Afyon Kocatepe Üniversitesi
FEN BİLİMLERİ DERGİSİ

Özel Sayı
245-250

Afyon Kocatepe University
JOURNAL OF SCIENCE

PRODUCTION OF LIGHTWEIGHT AGGREGATES FROM DIFFERENT TYPES OF BORON WASTES

Taner KAVAS[1,*], Angeliki CHRISTOGEROU[2], Yiannis PONTIKES[2],
Tuğba TUNÇ[1], George N. ANGELOPOULOS[2]

[1]Department of Materials Science and Engineering, Afyon Kocatepe University, Afyonkarahisar, Turkiye
[2]Laboratory of Materials and Metallurgy, Department of Chemical Engineering,
University of Patras, 26500 Rio, Greece

ABSTRACT

Four boron wastes (BW), named as Sieve (SBW), Dewatering (DBW), Thickener (TBW) and Mixture (MBW) waste, from Kirka plant (Turkey) were investigated for the formation of Artificial Lightweight Aggregates (LWA). The characterization involved chemical, mineralogical and thermal analyses. The bloating behavior was examined by heating microscopy. SBW and DBW expanded in two stages, at 300°C approximately and subsequently at 550°C with concurrent formation of liquid phase. However, at 650-700°C there is excessive liquid phase formed resulting in large, non uniform porosity of irregular shape. On the contrary, in the case of TBW and MBW no noticeable expansion or glassy surface was formed. An optimization route, involved the formation of a mixture with 20wt% clay, 40wt% SBW, 40wt% DBW and one with 20wt% clay, 35wt% SBW, 35wt% DBW, 10wt% quartz sand. The raw aggregates were fired in a rotating crucible at 650°C, 700°C, 710°C and 760°C for 2-5 min. It was observed that the clay addition leads to better plasticity and cohesion between the particles whereas the quartz addition shifts the softening point 50°C higher. Water absorption was 56.8-60.5%, apparent specific gravity 2.3-2.4g/cm^3 and bulk density 0.9-1.1g/cm^3. The analysis of microstructure with electron microscopy revealed a glassy phase matrix and an extended formation of both open and closed pores. The results indicate that SBW and DBW boron wastes can be utilized in LWA production.

Keywords: Boron wastes, Light weight aggregates, Recycling, Valorisation

---

1. INTRODUCTION

Lightweight aggregates are defined as natural or artificial materials, which are granular, porous and light in weight. They are categorized as normal LWA, ultra LWA and heavy LWA. The natural materials most frequently used for their production are clay (vermiculite, smectite, montmorillonite) and sedimentary rocks (slates, shales). Aggregates are used in concrete mixtures, where they can make up 70 to 80% of the concrete volume, as well as in asphalt mixtures (roadways-hot mix asphalt, cold mix asphalt, surface treatments). The typical properties of LWA are good thermal and acoustic insulation, as well as good fire resistance.

The formation of LWA is based on the “bloating” phenomenon at which two conditions must occur simultaneously: the formation of a viscous liquid phase during firing which is capable to entrap the gases produced from the decomposition of minerals. In addition, a glassy film on the outer surface should be developed during cooling making the LWA impervious to water [1].

Several wastes or industrial by-products have been used for the production of LWA, such as fly ash, bottom ash, red mud, waste glass, zeolites and other [2-7]. The goal is to replace the raw materials used for the LWA production by other materials presenting similar chemical composition. As a result, by-products will be utilised and their rejected amount will be reduced with obvious environmental benefits.

The largest boron deposits are found in west Turkey with a worldwide share of 72% (851Mt) in terms of B_2O_3 content, and are controlled by the national mining enterprise Eti Maden [8,9]. The principal borate minerals are tincalconite ($Na_2O·2B_2O_3·5H_2O$), ulexite ($Na_2O·2CaO·5B_2O_3·16H_2O$) and colemanite ($2CaO·3B_2O_3·5H_2O$) which are refined into pure chemical compounds. During this process, large quantities (~ 400.000t/y) of different types of boron wastes are formed and rejected in tailing dams [10]. These wastes contain important fluxing oxides such as SiO_2, MgO, CaO, Na_2O, B_2O_3 which are necessary for the formation of LWA.

The aim of this study is to investigate the possibility of using these boron wastes in the production of LWA.

2. MATERIALS AND METHODS

The raw materials used were boron wastes from the main production stages of Etibor Co. Kirka Borax plant in Turkey, named Sieve (SBW), Dewatering (DBW), Thickener (TBW) and Mixture (MBW) waste. A clay mixture as well as quartz sand were also used. The chemical composition of the boron wastes was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Optima 3200 XL, Perkin-Elmer, USA), whereas for the clay mixture an Atomic Absorption Spectrometer was used (AAnalyst 200, Perkin Elmer, USA). The crystalline phases were determined by X-ray diffraction analysis (XRD, Siemens Diffraktometer D5000, Germany).

All raw materials were dried at 110°C and milled at a particle size <125µm. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) was performed on powdered samples, in static air, with a heating rate of 10°C/min (TGA Q50, TA Instruments, USA and Linseis-L81, Germany, respectively). Firing behaviour was also examined by a custom made heating microscopy (HM), employing a heating rate of 40°C/min. Analysis was performed on cylindrical samples (dia=4.8mm, height=6mm) formed from different dry mixtures by adding 40wt% water approximately, drying at 110°C and heating up to 750°C with a rate of 40°C/min. Six body formulations were tested: the four raw materials (SBW, DBW, TBW and MBW) as well as two mixtures, M1 and M2, that resulted as an effort to optimize the firing behaviour and characteristics of the aggregates. Mixture M1 is comprised of 20wt% clay, 40% SBW, 40wt% DBW, whereas M2 of 20wt% clay, 35wt% SBW, 35wt% DBW and 10wt% quartz sand. Volume expansion was calculated from the pictures taken at several times and temperatures, with respect to the initial volume of the sample in room temperature.

Based on their behaviour as deduced by HM, raw aggregates were prepared with mixtures M1 and M2. The raw materials were mixed in a plastic bag for homogenization and subsequently 40wt% approximately water was added. From the plastic mass, spherical samples (dia=8-10mm) were formed by hand pelletising and dried at 110°C for 2h. Firing took place in a rotary crucible in two different conditions (Table 3): a) with a heating rate of 20°C/min from 25°C to 750°C, and b) with a heating rate of 22°C/min from 25°C to 300°C and flash heating at 650, 700, 710 and 760°C. Soaking time varied between 2 to 5 min.

Water absorption (A), porosity (P), apparent specific gravity (T) and bulk density (B) of the fired aggregates was determined according to the ASTM C373-88. The microstructure of fractured and polished cross-section as well as of the surface of the samples was examined by scanning electron microscopy (SEM, JSM-6300, Jeol, Japan).

3. RESULTS AND DISCUSSION

The chemical analysis of raw materials is presented in Table 1. In terms of mineralogy, all boron wastes are comprised of tincalconite ($Na_2B_4O_7{\cdot}5H_2O$) and dolomite ($CaMg(CO_3)_2$) as major phases, with albite ($NaAlSi_3O_8$), sanidine ($K(Si_3Al)O_8$) and microcline ($KAlSi_3O_8$) as minor ones. SBW and DBW have in addition calcite ($CaCO_3$). The major phases of the clay mixture are quartz, SiO_2, calcite, clinochlore ($(Mg,Fe)_6(Si,Al)_4O_{10}(OH)_8$) and albite, whereas illite [$(K,H_3O)Al_2Si_3AlO_{10}(OH)_2$] and muscovite [$(K,Na)(Al,Mg,Fe)_2(Si_{3.1}Al_{0.9})O_{10}(OH)_2$] are present as minor constituents.

Table 1. Chemical composition of raw materials (in wt%).

	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	SO_3	K_2O	Na_2O	B_2O_3	L.O.I.
SBW	19.10	0.75	8.06	0.28	9.25	0.55	0.64	11.87	19.58	29.92
DBW	14.51	0.48	12.01	0.26	16.09	b.d.l	0.72	9.32	15.11	31.49
TBW	26.13	1.42	8.55	0.43	9.17	0.92	1.39	5.49	10.41	36.07
MBW	19.79	0.47	12.32	0.23	5.95	0.41	0.61	11.66	16.14	32.42
Clay	46.29	13.11	12.33	5.79	3.01	b.d.l	2.29	0.58	b.d.l	12.87

b.d.l : below detection limit

From the TGA curves, Fig. 1, it is revealed that boron wastes have three characteristic steps of weight loss. In the first step, up to 160°C, the endothermic, Fig. 2, reaction of tincalconite's dehydration takes place. SBW, TBW and MBW present a comparable behaviour in this range, having a weight loss of 4% approximately. On the contrary, DBW presents the highest mass loss, 12%. At 520-550°C approximately, the dehydroxylation of tincalconite to anhydrous borax, $Na_2B_4O_7$, initiates as is evident by the accompanied weight loss, Fig. 1, and the strong endothermic peak, Fig. 2. The thermal behaviour of tincalconite resembles that of chemically pure borax ($Na_2B_4O_7{\cdot}10H_2O$) [11,12]. At 700°C approximately, the process of dissociation for calcite and dolomite, originally present in SBW and DBW, has been most probably completed, Fig. 1 and 2, and there is subsequently minimal weight loss up to the final temperature. The total weight loss ranges from 29-36%, with TBW presenting the highest value. In the case of clay the overall weight loss is 14% and is mainly due to dehydroxylation of the clay minerals and the dissociation of calcite.

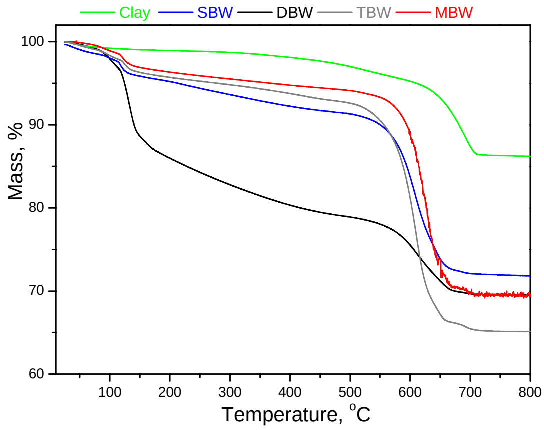

Fig. 1. TGA analysis of boron wastes and clay.

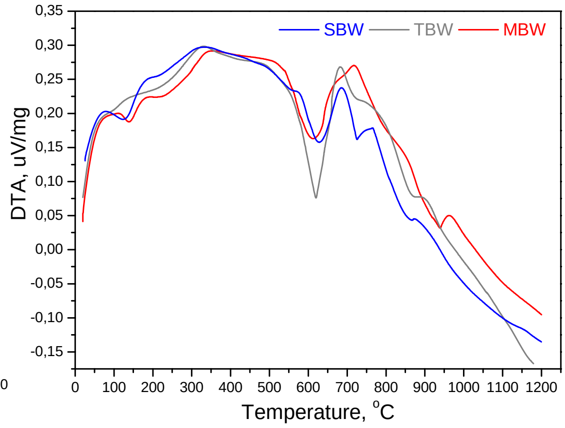

Fig. 2. DTA analysis of SBW, TBW and MBW.

Tests with the HM indicate two major bloating stages for SBW and DBW. In the case of SBW, volume expansion was observed at 300°C and bloating at 500°C. The softening point was observed at 550°C and the melting point at 750°C. DSW presented volume expansion at 300°C, bloating at 550°C, softening point at 400°C and melting at 700°C.

TBW and MBW samples demonstrated a different behaviour compared to SBW and DBW. TBW and MBW presented the two characteristic bloating stages at 300 and 500°C. At 650°C samples start to shrink, whereas for firing even up to 835°C, the samples retain their structural integrity. No formation of glassy surface was observed.

In order to examine the phase transition during heating, samples of DBW were quenched from 300, 500 and 700°C to air temperature, Fig. 3, pulverized and analyzed by XRD, Fig. 4. It was observed that at 300°C the initial minerals identified in DBW, tincalconite and dolomite, still exist. The samples fired to 500°C present a decrease in the peak of tincalconite and an increase of amorphous phase. This reveals that dehydroxylation of tincalconite has not been yet completed. Samples fired at 700°C result in significant increase of the amorphous phase and in the formation of new crystalline phases, such as sodium borate ($Na_2B_4O_7$), calcium silicate (Ca_2SiO_4) and calcium borate ($Ca_2B_2O_5$).

From these results, it was concluded that SBW and DBW demonstrate good bloating behaviour. However, the fired samples presented a microstructure with porosity of irregular shape and uneven distribution. Moreover, the external surface was blown off by gas bubbles produced during firing.

In order to improve the characteristics of the process and the final body, mixture M1 was formulated by using 20wt% clay, 40wt% SBW and 40wt% DBW. The addition improved the cohesion between the particles and the shaping ability. Moreover, a simultaneous formation of liquid phase and gases was achieved, resulting in a uniformly distributed internal pore structure.

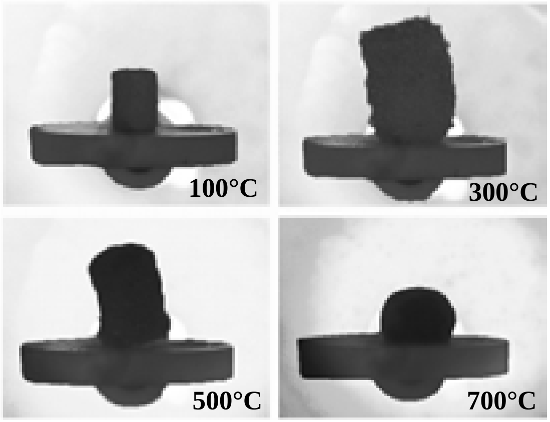

Fig. 3. DBW sample, fired in heating microscope.

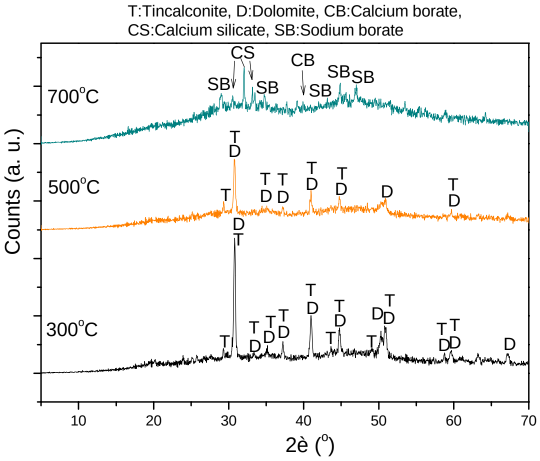

Fig. 4. XRD patterns of DBW sample fired at 300, 500 and 700°C. Only major phases annotated in the graph.

In mixture M2, quartz was added to mixture

M1, in order to investigate its influence on the glassy phase formation and bloating. As a result, bloating and softening point were shifted to 50°C approximately higher. The produced gas bubbles were entrapped inside the body more effectively, probably due to an increase of the viscosity of the liquid phase formed. Deformation of the samples started above 720°C. The final volume expansion after 15min firing at 700°C was 65% approximately. The surface of the aggregate was vitrified whereas the internal structure was characterised by uniformly distributed open and closed pores.

In the second experimental part, aggregates were formed according to the best formulations tested by HM, M1 and M2. The physical properties of the fired pellets are presented in Table 2. For comparative reasons, the values for natural lightweight aggregates-NLWA (pumice from Greece) are also included.

The increased bulk density value for the M1 aggregates, 1.25g/cm^3, can be attributed to the slow heating rate from room temperature to 750°C which provides sufficient time for gas escape and reduces volume expansion, Fig 5(b) and (c).

Table 2. Physical properties of LWA fired at different temperatures and times.

Mixtures	*Temperature (°C)*	*Time (min)*	*P (%)*	*A (%)*	*T (g/cm^3)*	*B (g/cm^3)*
M1	25-750	12	39.6	31.7	2.1	1.25
M2	650 (feeding)	4-5	58.7	60.5	2.4	0.97
M2	700	2-3	48.3	43.4	2.3	1.00
M2	710	4	57.4	56.5	2.4	1.03
M2	760	3-5	56.1	56.8	2.3	0.97
NLWA	-		42.2	48.9	1.6	0.94

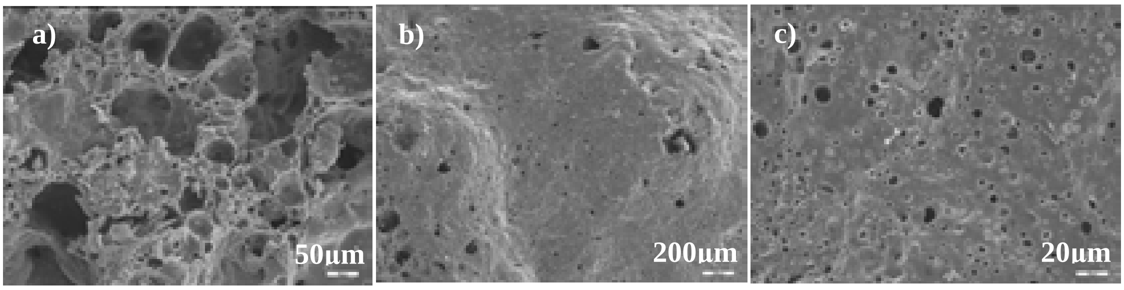

Fig. 5. SEM images of fired M1 aggregate; a) core, b) and c) external surface.

Flash firing which was applied for M2 aggregates, resulted in an increase of apparent specific gravity and in a decrease of bulk density <1g/cm^3, a value similar to the natural LWA. SEM observation of cross-sections for the M2 samples is presented in Fig. 6. A fine distribution of both closed and open pores, in a matrix of highly vitrified phase is observed.

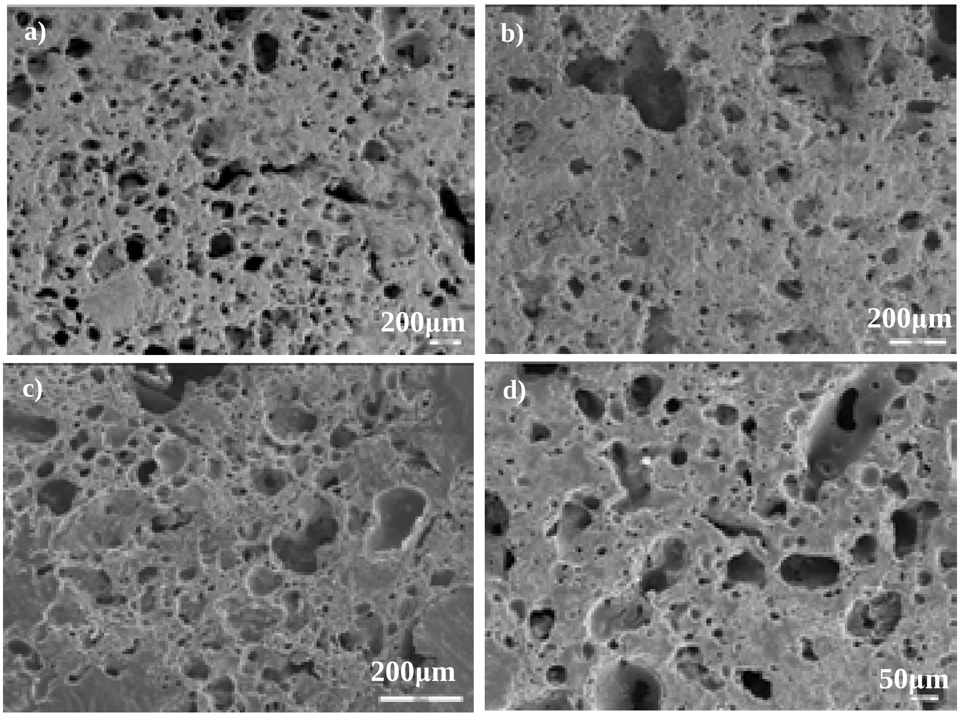

Fig. 6. SEM images of cross section of samples M2 fired at 650 (a), 700 (b), 710 (c) and 760°C (d) respectively.

4. CONCLUSIONS

Two types of boron wastes, SBW and DBW, can be used for the production of lightweight aggregates after adjustment of the final mixture. The best results were obtained from a mixture consisting of 20wt% clay, 35wt% SBW, 35wt% DBW and 10wt% quartz sand. Flash firing at 650, 700, 710 and 760°C resulted in porous LWA with bulk density values of 0.97, 1.00, 1.03 and 0.97g/cm^3 respectively. Boron wastes obviously decrease the firing temperature for LWA production.

5. REFERENCES

1. E. G. Ehlers, The Mechanism of Lightweight Aggregate Formation, Ceramic Buletin, Vol. 37, No.2, 95-99, 1958
2. Su-Chen Huang et al, Production of lightweight aggregates from mining residues, heavy metal sludge, and incinerator fly ash, J. Hazard. Mater. 144, 52-58, 2007
3. M. Aineto, A. Acosta, J. M. Rincon, M. Romero, Production of Lightweight Aggregates from Coal Gasification Fly Ash and Slag, Submitted for consideration in the 2005 World of Coal Ash 11-15, Lexington, Kentucky, USA, 2005
4. I. Anagnostopoulos, V. Stivanakis, Utilization of lignite power residues for the production of lightweight aggregates, J. Hazard. Mater. (2008), doi:10.1016/j.jhazmat.2008.06.125
5. H. R. Blank, Red Mud from Alumina Plants as a Possible Source of Synthetic Aggregate, Journal of Testing and Evaluation, JTEVA, Vol. 4, No. 5, 355-358, 1976
6. V. Ducman, A. Mladenovič, J. S. Šuput, Lightweight aggregate based on waste glass and its alkali-silica reactivity, Cem. Conr. Res. 32, 223-226, 2002
7. R. de Gennaro, P. Cappelletti, G. Cerri, M. de Gennaro, M. Dondi, A. Langella, Zeolitic tuffs as raw materials for lightweight aggregates, App. Clay Sci. 25, 71-81, 2004
8. http://www.etimaden.gov.tr
9. P. M. Mobbs, The Mineral Industry of Turkey, U.S. Geological Survey Minerals Yearbook-2004.
10. European Commission, Reference Document on Best Available Techniques for Management of Tailings and Waste-Rock in Mining Activities, Chapter 3, July 2004.
11. A. Ekmekyapar, A. Baysar, A. Künkül, Dehydration Kinetics of Tincal and Borax by Thermal Analysis, Ind. Eng. Chem. Res. 36, 3487-3490, 1997
12. I. Waclawska, Thermal decomposition of borax, J. Therm. Anal., 43, 261-269, 1995

6. ACKNOWLEDGEMENTS

The authors acknowledge the support obtained within the framework of Erasmus and Turkish-Greek bilateral projects (TÜBİTAK-105M330).