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Utilization of Industrial Borax Wastes (BW) for Portland Cement Production

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Abstract

Industrial borax wastes (BWs) are formed as solid waste during the production of borax from tincal [$Na_2B_4O_5(OH)_4.8H_2O$] in Bandırma, Turkey. These wastes cause different environmental problems and lead to economic losses because of high boron oxide (B_2O_3) content. The primary aim of this study is the removal of $B_2O_3$from BWs and the second aim is the usage of BWs with low boron content in cement as an additive material. For this purpose, the BW was treated with water for removal of boron oxide and to reduce its toxic effects. After washing, treated and untreated BW was added to the Portland cement (PC42.5 type) at a ratio of 5%. The final products were tested for compressive strength, setting time, Le Chatelier expansion and fineness properties and the results were compared with Portland cement properties and European Standards (EN 196). The results showed that BW that has a high boron level caused a decrease in compressive strength and increase the soundness expansion in Portland cement. It was concluded that BW can be used as a cement additive after decreasing boron oxide and water-soluble impurities.

Key words: B_2O_3, Borax wastes, Cement, Compressive strength.

Introduction

Boron minerals occur in a few locations in the world. Approximately, 63% of the known world boron reserves are found in the western part of Turkey. The hydrated boron minerals, which have a big potential in Turkey, are the main materials of the chemical industry. In particular, tincal [$Na_2B_4O_5(OH)_4.8H_2O$], used in the production of borax ($Na_2B_4O_7.10H_2O$), is very important economically. Boron and its compounds have a wide field of applications in the industry. Borax has found wide areas of use such as borosilicate glasses, glass wool, ceramics, detergents, cement and fire proof materials (Pişkin, 1983; Ekmekyapar *et al.,* 1997; Çetin *et al.,* 2001).The production of borax is a batch process. In the process, tincal concentrate, having about 10 mm particle size, is fed to a stirred reactor containing water heated to 95-100 °C. The clay part in the tincal becomes colloidal in the reactor and the colloidal part passes to the thickener. The precipitation in the thickener is called borax waste (BW) (Figure 1) (Erdoğan *et al.,* 1993; Boncukçuoğlu *et al.,* 1998; Boncukçuoğlu *et al.,* 2003). Annually, 25,000 t of BW is formed and discharged into the waste dams near the plant area. The content of boron oxide (B_2O_3) in BW obtained during borax production increases up to 17%. Therefore, it is recognized as valuable industrial raw material. Discharge of this waste causes soil pollution as well as economic loss due to dissolution of the boron compounds by means of rain waters. Although boron is an essential nutrient for plants, it can be toxic to organisms when accumulated in high concentrations (Çöl *et al.,* 2003). Therefore, materials with a high boron concentration are considered pollutants due to their toxicological effects. For these reasons, some useful methods have been developed and tested for the removal of $B_2O_3$from BWs (Erdoğan *et al.,* 1993; Boncukçuoğlu *et al.,* 2002; Elbeyli *et al.,* 2003).

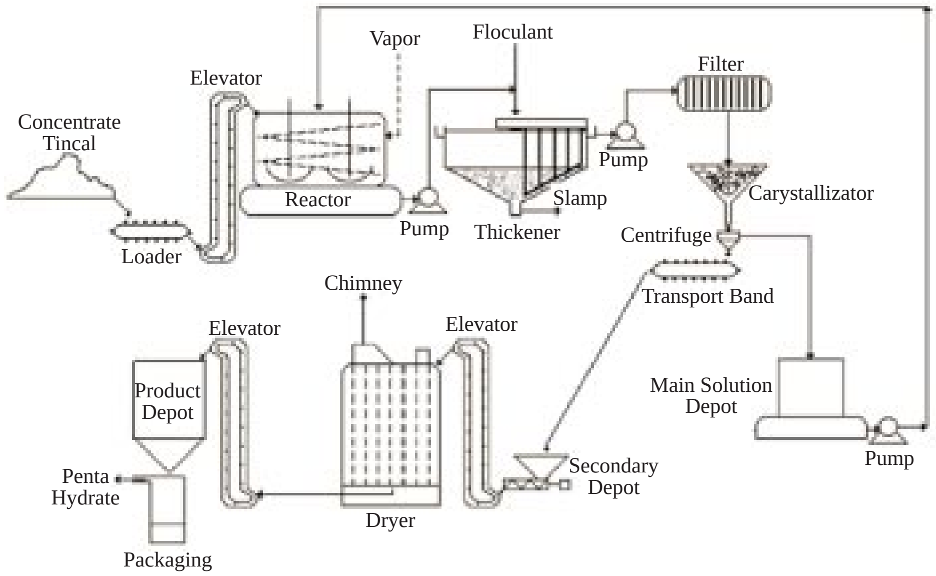

Figure 1. A process diagram of borax production from tincal (Boncukçuoğlu et al., 2003).

In order to solve environmental and storage problems at borax plants, various applications concerning the use of BW in different ways have been developed. Utilization of BW as a resource has been studied for decades in many areas such as in boron extraction and in building products (bricks and cement). In brick studies, BW is used as an additive in the brick body because it has properties similar to those of brick clays (Elbeyli *et al.,* 2000). In addition to these studies, solid and liquid wastes of the boron industry were investigated with cement, lime and sand, their effects on some properties of the concrete and cement were determined (Erdoğan *et al.,* 1993; Shaio *et al.,* 1998; Boncukçuoğlu *et al.,* 1999; Elbeyli *et al.,* 2000; Boncukçuoğlu *et al.,* 2002; Elbeyli *et al.,* 2003). It was found that concrete obtained from cement with BW has better mechanical strength than other traditional cements. Furthermore, the main characteristics of cements produced by the addition of borate are high resistance to nuclear radiation, development of strength and decrease in heating temperature (Shaio *et al.,* 1998; Boncukçuoğlu *et al.,* 1999). On the other hand, there are various studies on the removal of boron from BWs. In these studies, boron wastes are used to produce various borax compounds and approximately 90% of its boron content is recovered (Yamık *et al.,* 1995; Boncukçuoğlu *et al.,* 1998).

The aim of this research was to investigate the effects of BWs, which have high and low B_2O_3content, on the physical and mechanical properties of Portland cement.

Materials and Methods

Materials

Portland cement is obtained from the burning of mixtures of calcareous and argillaceous, or other silica, alumina, and iron oxide-bearing materials, at a clinkering temperature, and grinding of the final clinker. The ordinary Portland cement (PC 42.5 type) (OPC) used in the experiments was supplied by the Akçansa Cement Plant in İstanbul, Turkey.

The BW used in the study was provided by the Eti Holding Borax Plant in Bandırma, and was taken from the outlet of the thickener unit (Figure 1). The chemical compositions of the BW and OPC used in the experiments are given in Table 1.

Characterization of BW by XRD, SEM and DTA-TG

Before the preparation of the mortar specimens from the cements produced with BW, its properties were investigated by X-ray diffractometry (XRD), which is used for the determination of minerals, and by scanning electron microscope (SEM) and differential thermal analysis-thermogravimetric analysis (DTA-TG), which are used for the observation of microstructures and determination of thermal behaviors.

Table 1. The chemical composition of cement and borax waste by weight (%).

Compounds	Portland cement (PC42.5)	Borax waste (BW)
SiO_2	21.18	18.24
Al_2O_3	4.97	2.05
Fe_2O_3	3.16	1.04
MgO	1.1	15.84
CaO	62.68	13.97
SO_3	2.5	0.75
Na_2O	-	2.98
K_2O	-	1.01
B_2O_3	-	14.09
Heating lost	2.45	30.84

The XRD analyses were performed using CuKα radiation (40 kV and 20 mA) on Philips diffractometer equipment. Silicon was used as a calibration material. The DTA-TG analyses of the samples were performed using a Setaram Labsys model thermal analyzer. Air atmosphere was used as a carrying gas and a heating rate of 10 °C min^{-1} was used. The samples were heated from 25 to 500 °C in platinum crucibles. Surface structural information of the BW sample was provided using a Jeol JSM-5410 model SEM.

Removal of Boron Oxide from BW

Washing by water was applied for the removal of $B_2O_3$and other water-soluble impurities in BW. Before the washing, the waste was dried in an oven and ground to a particle size of -200 μm. For the removal of boron, experiments were carried out at 80 °C with a solid/liquid ratio of 1/5 and dissolved in water for 40 min. Solid and liquid parts of the waste were separated with a vacuum filtration system. B_2O_3 component and water-soluble materials were passed to the filtrate. Finally, boron was removed by decreasing its content in the waste. The amounts of boron remaining in the cake and filtrate were determined by potansiometric titration (Pişkin, 1983).

Preparation and testing of Portland cement

OPC, treated BW (low boron content) and untreated BW (high boron content) samples after drying were homogenized in a ball mill. In the experiments, a 3-cell mold (4 x 4 x 16 cm) was used. In the first stage, untreated BW was added to OPC at a ratio of 5% (w/w) and cement samples were formed by intergrinding OPC and untreated BW samples. At the second stage, mortars were prepared with 450 g of cement, 1350 g of fine aggregate (natural sand, 2.93 modulus fineness) and 200 ml of water. Mixtures were put in a mold to obtain three 16 x 4 x 4 cm^3 specimens and stored in a moisture room (20 ± 1 °C) for 24 h; after demolding, the specimens were stored under water at 20 ± 1 °C until the test day (2, 7, 28). After this procedure, compressive strengths, setting time, Le Chaletier expansion and the fineness properties of cement mortars were tested and recorded according to European Standards (European Standards EN 196, 1989). The specific gravity and fineness (Blaine method) were also measured. The compressive strength values were measured in a universal testing machine and the setting times of cement samples were measured using a Vicat apparatus. In addition to this procedure, treated BW was added to OPC at a ratio of 5% (w/w) and cement samples were formed by intergrinding OPC and treated BW samples. The same methods were used in the preparation of mortars and they were tested according to the same standards. All of these experiments were carried out in the Akçansa Cement Factory in İstanbul. The results are given in Table 2.

Results and Discussion

SEM photographs and X-ray diffraction data confirm variations in mineral composition and heterogeneous structure (Figures 2 and 3). Figure 3 shows that the XRD pattern of BW proes the presence of different minerals such as dolomite [$CaMg(CO3)_2$], tincalconite [$Na_2B_4O_7.5H_2O$], quartz [SiO_2], ankerite [$Ca(Fe{+}{+},Mg,Mn)(CO_3)_2$] and calcite [$CaCO_3$]. DTA-TG curves for BW at 10 °C min^{-1} are presented in Figure 4. In the DTA curve, there were 3 basic endothermic peaks. The first one is observed in the range from 81.5 °C to 115.3 °C, with a peak at 94.6 °C. The second endothermic peak is observed in the range from 115.3 °C to 168.4 °C, with a peak at 138.3 °C. The last endothermic peak occurred in the range from 168.4 °C to 195 °C, with a peak at 180 °C. This loss corresponds to the elimination of the water hydration in tincalconite.

In the first stage of experiments, washing was used to remove B_2O_3 from the BW. The proportion of $B_2O_3$was decreased to 3.55% from 14.09% by the washing process. Removal of B_2O_3 was achieved with a yield of 75%.

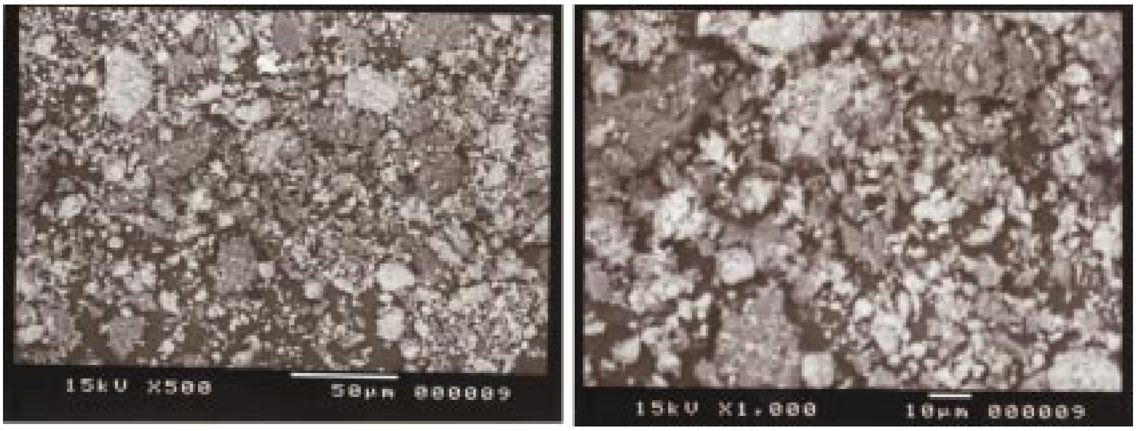

Figure 2. SEM photograph of borax waste (BW) at X500 and X1000.

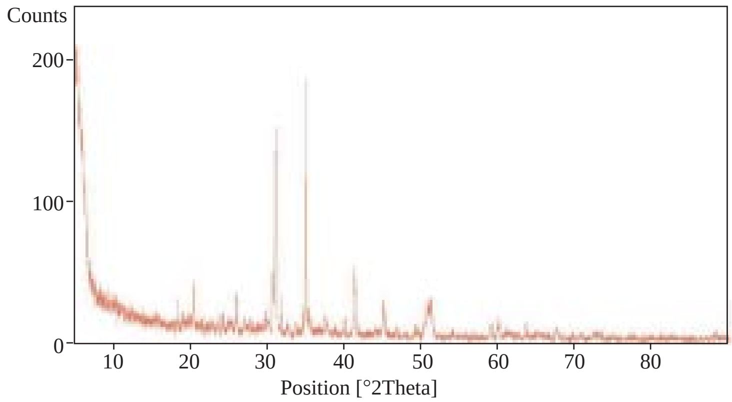

Figure 3. XRD pattern of borax waste (BW).

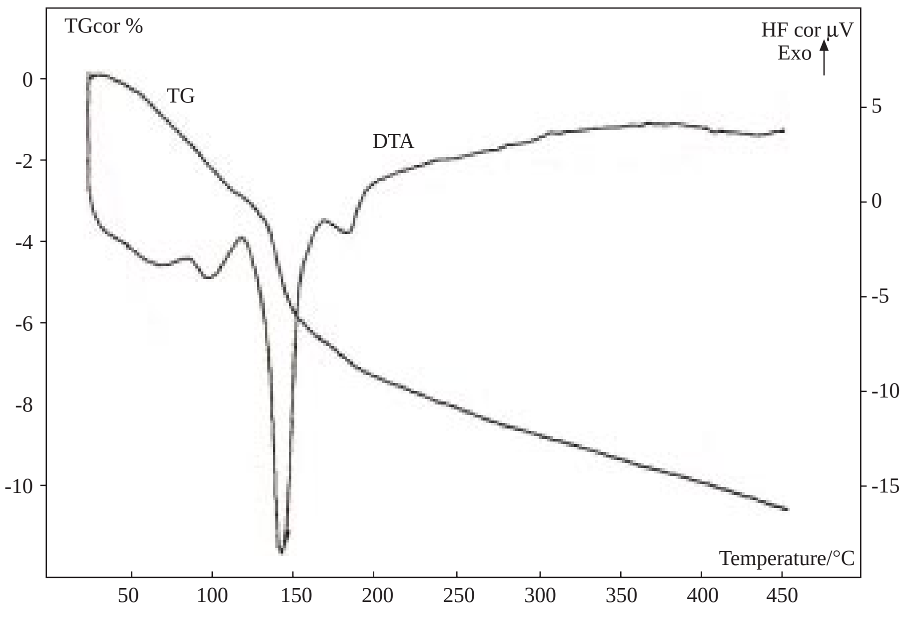

Figure 4. DTA-TG curves of borax waste (BW).

Table 2. Physical and mechanical properties of the cements produced.

Sample no.	M1	M2	M3
Fineness (cm^2/g), Blaine method,	3690	3520	3550
Consistency of standard paste (water %), Vicat apparatus	25.2	28.0	31.8
Setting time (min),			
Initial	91	60	174
Final	122	93	266
Soundness expansion (mm), Le Chaletier	5	11	3
Compressive strength (N/mm^2),			
RILEM-CEMBUREAU Method			
2 days	22.6	8.4	24.8
7 days	36.7	27.6	37.6
28 days	43.2	37.2	48.0
Weight of liter (g)	1150	1185	1185
Sieve analysis			
45 (μm)	12.7	23.2	22.4
90 (μm)	1.4	5.9	4.4
200 (μm)	0.5	2.8	0.2
Specific Gravity (g/cm^3)	3.14	3.11	3.11

M1: OPC (PC 42.5)
M2: 95% PC 42.5 + 5% untreated BW (14.09% B_2O_3)
M3: 95% PC 42.5 + 5% treated BW (3.55% B_2O_3)

At the second stage of experiments, cement samples were prepared by mixing separately untreated BW (14.09% B_2O_3) (M2) and treated BW (3.55% B_2O_3) with OPC. Mortars produced by these mixtures showed different physical and mechanical properties. These results indicated that the setting time of OPC pastes (M3) is remarkably retarded when mixed with treated BW. On the other hand, it was observed that the setting time of OPC prepared with untreated BW (M2) paste was shorter than that of the control cement, OPC (M1). For both cement samples mixed with BW, the setting was found to be different. It was found that the setting time was a function of the percentage of B_2O_3in the BW.

Cement obtained by adding treated BW to OPC has a compressive strength higher than that of mortar produced with other cements. The 28-day compressive strength of the mortar produced by using OPC was 43.2 N/mm^2, whereas the compressive strength achieved by the addition of 5% of treated BW to the OPC was 48 N/mm^2 at 28 days (Table 3). It was seen that the cement containing 5% of treated BW has compressive strength 11% higher than that of the OPC control at 28 days. Comparatively, the treated BW used in cement caused greater strength and stability of mortar than the untreated BW. As BW is treated after being washed with water, it can give better results because the water-soluble impurities, especially B_2O_3 are removed from the BW. The results show that washing the BW caused a decrease in the soundness expansion and an increase in the setting time and compressive strength. Additionally, OPC mixed with untreated BW (5%) had the highest soundness expansion, 11 mm, in all mixtures (Table 2). For the cement produced with the addition of 5% of untreated BW, decreases in the setting time and compressive strength were obtained (37.2 N/mm^2 at 28 days). It was seen that the utilization of treated BW in cement production gives better results than untreated BW. Le Chatelier volume expansion tests on OPC indicate that the expansion varies from 0 to 4 mm. These results are in European Standard EN 196-3 and 14.09% B_2O_3 content of BW affected volume expansion worse.

Conclusions

In this study, the effects of treated and untreated BW addition on the mechanical and physical properties of OPC prepared by adding BW to PC 42.5 were determined. The following conclusions can be drawn from the experimental results:

1- All water-soluble impurities, especially B_2O_3, can be removed from BW by a simple washing process. Removal of B_2O_3 is an important process in the prevention of water and soil pollution, recycling of raw materials in borax production and the utilization of waste.

2- Utilization of treated BW in cement production gives better results than untreated BW. The physical and mechanical properties of cements prepared with BW samples, which have high and low B_2O_3 content, show differences. The compressive strength, expansion and the setting time properties of the OPC are affected negatively by increasing the B_2O_3contentin the waste. It is concluded that BWs could be used for OPC as an additive if the B_2O_3 content is low.

3- It has been reported that an increased B_2O_3 amount in cement causes a fall in strength values. Borax and other borates are often used as retarding aids to extend the temperature range of effective use of concretes. It is known that the obtained cements and concretes are resistive to microbial decomposition because boron compounds are antiseptics, and they decrease the radioactive permeability of the concrete (Boncukçuoğlu *et al.,* 1999). Therefore, BW can be used as additive to cement (5% by weight) after the limitation of boron content.

4- It is concluded that all water-soluble impurities, especially B_2O_3, are removed from BW by water leaching and the mechanical properties of OPC mixtures are improved.

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