Pergamon

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Cement and Concrete Research 33 (2003) 1659–1661

CEMENT AND CONCRETE RESEARCH

Utilization of clay wastes containing boron as cement additives

Mine Özdemir*, Neşe Uygan Öztürk

Department of Chemical Engineering, Faculty of Engineering and Architecture, Osmangazi University, 26480 Eskişehir, Turkey

Received 16 September 2002; accepted 9 April 2003

Abstract

The utilization of clay wastes (CW) containing boron as cement additives was investigated. The effect of CW on mechanical and chemical properties of cement prepared by adding CW to clinker and gypsum was determined. The results obtained were compared with Portland cement properties and Turkish standards (TS) values. It was determined that the first clay waste (CW1) and the second clay waste (CW2) may be used as cement additives up to 5% and 10%, respectively.

Keywords: Boron wastes; Cement; Mortar; Waste management

1. Introduction

Turkey has 803 million tons of boron reserves, which consist of 63% of the total world boron reserves. The most important boron ores in Turkey are tincal, colemanite and ulexite. Products obtained from these ores are concentrated tincal, borax pentahydrate, borax decahydrate, anhydrous borax, boric acid and sodium perborate. Turkey is the second producer following the United States with 1.72 million tons boron minerals and compounds production. In Etibank Kýrka Borax Plants, 800,000 tons/year of concentrated tincal, 160,000 tons/year of borax pentahydrate, 60,000 tons/year of anhydrous borax, 17,000 tons/year of borax decahydrate are obtained from tincal [1,2]. Annually, 120,000 tons clay wastes (CW), known as the first clay waste (CW1) and the second clay waste (CW2), form in the concentrated tincal unit and the borax pentahydrate unit during the production. CW containing about 8–22% B_2O_3 are discharged to the plant area. These wastes contain boron oxide in quite high concentration, so this is an environmental pollution problem as well as an economical loss.

The utilization of various industrial wastes is important to saving the environment from degradation. Thus, their use as additives in the production of cement and mortar has been the subject of investigation in recent years. In these studies, boric acid wastes including reactor waste, borogypsum and sludges as well as colemanite concentrator wastes, tincal concentrator wastes and borax pentahydrate wastes were added to Portland and trass cements and clinker in various ratios. The effect of wastes on the physical and mechanical properties of cements was investigated [3–13].

The aim of this study is to investigate the use of CW containing boron as a cement additive.

2. Materials and methods

CW used in this study were provided from Etibank Kýrka Borax Plant, while clinker and gypsum from Eskişehir Cement Plant in Eskişehir, Turkey. CW1 and CW2 were provided from the concentrated borax unit and the borax pentahydrate unit. These CW were dried in the air. The chemical compositions of CW1, CW2, clinker and gypsum used in the experiments are given in Tables 1 and 2. Cement samples used in the study were prepared by adding CW1 and CW2 to clinker and gypsum mixtures separately. The weight

Table 1
Chemical composition of CW and clinker (%, w/w)

Component	CW1	CW2
B_2O_3	22.48	8.23
CaO	16.43	22.10
MgO	14.12	18.16
SiO_2	14.01	10.46
Na_2O	8.32	4.47
Al_2O_3	1.68	1.04
Fe_2O_3	1.57	1.40
K_2O	1.39	0.56
Loss on ignition	20.00	33.58

* Corresponding author. Tel.: +90-222-2393750; fax: +90-222-2393613.

E-mail address: mnozdemi@ogu.edu.tr (M. Özdemir).

0008-8846/03/$ – see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0008-8846(03)00138-8

Table 2
Chemical composition of clinker and gypsum (%, w/w)

Component	Clinker	Gypsum
CaO	65.56	32.46
MgO	1.17	0.54
SiO_2	20.88	1.74
Al_2O_3	4.91	0.51
Fe_2O_3	3.76	0.27
Na_2O	0.08	0.05
K_2O	0.57	0.07
SO_3	1.76	43.99
Loss on ignition	0.31	20.36

ratio of gypsum in the mixtures was 3.5%. Five hundred gram samples were used in the experiments and CW1 and CW2 ratios in the sample mixtures were 1%, 2.5%, 5%, 10%, by weight. These mixtures were ground in definite particle size with Herzog mill. Thus, eight types of cement samples containing CW in various ratios were prepared. The cement samples prepared were mixed with 450 g of cement, 1350 g of sand and 225 ml of water in Seger mortar mixer. The mortar prepared was put into $4 \times 4 \times 16$ cm molds with three cells. Spaces between grains were decreased with a vibrator and the top surfaces of molds were smoothed.

The cement mortar samples obtained in this way were left 24 h for the first hydration under 20 ± 1 °C and 90% water saturated air. The mortar samples demolded were left in water at 20 °C for 28 days. After these treatments, mortar samples were dried and tested for tensile strength and the compressive strength was applied on them in Toniteknik equipment. The preparation of mortar samples, the physical tests and chemical analyses were carried out according to TS [14]. The values obtained were compared with those of Portland cement and TS 19.

3. Results and discussion

Eight types of cement samples were obtained by adding CW1 and CW2 to clinker and gypsum at various ratios. The tensile strength and the compressive strength values of the mortar samples prepared with these cements were determined. The results obtained are given in Table 3 and Figs. 1 and 2.

As seen in Table 3, it is observed that the mortar of cement obtained by adding CW to clinker and gypsum had lower tensile strength and compressive strength than that of the Portland cement, except the sample containing 1% CW1. However, the tensile and compressive strength values of these mortar samples were higher than the TS values, except for the sample containing 10% CW1.

The tensile strengths with increasing CW1 and CW2 ratios are 8.73, 8.07, 6.63, 4.10 (N/mm^2) and 8.00, 8.13, 7.20, 6.47 (N/mm^2), respectively, while being 8.30 (N/mm^2) for Portland cement and 5.5 (N/mm^2) at TS [14].

The compressive strengths by increasing CW1 and CW2 ratios are 57.02, 46.73, 36.15, 23.20 (N/mm^2) and 52.70, 51.77, 39.13, 32.90 (N/mm^2), respectively, while being 54.5 (N/mm^2) for Portland cement and 32.50 (N/mm^2) at TS [14].

The fineness of the cement sample with 10% CW1 is 319.9 mm^2/kg. By grinding this cement up to 350.0 mm^2/kg, it is possible for the tensile strength and the compressive strength values to exceed 5.5 and 32.5 (N/mm^2), respectively.

It has been seen that the tensile strength and the compressive strength of the mortar decrease with increasing CW ratio and the B_2O_3 ratio in the CW, except 1% CW1 (Figs. 1 and 2). These results are in agreement with the previous studies [7,11,13].

The chemical compositions of cement samples are given in Table 4. The chemical compositions of cement samples

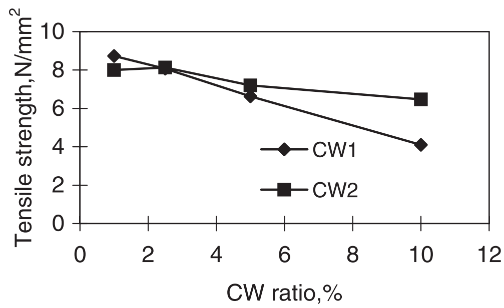

Fig. 1. Tensile strength of mortar with CW.

Table 3
Physical and mechanical properties of cement samples

	Waste ratio (%, w/w)	Specific surface (mm^2/kg)	Tensile strength (N/mm^2)	Compressive strength (N/mm^2)
CW1	1.0	352.4	8.73	57.02
	2.5	316.3	8.07	46.73
	5.0	304.2	6.63	36.15
	10.0	319.9	4.10	23.20
CW2	1.0	320.5	8.00	52.70
	2.5	352.3	8.13	51.77
	5.0	290.3	7.20	39.13
	10.0	302.0	6.47	32.90
Portland cement	0.00	326.2	8.30	54.50
TS requirements	–	–	Min. 5.5	Min. 32.50

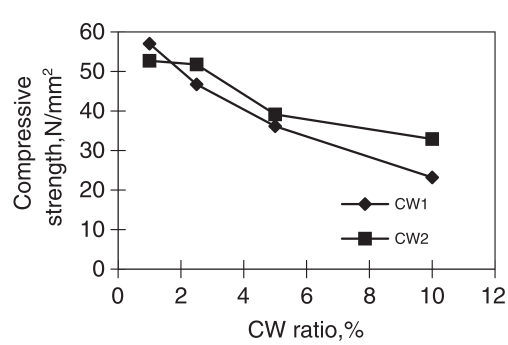

Fig. 2. Compressive strength of mortar with CW.

Table 4
Comparison of cement samples with Portland cement and TS

Component (%, w/w)	CW1	CW2	Portland cement	TS 19
$SiO_2 + R_2O_3$	29.38	29.46	29.89	Min 70
CaO	65.83	65.87	64.80	–
MgO	1.34	1.41	1.27	Max 5.0
SO_3	1.81	1.78	2.37	Max 3.5
B_2O_3	0.22	0.08	–	–
Loss on ignition	0.86	0.85	0.98	Max 4.0

containing CW1 and CW2 are in agreement with the Portland cement and TS values.

4. Conclusions

The possibility of using CW as a cement additive has been investigated. The major conclusions are as follows:

1. The mortar containing 1% of CW had higher compressive strength than that of Portland cement. At other conditions, the cement mortar showed the best result. The mortar containing up to 5% of CW1 and 10% of CW2 exhibited comparable results with the TS value.
2. The mechanical strength of the mortar decreased with increasing CW ratio and the B_2O_3 ratio in the CW, except 1% CW1.
3. As a result, it is suggested that CW1 and CW2 can be used as cement additives up to 5% and 10%, respectively.

Acknowledgements

We thank Osmangazi University Research Foundation (Project No. 2000/6) for financial support, Etibank Kýrka Borax Plant for CW and Eskişehir Cement Plant for laboratory facility.

References

[1] The State Planning Organization, DPT, Report No. 2414, Ankara, Turkey, 1995.
[2] The State Planning Organization, DPT, Report No. 2427, Ankara, Turkey, 1996.
[3] S.J. Shiao, C.M. Tsai, The study on improving Masonry cement for the solidification of borate wastes, Radioact. Waste Manag. Nucl. Fuel Cycle 11 (4) (1989) 319–331.
[4] 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) 377–388.
[5] M. Singh, M. Garg, Cementitious binder from fly ash and other industrial wastes, Cem. Concr. Res. 29 (1999) 309–314.
[6] Y. Erdoğan, A. Demirbaş, H. Genç, Partly-refined chemical by-product gypsum as cement additives, Cem. Concr. Res. 24 (4) (1994) 601–604.
[7] A. Demirbaţ, S. Karslýoðlu, The effect of boric acid sludges containing borogypsum on properties of cement, Cem. Concr. Res. 25 (7) (1995) 1381–1384.
[8] Y. Erdoğan, M.S. Zeybek, A. Demirbaş, Cement mixes containing colemanite from concentrator wastes, Cem. Concr. Res. 28 (4) (1998) 605–609.
[9] R. Boncukçuoğlu, M.M. Kocakerim, V. Tosunoğlu, Utilization of industrial boron wastes in cement production for the stabilization, Energy Educ. Sci. Technol. 3 (1) (1999) 48–54.
[10] I. Kula, A. Olgun, Y. Erdoğan, V. Sevinç, Effect of colemanite waste, cool bottom ash, and fly ash on the properties of cement, Cem. Concr. Res. 31 (2001) 491–494.
[11] I. Kula, A. Olgun, V. Sevinç, Y. Erdoğan, An investigation on the use of tincal ore waste, fly ash, and coal bottom ash as Portland cement replacement materials, Cem. Concr. Res. 32 (2002) 227–232.
[12] R. Boncukçuoğlu, M.T. Yılmaz, M.M. Kocakerim, V. Tosunoğlu, Utilization of borogypsum as set retarder in Portland cement production, Cem. Concr. Res. 32 (2002) 471–475.
[13] R. Boncukçuoğlu, M.T. Yılmaz, M.M. Kocakerim, V. Tosunoğlu, Utilization of trommel sieve waste as an additive in Portland cement production, Cem. Concr. Res. 32 (2002) 35–39.
[14] Turkish National Standards, Portland cements, TS 19 (1985), Mortar cement, TS 22 (1983), Physical and mechanical testing methods of cement, TS 24 (1985), Chemical analysis methods of cement TS 687 (1979), Turkish Standard Institute, Ankara, Turkey.