Pergamon

CEMENT AND CONCRETE RESEARCH

Cement and Concrete Research 32 (2002) 471–475

Utilization of borogypsum as set retarder in Portland cement production

Recep Boncukcuoğlu[a,*], M. Tolga Yılmaz, M. Muhtar Kocakerim[b], Vahdettin Tosunoğlu[a]

[a]Atatürk University, Faculty of Engineering, Department of Environmental Engineering, 25240 Erzurum, Turkey
[b]Atatürk University, Faculty of Engineering, Department of Chemical Engineering, 25240 Erzurum, Turkey

Received 22 February 2001; accepted 15 October 2001

Abstract

Boron ores are used in the production of various boron compounds such as boric acid, borax and boron oxide. Boric acid is produced by reacting colemanite($2CaO{\cdot}3B_2O_3{\cdot}5H_2O$) with sulphuric acid and a large quantity of borogypsum is formed during this production. This waste causes various environmental problems when discharged directly to the environment. Portland cement is the most important material in the building industry. This material is produced by adding about 3–5% gypsum ($CaSO_4{\cdot}2H_2O$) to clinker as a set retarder. The aim of this study was to stabilize borogypsum, and to produce cements by adding borogypsum instead of natural gypsum to clinker. Concrete using cement produced with borogypsum was tested to find the mechanical properties and the test values were compared with those of concrete from cement with natural gypsum. Compressive strength of concrete from cement produced with borogypsum was found to be higher than that of natural gypsum. Also, the setting time of cement with borogypsum was longer than that of the Portland cement.

Keywords: Borogypsum; Cement; Concrete; Waste management; Set retarder

1. Introduction

About 53% of the world's boron ores are in Turkey. The average boron ores production of Turkey is about 1.3 billion tons per year. The most important boron ores in Turkey are colemanite, ulexite and tincal. Products such as borax, boric acid and sodium perborate are obtained from these ores. Borogypsum is formed by reacting colemanite with sulphuric acid in the production of boric acid and obtained by filtering the reaction mixture on the filter presses. The amount of these wastes is about 550,000 tons/year. Hence, there is a necessity of making use of this waste in large amount to avoid environmental problems [1].

Cement is a hydraulic binder obtained by grinding gypsum, which is added as 3–5% (wt/wt) to clinker. In the cement industry, gypsum is added into the clinker in order to delay the rapid reaction between $C_3A(3CaO{\cdot}Al_2O_3)$ and water. Conventionally, natural gypsum is used as a retarder; however, in some countries, because of lack of gypsum deposits, new sources of gypsum, such as industrial gypsum is utilized in cement production. Various industrial gypsums, such as phosphogypsum, fluorogypsum, desulphogypsum and borogypsum have the same chemical composition as the natural one [2]. In addition, it is possible to produce building materials that have different characteristics with the addition of various admixtures in different ratios. These admixtures can be either natural or industrial wastes.

Utilization of various industrial wastes produced, such as fly ash, phosphogypsum, fluorogypsum, lime sludge, red mud and borogypsum is important to save the environment from degradation [3,4]. To reduce pollution and disposal of these industrial wastes, there is an urgent need to develop useful building materials from them. With this view, investigations were undertaken to produce cementitious binders by blending fly ash with Portland cement as well as by suitably proportioning the fly ash

* Corresponding author. Tel.: +90-442-231-2283; fax: +90-442-233-1133.

E-mail address: rboncuk@yahoo.com (R. Boncukcuoğlu).

0008-8846/02/$ – see front matter
PII: S0008-8846(01)00711-6

with calcinated borogypsum, phosphogypsum and chemical additives.

A number of researchers [5,6] attempted to remove or stabilize the impurities in chemical gypsums of borogypsum or phosphogypsum. It is very important to select the mixing ratios and the properties of concrete materials to obtain a suitable mixture economically and to product a concrete having optimum characteristics. The workability of wet concrete and durability and strength of hardened concrete are the main functional requirements. There are various methods dealing with the calculation of mix proportions and the information about main characteristics of concrete. Whatever methods are used, it is essential that the theoretical mix proportions should be controlled with experimental ones and necessary corrections must be made. Cement that is produced by adding borogypsum to clinker has important characteristics. In some studies on the removal of solid boron wastes, the recovery of boron from boron wastes or the stabilization of boron wastes with cement, lime and sand has been studied [7,8].

The aims of this research are to investigate the use of borogypsum as a cement set retarder and to stabilize this waste.

2. Material and methods

2.1. Materials

The materials used in the study are provided by Eti Holding Bandırma Borax and Acid Factories in Turkey. Borogypsum is the solid part on filter press in boric acid production, which forms in the reaction of colemanite ($2CaO{\cdot}3B_2O_3{\cdot}5H_2O$) with H_2SO_4 as follows;

$$2CaO{\cdot}3B_2O_3{\cdot}5H_2O + 2H_2SO_4 + 6H_2O \rightarrow 6H_3BO_3 + 2CaSO_4{\cdot}2H_2O$$

This damp waste was dried in air and then crushed and ground by mechanical means. The particle size of borogypsum was not taken into account since it has a crushable structure and completely sieved in a 100-mesh sieve. Some physical and chemical features of borogypsum used in the research are presented in Table 1. In the experiments, clinker, cement and modular sand provided by the Erçimsan-Aşkale Cement Factory were used. The chemical analysis of clinker and cement are given in Table 2.

Table 1
Chemical analyses of borogypsum and natural gypsum

Parameters	Borogypsum	Natural gypsum
B_2O_3 (%)	1.50	–
SiO_2 (%)	6.820	0.61
SO_3 (%)	37.940	34.05
CaO (%)	22.830	36.23
MgO (%)	1.420	1.480
Fe_2O_3 (%)	0.410	0.110
Al_2O_3 (%)	0.800	0.110
Na_2O (%)	0.163	–
SrO (%)	0.860	–
As_2O_3 (%)	0.219	–
Water (%)	27.03	27.41

Table 2
Chemical analyses of clinker and cement

Parameters	Clinker	Cement
SiO_2 (%)	20.710	19.580
CaO (%)	64.200	55.400
MgO (%)	3.470	3.380
Fe_2O_3 (%)	3.200	3.000
Al_2O_3 (%)	5.940	4.880
SO_3 (%)	1.620	3.000
Undissolved solid (%)	0.360	7.620
Loss on heating (%)	0.330	3.360

2.2. Preparation and testing of Portland cement

To produce the cement, borogypsum both dried in air and heated at 105 °C for 2 h after drying in air was added to clinker in ratios of 2.5%, 5%, 10%, 15%, 25%, 40% and 50% (wt/wt). In the experiments a three cell mold with $4 \times 4 \times 12$-cm inner dimensions was used to prepare the compressive and tensile strength the specimens. Cement with borogypsum, sand and water was well mixed and the mortar obtained was put into the molds according to Turkish Standards [9] and were vibrated by a mechanical vibrator. After the top surface of the mold was smoothed by an iron plate, the sample was left for hydration under suitable conditions. In order to reduce the loss of dampness in the samples, the mold

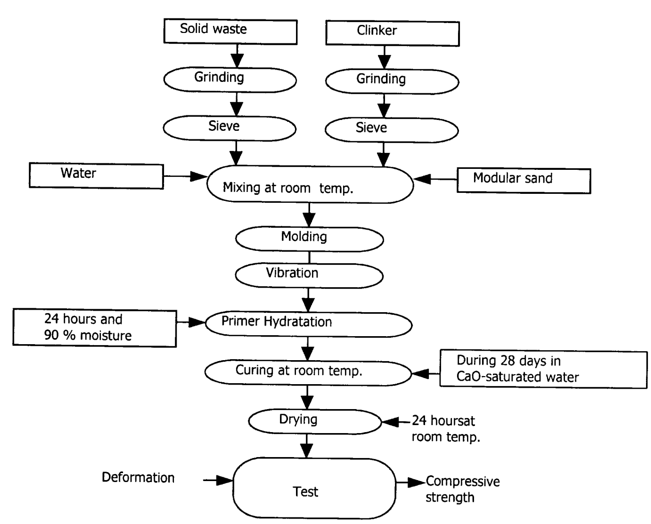

Fig. 1. Flow diagram.

Table 3
Experimental results

	Waste ratio (%)	Tensile strength (kg_f/cm^2)			Compressive strength (kg_f/cm^2)		
		2 Days	7 Days	28 Days	2 Days	7 Days	28 Days
Heated borogypsum	2.5	49	60	78	230	325	430
	5.0	33	54	70	188	311	378
	10.0	27	31	60	145	165	325
	15.0	20	25	50	108	135	270
	25.0	12	17	38	–	92	205
	40.0	–	13	29	–	70	151
	50.0	–	–	12	–	–	65
Unheated borogypsum	2.5	25	36	55	135	195	310
	5.0	20	35	54	110	185	290
	10.0	17	20	47	90	105	255
	15.0	15	20	37	78	110	190
	25.0	5	13	28	25	70	150
	40.0	–	–	20	–	–	105
	50.0	–	–	–	–	–	–
Portland cement		43	56	72	183	279	350
Clinker		52	69	78	221	346	453

was covered by a polyethylene film and left for 24 h for hydration under 20–25 °C and 90% water-saturated air. The samples were left in lime-saturated water for 2, 7 and 28 days and then, dried in air. The surfaces of the dried samples were smoothed by carborundum, surface areas were measured by a compass and their weight were determined by a precision balance. After this procedure mechanical properties such as compressive strengths, tensile strengths (direct tension) and setting time were recorded. The procedure is shown in Fig. 1 schematically. The compressive strengths were measured in a universal testing machine (marked Tonindustrie), which has a maximum capacity of 10,000 kg/cm^2 [9]. The tensile strengths were measured in a universal testing machine (marked Buehl & Faubel) [9]. Also, the setting time measurements of cement were carried out using a Vicat apparatus [9]. Standard methods were employed both in the preparation of the mixtures and the measurements and analysis during the experiments [9–13]. All of these experiments were carried out in Erçimsan-Aşkale Cement Factory in Erzurum, Turkey under industrial conditions.

3. Results and discussions

In the study, cements were obtained by adding borogypsum to the clinker in certain ratios. The compressive strengths, tensile strengths and setting time of the concretes from these cements were determined.

The results obtained are given in Table 3 and Figs. 2–6. In Fig. 2, it is seen that compressive strength was decreased with increasing air-dried borogypsum ratio in cement. Also, the same tendency was obtained by using borogypsum heated at 105 °C (Fig. 4). The change of

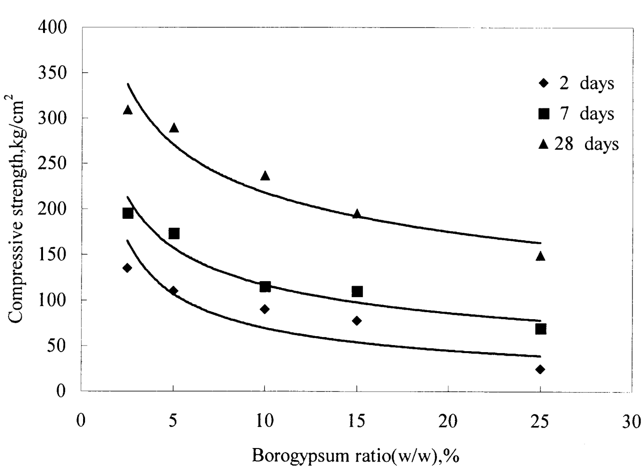

Fig. 2. Compressive strength of concrete with unheated borogypsum.

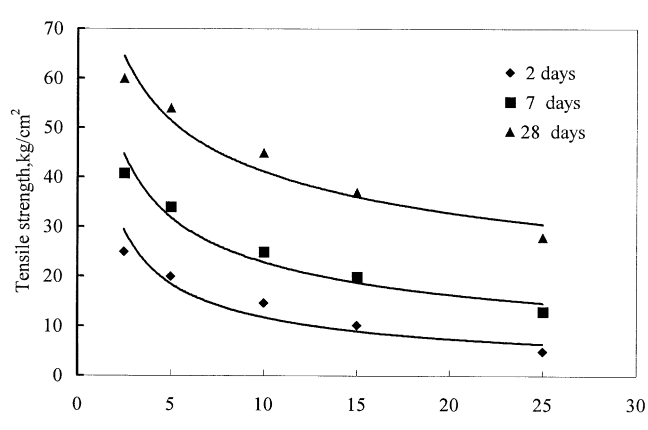

Fig. 3. Tensile strength of concrete with unheated borogypsum.

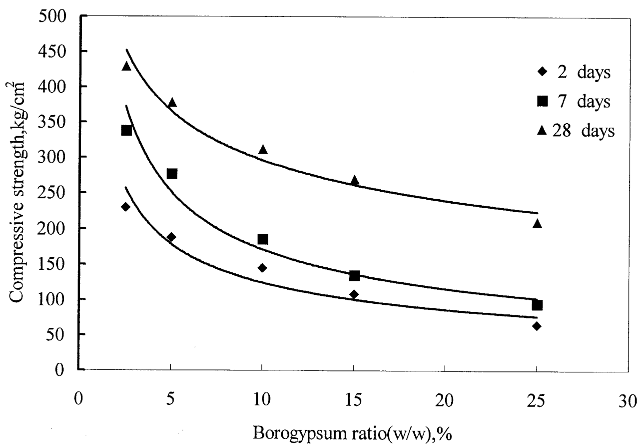

Fig. 4. Compressive strength of concrete with borogypsum.

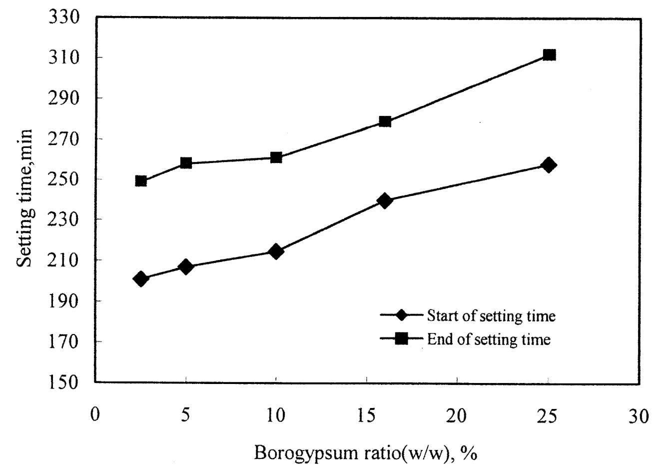

Fig. 6. Change of setting time with borogypsum ratio.

tensile strength with borogypsum ratio is given in Figs. 3 and 5 for air-dried borogypsum and heated borogypsum at 105 °C. It was determined that tensile strength decreased with borogypsum ratio for two situations. Concrete produced with heated borogypsum had better compressive and tensile strengths than that with the air-dried borogypsum. As a result, the cements produced by adding borogypsum to clinker had better performance than those of the natural gypsum in mechanical properties and workability, because it causes the concrete to disperse into the mold, and obtain more homogeneous matrix in the concrete. For example, the compressive strength of the concrete with 2.5% borogypsum was found to be 430 kg/cm^2, compared to 325 kg/cm^2 for the Portland cement. The effect of borogypsum ratio on setting time is shown in Fig. 6. It is seen that the setting time increased with increasing borogypsum ratio. Furthermore, the borogypsum provides easier processing due to increased setting time. For example, the starting of the setting time of cement with 2.5% borogypsum was 207 min compared to 201 min for the Portland cement.

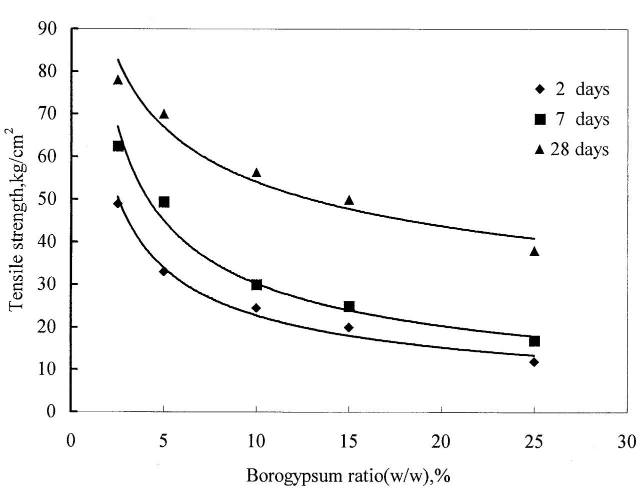

Fig. 5. Tensile strength of concrete with heated borogypsum.

4. Conclusions

Concrete prepared with borogypsum–cement gives better mechanical strength than that of natural gypsum cements. It has been shown that the mechanical strength of the concrete decreases with increasing borogypsum ratio, as well as natural gypsum. Ground natural gypsum is added to clinker as retarder in the cement production. However, its dehydration during grinding causes pseudo-setting and cement quality is affected badly. Because borogypsum has a loose structure, an important power is not required; its mass does not heat and it does not lose crystal water while grinding. As a result, cement quality does not decrease. Also, it is known that the obtained cements and concretes are resistant to microbial decomposition because boron compounds are antiseptics [14], and boron compounds also decrease radioactive permeability of the concrete [15].

It is suggested that borogypsum can be used as set retarders up to 10% by weight of cement. Hence, borogypsum, like other industrial gypsums such as phosphogypsum, desulphogypsum, citrogypsum, fluorogypsum, etc. [2] can be added to the clinker in the production of cement, and a cement having better properties than those of other waste gypsums can be obtained.

References

[1] R. Boncukcuoğlu, M.M. Kocakerim, V. Tosunoğlu, Utilization of industrial boron wastes cement production for the stabilization, Energy Educ. Sci. Technol. 3 (1) (1999) 48–54.

[2] H.M. Özkul, Utilization of citrı- and desulphogypsum as set retarders in Portland cement, Cem. Concr. Res. 30 (2000) 1755–1758.

[3] M. Singh, M. Garg, Cementitious binder from fly ash and order industrial wastes, Cem. Conc. Res. 29 (1999) 309–314.
[4] V. Tosunoğlu, R. Demirbağ, R. Boncukcuoğlu, Ö. Anapalı, Ç. Öztepe, Pozzolanic properties of natural pasa, Energy Educ. Sci. Technol. 8 (2) (2002) 77–84
[5] H. Ölmez, E. Erdem, The effect of phosphogypsum on the setting and mechanical properties of Portland cement and trass cement, Cem. Concr. Res. 19 (3) (1989) 377–384.
[6] Y. Erdoğan, A. Demirbaş, Partly-refined chemical by-product gypsum as cement additives, Cem. Concr. Res. 24 (4) (1994) 601–604.
[7] R. Boncukcuoğlu, M.M. Kocakerim, M. Alkan, Water Air Soil Pollut. 104 (1998) 103–112.
[8] R. Boncukcuoğlu, M.M. Kocakerim, H. Erşahan, Upgrading of the reactor waste obtained during borax production from tincal, Miner. Eng. 12 (10) (1999) 1275–1280.
[9] Turkish Standards, TS 24, Physical and mechanical testing methods of cement, The Institute of Turkish Standards, Ankara, 1985.
[10] Turkish Standards, TS 687, Chemical analysis methods of cement, The Institute of Turkish Standards, Ankara, 1979.
[11] Turkish Standards, TS 22, Mortar cement, The Institute of Turkish Standards, Ankara, 1983.
[12] A.M. Neville, Properties of Concrete, third ed., ELBS Press, Essex, England, 1995.
[13] Y. Erdoğan, M.S. Zeybek, A. Demirbaş, Partly-refined chemical by-product gypsum as cement additives, Cem. Concr. Res. 24 (4) (1994) 601–604.
[14] H.G. Seiler, H. Sigiel, A. Sigel, Handbook of Toxicity of Inorganic Compounds, Marcel Dekker, New York, USA, 1988.
[15] S.J. Shiao, C.M. Tsai, The study on improving masonry cement for the solidification of borate wastes, Radioact. Waste Manage. Nucl. Fuel Cycle 11 (4) (1989) 319–331.