are shown in Fig. 2. In the DTA curve of borogypsum, there were two basic endothermic peaks, which appear at 170 and 200 °C. On the TGA curve, it is noticed that a mass loss is occurred through several stages. The first mass loss, which is related to the humidity of sample, is between 70 and 140 °C that represents 1.6% of initial mass. The second mass loss is between 140 and 190 °C, corresponding to the elimination of water of hydration that represents 13.5% initial mass. The third stage starts at 190 °C and finishes at 220 °C. It represents

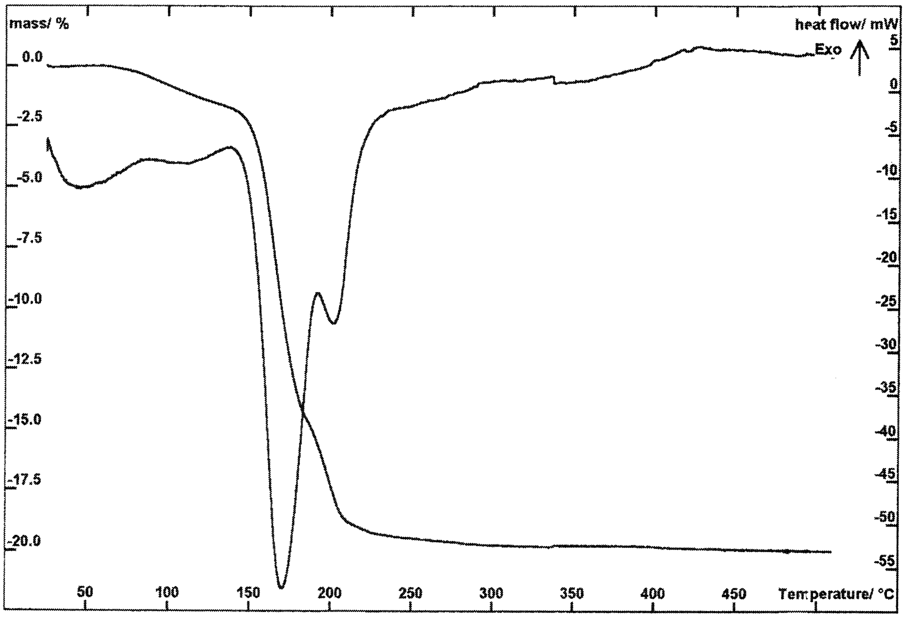

Fig. 2. DTA–TGA curves of the borogypsum.

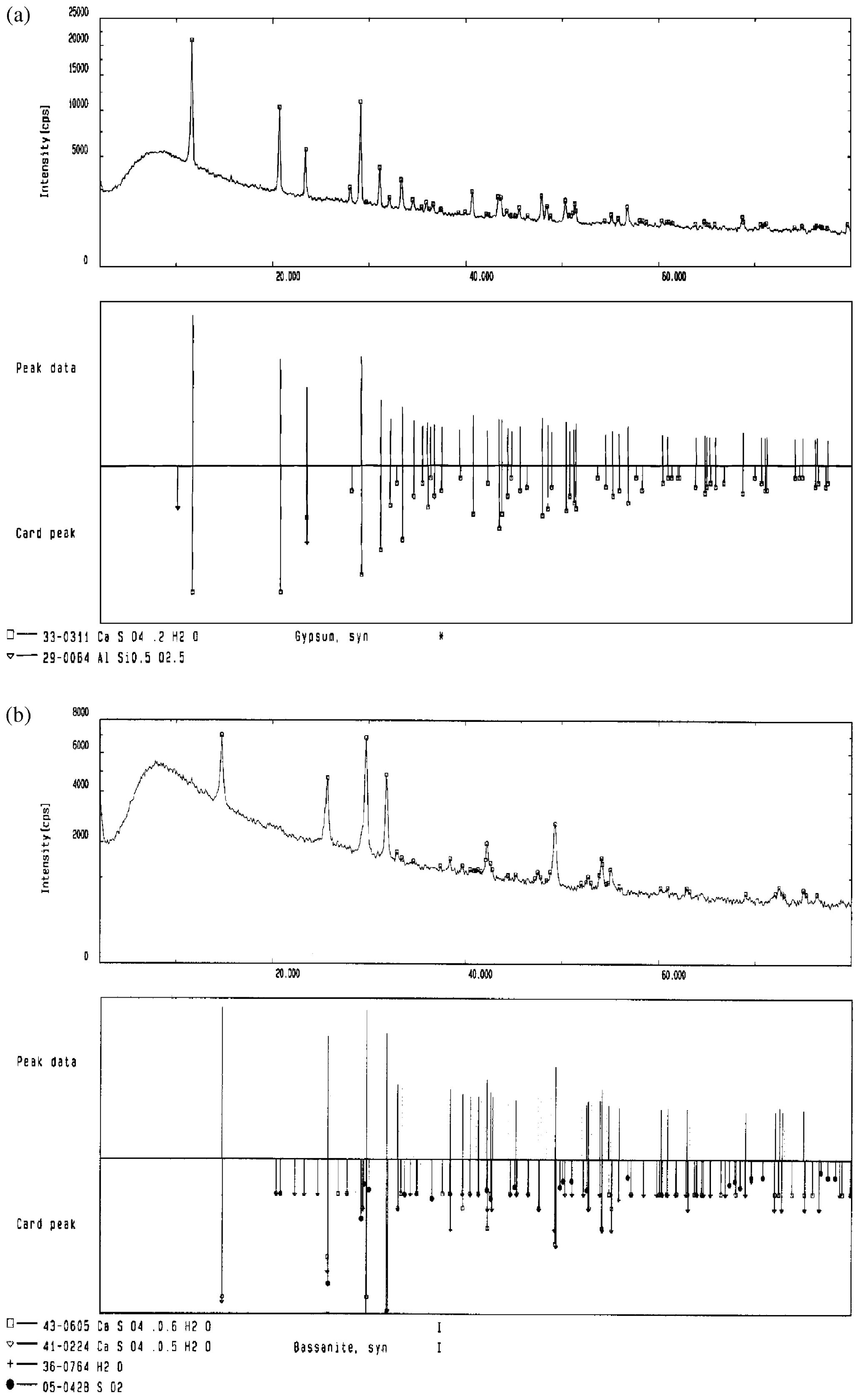

Fig. 3. X-ray diffractograms of borogypsum before and after thermal treatments (a) raw borogypsum (b) calcined borogypsum at 190 °C (hemihydrate) (c) calcined borogypsum at 220 °C (soluble anhydrite).

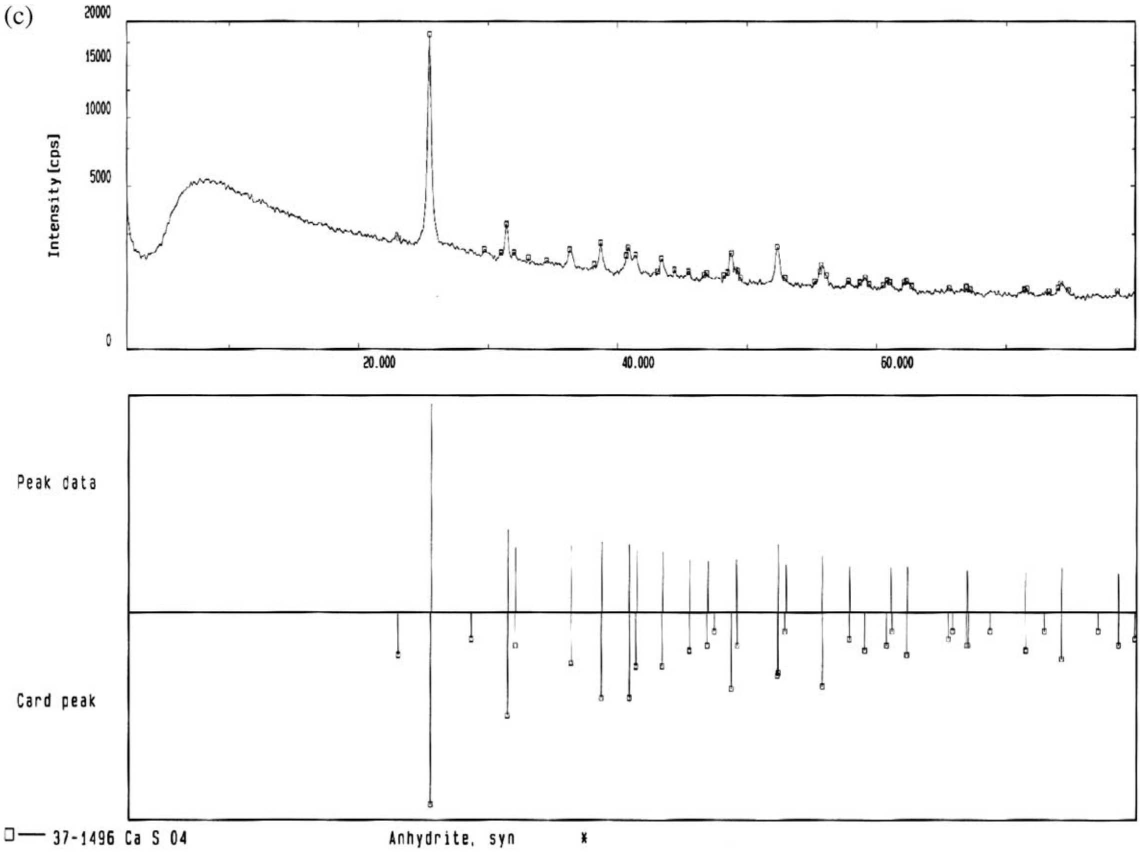

Fig. 3 (*continued*).

4.5% initial mass. The total loss obtained at 220 °C is of 20% total mass. The temperature values and the nature of each borogypsum transformation studied are presented in Table 2. The enthalpies of the endothermic reactions are calculated as 196.90 and 26.89 J/g at the first and second stages, respectively. Heating borogypsum at an atmospheric pressure up to 220 °C leads to an anhydrous hexagonal or soluble anhydrite form: $CaSO_4$.

3.3. The determination of conversion of borogypsum to hemihydrate and anhydrite by XRD

X-ray diffractograms of borogypsum before and after thermal treatments: (a) raw borogypsum, (b) calcined borogypsum at 190 °C (hemihydrate), (c) calcined borogypsum at 220 °C (soluble anhydrite) structures are given in Fig. 3. Conversion of borogypsum to hemihydrate and soluble anhydrite structure is confirmed by the XRD determinations.

3.4. Physical and chemical properties of cement with borogypsum additives

The cement samples were obtained by mixing separately borogypsum (5% and 7%), hemihydrate borogypsum (5%) and natural gypsum (5%) with Portland cement clinker on the industrial scale (Table 4). The compressive strength, setting time, Le Chatelier expansion, fineness and the chemical properties of mortars produced by these

Table 3
Physical properties of the cement produced

Sample no.	M1	M2	M3	M4
Fineness (cm^2/g), Blaine method	3690	3610	3590	3500
Consistency of standard paste (water %), Vicat apparatus	25.2	28.5	30.5	26.0
Setting time (min)				
Initial	91	144	174	256
Final	122	196	266	340
Soundness expansion (mm), Le Chatelier	5	4	3	2
Compressive strength (N/mm^2), RILEM—CEMBUREAU Method				
1 day	12.3	9.0	11.9	9.2
2 days	22.6	17.6	21.4	19.8
7 days	36.7	33.0	33.9	40.7
28 days	43.2	45.1	40.7	54.1
Weight of liter (g)	1150	1065	1160	1175
Sieve analysis				
45 (μm)	12.7	15.3	13.0	14.1
90 (μm)	1.4	1.8	1.1	1.1
200 (μm)	0.5	0.7	0.3	0.4
Specific gravity (g/cm^3)	3.14	3.14	3.13	3.17

M1 = 95% clinker + 5% gypsum; M2 = 95% clinker + 5% borogypsum; M3 = 93% clinker + 7% borogypsum; M4 = 95% clinker + 5% hemihydrate borogypsum.

Table 4
Chemical properties of the cement produced

Compounds (%)	95% K + 5% G	95% K + 5% BG	93% K + 7% BG	95% K + 5% HBG
SiO_2	21.300	21.220	21.270	21.280
Al_2O_3	5.600	5.470	5.050	5.300
Fe_2O_3	3.310	3.560	3.420	3.480
CaO	64.130	63.940	62.280	64.050
MgO	1.180	1.160	1.180	1.220
SO_3	2.190	2.050	2.560	2.100
Cl^-	0.015	0.025	0.020	0.012
Na_2O	0.160	–	–	–
K_2O	0.870	–	–	–
Loss on ignition	1.200	1.380	1.470	0.800
Free CaO	1.550	1.800	1.700	1.400
B_2O_3	–	0.350	0.490	0.440

K = clinker; G = gypsum; BG = borogypsum; HBG = hemihydrate borogypsum.

mixtures were determined. Results are given in Tables 2 and 3, respectively. It is observed that the cement obtained by adding hemihydrate borogypsum to clinker had a higher compressive strength than mortar produced with other cements. The 28-day compressive strength of the mortar produced using natural gypsum (5%) was 43.2 N/mm^2, whereas the compressive strength achieved by the addition 5% of hemihydrate borogypsum to the clinker was 54.1 N/mm^2 at 28 days (Table 3). It was seen that the cement containing 5% hemihydrate borogypsum had 25% higher compressive strength than the ordinary Portland cement (OPC) control at 28 days. When hemihydrate mixes with water, it can give higher strength and stability than gypsum because the particles in hemihydrate are in close contact and the crystals produced form a dense and hardened mass [20]. Also, increase of setting time, compressive strength and a decrease of soundness expansion for cement produced with additive 5% hemihydrate borogypsum were obtained.

The results show that increasing the borogypsum level from 5% to 7% caused an increase in setting time, and a decrease in soundness expansion and compressive strength. Additionally, Portland clinker mixed with borogypsum (5%) was found to have similar strength properties compared to the samples obtained with natural gypsum (Table 3). Additionally, the 28-day compressive strength of the mortars produced with 5% borogypsum additive was 45.1 N/mm^2, compared to 40.7 N/mm^2 for cement produced with 7% borogypsum (Table 3). It is concluded that hemihydrate borogypsum could be used for Portland cements manufactured on an industrial scale. This would play an important role in reducing environmental pollution.

As it can be seen from DTA–TGA curves, borogypsum and gypsum are completely transformed into the hemihydrate structure at 190 and 188 °C, respectively. The surface water is evaporated at about 150 °C totally. Nevertheless, crystal water is evaporated at higher temperatures (Figs. 1 and 2).

4. Conclusions

The following conclusions can be drawn from the experimental results.

The mortar obtained from the cement with hemihydrate borogypsum gives better mechanical strength than cement prepared using natural gypsum as untreated borogypsum. Hemihydrate borogypsum can be used as an additive material to cement 5% by weight, and the evidence suggests 28-day strengths may be enhanced. However, the addition of hemihydrate borogypsum to clinker decreases the soundness expansion and markedly increases the setting time. The retardation of setting time was more pronounced with hemihydrate borogypsum than with borogypsum as produced. An increase in borogypsum addition from 5 to 7 decreases compressive strength and soundness expansion, and increases the setting time. It has been reported that an increased B_2O_3 amount in cement causes a rise in setting time and a fall in strength values [18]. In this study, when borogypsum amounts were increased from 5% to 7%, the same effect was observed. It is concluded that hemihydrate borogypsum could be used as a retarder for Portland cement on an industrial scale. This would play an important role in preventing environmental pollution. Hemihydrate borogypsum may also be useful for decreasing the radioactive permeability of concrete due to the boron content. As it is known, colemanite, borax and ulexite which have high boron content are used in nuclear reactors as shielding materials for radiation [21].

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