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Use of boron wastes in the production of heavy clay ceramics

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Abstract

Colemanite, ulexite and tincal are the main boron ores found in Turkey and account to 63% of the world estimated reserves. The production route of boron products results in significant amounts of different types of Boron Wastes, BW. Their open field disposal raises substantial environmental concerns in fear of leaching and groundwater pollution. The heavy clay ceramic industry can potentially absorb substantial quantities of BW. In the present study, BW produced from Kirka borax plants in Turkey, with 12.6 wt.% B_2O_3 was introduced in 0 wt.%, 5 wt.% and 15 wt.% in a heavy clay body mixture. Four peak temperatures, 800 °C, 850 °C, 900 °C and 950 °C, were examined for the dry pressed samples. The thermal behaviour analyzed by dilatometry and TGA shows that major loss in weight starts about 600 °C and continues to 700 °C approximately. For 5 wt.% BW addition and firing at 900–950 °C, the sintered bodies present comparable or improved physical and mechanical properties with respect to the reference formulation. The microstructure was analyzed by SEM whereas the main crystalline phases were identified by XRD. Samples fired at 900 °C with 5 wt.% BW present comparable properties with the reference ones. At 950 °C, the obtained properties were improved. Deformation occurs for samples with 15 wt.% BW when fired at >900 °C.

Keywords: Heavy clay ceramics; Boron waste utilization

1. Introduction

Borates are naturally occurring minerals, containing or supplying boric oxide, which can be found mainly in sediments and sedimentary rocks. The commercially most important boron minerals are tincalconite ($Na_2B_4O_7{\cdot}10H_2O$), colemanite ($Ca_2B_6O_{11}{\cdot}5H_2O$) and ulexite ($NaCaB_5O_9{\cdot}8H_2O$) [1]. These ores can be refined into pure chemical compounds such as boric acid, anhydrous boric acid, anhydrous borax, borax pentahydrate, borax decahydrate and sodium perborate. The largest boron deposits in the world are known to be in west Turkey with a worldwide share of 72% (851 Mt), in terms of B_2O_3 content, and are controlled by the national mining enterprise Eti Maden (Eti mine) [2–4]. The production route of boron products, results in significant amounts of different types of boron wastes, BW. Taking into account, an expected increase of ~3% annually on the total borate demand [1], it becomes obvious that the handling of BW will result more demanding in the future. At the present, BW are disposed in tailing dams; however, this raises substantial environmental concerns in fear of leaching and groundwater pollution [5].

A potential candidate for the BW could be the heavy clay ceramic industry due to the high volume production. Small additions in the raw mixture will result in significant BW utilization. In fact, several studies on the utilization of BW in ceramics have been published that concern wastes from different stages of the borates production route as well as from different geographical regions. This results in differences in chemical and mineralogical composition of BW with the B_2O_3 content varying from 3.5 wt.% to 26 wt.%. Uslu and Arol [6] report on the utilization of clay containing tailings in a clay mixture suitable for red brick production. They found that additions up to 30 wt.% of this BW enhances the glassy phase and improves the overall brick quality. Higher additions reduce the compressive strength and make rough the surface of the bodies. Kavas [7] reports that increasing up to 15 wt.% the content of clay and fine boron wastes in mixtures with red mud, the formation of glassy phase improves the mechanical

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Table 1
Chemical composition, in wt.%, of W and BW

Material	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	K_2O	Na_2O	B_2O_3	L.O.I.
W	48.3	13.6	12.7	5.3	3.1	2.5	0.6	–	13.6
BW	15.1	1.7	16.8	0.2	14.2	0.6	4.1	12.6	34.1

properties of the sintered bodies. Kurama et al. [8] studied a mixture consisting of dewatering sieve waste with ball clay and sanitaryware waste for the production of a terracotta floor tile body. It was found, also in this case, that the addition of BW promotes vitrification. The authors ascribe the improved physical and mechanical properties apart from the presence of boron to the high alkaline-earth oxides content in BW that decreases the viscosity of the developed liquid phase. In addition, Cave [9] made a survey on the use of BW in ceramic tile bodies. It was concluded that the ceramic industry is not yet ready to welcome a by-product in their production route, because of the critical variations in chemical composition. Olgun and co-authors [10] examined the effect of coal fly ash and borax solid waste (TW) on the properties of wall tiles. Fly ash and TW were introduced in a range of 2–10% replacing potassium feldspar. The results showed increased firing strength when TW was added up to 6%.

Borates can benefit the heavy clay ceramic industry due to their glass-forming effects. Moreover, reduction of the firing temperature is anticipated. However, use of water-soluble borax and boric acid is disadvantageous as they are water soluble. Tests with the above products showed a large degree of migration of the borate to the surface as water is expelled during drying process. As a consequence, glass is formed on firing at the surface creating several problems in the production. In order to face this problem borate containing products have been developed and are commercially available such as Evansite® which minimize migration problems to the surface.

Summarizing the above findings, it is evident that: (a) BW functions as a flux promoting the liquid phase formation in the body and (b) an excess in the body mixture or a high sintering temperature may deteriorate the sintered bodies. Nonetheless, there is only one work focusing on BW in bricks and there is room for contribution especially in the area of thermal behaviour and microstructural development.

To address these issues, mixtures of BW and a clay mixture used in the heavy clay industry for the production of roofing tiles were prepared following the state-of-the-art guidelines in mixture design. The samples were formed by dry pressing with 6 wt.% water addition in order to minimize the borate migration towards the surface. BW content and firing temperature were moderate, up to 15 wt.% and up to 950 °C, respectively. The physical and mechanical properties, as well as the thermal behaviour and the microstructure of the final products were studied.

2. Experimental

The raw materials used were clay body mixture, W, industrially used for the production of white-cream bricks, and BW (sieve waste) obtained from Eti Holding Kirka Borax Inc. The chemical composition of W and BW was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES Optima 3200 XL, PerkinElmer, USA), and is reported in Table 1. The crystalline phases of raw materials were determined by X-ray diffraction analysis (PW 1830, Philips), Table 2.

For the preparation of the raw materials, both clay mixture and BW were milled at a particle size $<125\ \mu m$ and thoroughly homogenized. Three mixtures were prepared: the reference body W, and two with 5 wt.% BW (W5) and 15 wt.% BW (W15) replacing W. In the resulting mixtures, 6 wt.% of distilled water was added and they were left to rest for 24 h in a hermetically closed plastic bag. Rectangular samples, $101\ mm \times 20\ mm \times 8\ mm$, were shaped under a load of 225 bar. The pressed samples were dried initially at room temperature for 24 h and then in a drying oven at 110 °C till constant weight. Sintering was performed in a laboratory muffle furnace at four peak temperatures: 800 °C, 850 °C, 900 °C and 950 °C. The thermal cycle was similar to the industrial one with 4 h soaking time and total duration of ~36 h.

For the sintered ceramics the standards ASTM C326-82 and ASTM C373–88 were followed for the measurement of total linear shrinkage after firing, apparent porosity, water absorption and bulk density. Bending strength was determined using a testing machine (DTM, Dillon, USA) equipped with a three point bending fixture. The mineralogical compositions of the fired samples were determined by X-ray diffraction analysis (PW 1830, Philips) on pulverized bodies. For the thermal analysis, thermogravimetry, TGA, (TGA Q50, TA Instruments) and dilatometry (402ES, Netzsch) were performed. TGA analysis was performed in powdered samples $<125\ \mu m$, in static air with a heating rate of 10 °C/min. Dilatometry was conducted in static air with a heating and cooling rate of 5 °C/min. The specimens were rods, 25 mm long and 3 mm diameter. Observation of microstructures was performed with a scanning electron microscope SEM (JSM-6300, Jeol) on polished surfaces, whereas energy dispersion spectroscopy, EDS (Oxford Instruments), was used for microanalysis.

Table 2
Crystalline phases of the raw materials

Material	Major	Minor
W	Quartz, calcite, Fe-chlorite, albite	Illite, mixed smectite interlayer, minerals, K-feldspar
BW	Dolomite ($CaMg(CO_3)_2$), ulexite ($NaCaB_5O_9\cdot 8H_2O$), tincalconite ($Na_2B_4O_7\cdot 5H_2O$), calcite	Montmorillonite, borax ($Na_2B_4O_7\cdot 10H_2O$)

3. Results and discussion

The chemical composition of raw materials is given in Table 1. W presents a typical composition for Ca-rich clay mixtures. BW is rich in CaO, MgO SiO_2 and B_2O_3.

In terms of mineralogy, Table 2, quartz, calcite, Fe-chlorite and albite are the main phases in the case of W, with illite, mixed smectite interlayer minerals and K-feldspar present in minor quantities. For BW, the main identified phases were dolomite ($CaMg(CO_3)_2$), ulexite ($NaCaB_5O_9\cdot8H_2O$), tincalconite ($Na_2B_4O_7\cdot5H_2O$) and calcite; as minor constituents, montmorillonite and borax ($Na_2B_4O_7\cdot10H_2O$) were present.

The TGA curves for W and BW are depicted in Fig. 1. For W, a continuous weight loss occurs up to 710 °C that coincides with the completion of the decomposition of calcite. The curve for BW is characterised by two abrupt zones, one up to 160 °C and the second between 550 °C and 750 °C and is comparable with other references [8]. In the first zone, the water removal from ulexite and tincalconite takes place [11], whereas in the second zone, the decomposition of dolomite and calcite occurs. The overall weight loss in the case of BW is 34% approximately. Compared to 14% approximately for the case of W, this value is rather high and a great amount of porosity is expected to evolve in the body.

The results from dilatometry are presented in Fig. 2. In the temperature interval 80 °C to 160 °C, W5 and W15 show a more intense shrinkage compared to W, in agreement with their higher weight loss as presented in Fig. 1. At a higher temperature, all mixtures show comparable behaviour, however W5 and W15 undergo an expansion at 750 °C approximately. This expansion can be attributed to entrapped CO_2, resulting after the decomposition of calcite and dolomite. It is observed in the case of mixtures with BW, due to the higher amount of carbonates in the body in conjunction with an early formation of liquid phase which obstructs the pathways for gas escape. Similar behaviour has been reported in the case of soda–lime–silica glass addition in traditional ceramics [12]. Shrinkage initiates at 760 °C and 780 °C for W15 and W5, respectively, and at higher temperature, 820 °C, for W. For W15, further shrinkage occurs before 950 °C, most probably due to the extended formation of liquid phase. The overall firing shrinkage is slightly higher for the mixtures with BW; W5 presents the highest value.

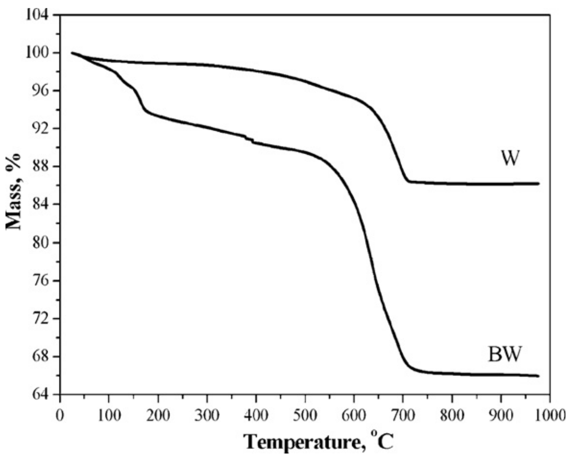

Fig. 1. TG curves for the clay body mixture W and for the BW material.

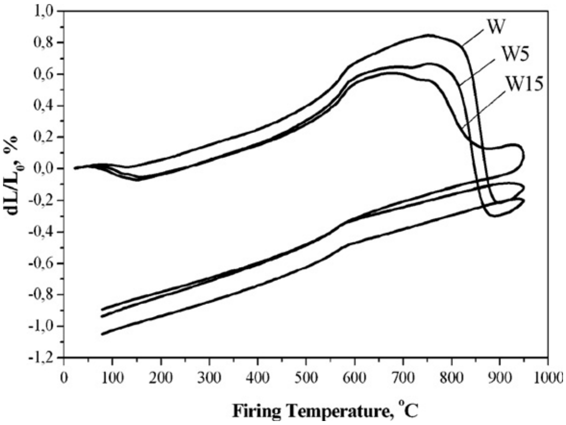

Fig. 2. Dilatometry curves for the clay body mixture W and for the mixtures of W with 5 wt.% and 15 wt.% BW substitution.

The water absorption and shrinkage after sintering is shown in Fig. 3. At 800 °C, W presents the minimum of all three bodies tested, 18.6%, whereas W5 and W15 follow, with 19.8% and 23.6%, respectively. This was anticipated in view of the high content of dolomite and calcite in BW, as also reflected in the weight loss during sintering. For a higher temperature, up to 900 °C, all mixtures demonstrate similar dependence from the sintering temperature. In fact, at 900 °C, W and W5 have their minima and comparable values, 16.5% and 17.5%, respectively. At 950 °C, the water absorption of W and W5 increases, compared to sintering at 900 °C, in line with other references on a similar W body [13] or calcite- and dolomite-rich clay mixtures [14]. On the other hand, W15 presents a notable decrease in water absorption of ~43%, due to enhanced formation of liquid phase. However, the viscosity was not sufficiently high and the samples were deformed. In terms of shrinkage, W demonstrates a small increase at 850 °C,

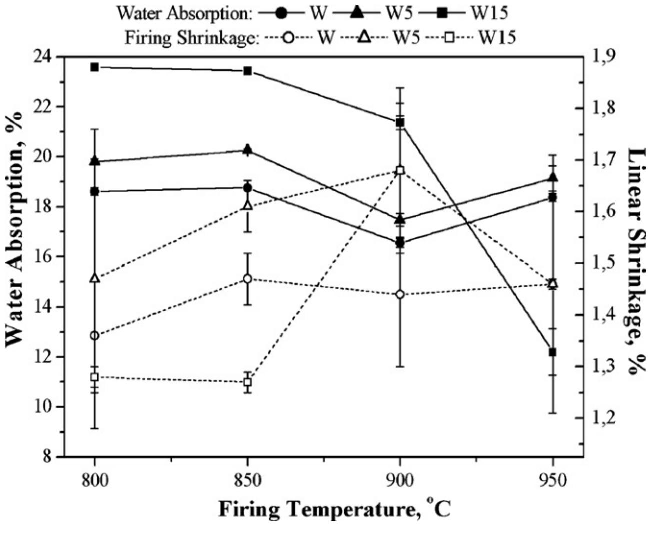

Fig. 3. Water absorption (continuous line) and linear shrinkage (dashed line) as a function of sintering temperature for the tested samples.

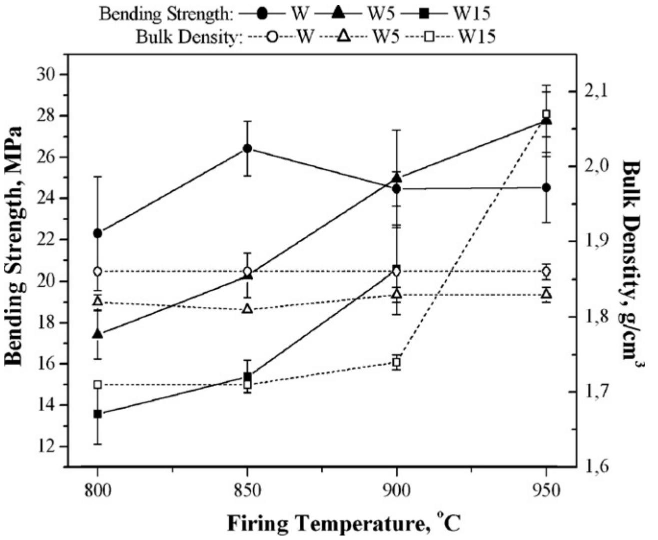

Fig. 4. Bending strength (continuous line) and bulk density (dashed line) as a function of sintering temperature for the tested samples.

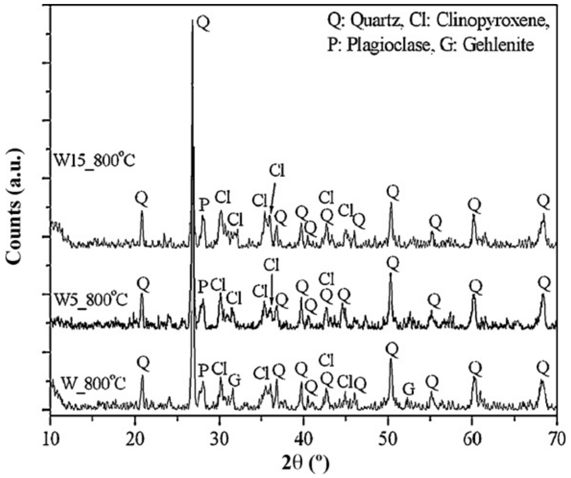

Fig. 5. XRD spectra of the samples W, W5 and W15, fired at 800 °C.

compared to 800 °C, which remains constant until 950 °C. W5, presents a continuous increase in shrinkage up to 900 °C and an expansion takes place for sintering at 950 °C, reducing the shrinkage from 1.7% (at 900 °C) to 1.5%. This behaviour is rather common when over-firing porcelain bodies, where gases are entrapped in the aluminosilicate melt.

The results of the three point bending strength and the bulk density are presented in Fig. 4. For the reference body W, the maximum value is observed at 850 °C, 26.4 ± 1.3 MPa. For sintering at 900 °C and 950 °C the bending strength is 24.5 ± 0.8 MPa and 24.5 ± 1.7 MPa, respectively. For the mixtures with BW, increase of firing temperature results in increased bending strength. The best results were achieved for W5 sintered at 950 °C, 27.8 ± 1.7 MPa, a value higher than one of the reference body. In terms of bulk density, W has a constant value of 1.86g/cm^3 for all firing temperatures. The samples with BW showed limited dependence from sintering temperature up to 900 °C. At 950 °C, bulk density for W5 remains constant, 1.83 ± 0.03 g/cm^3, as for sintering at lower temperatures, whereas W15 presents an increase from 1.71 ± 0.01 g/cm^3 to 2.07 ± 0.03 g/cm^3.

The results from the XRD analysis for the mixtures W, W5 and W15, fired at 800 °C, are presented in Fig. 5. The main phases identified for W are quartz, plagioclase (anorthite), clinopyroxene (aluminium diopside) and gehlenite. The addition of BW in the clay body mixture had no significant change in the phase formation at 800 °C, being qualitatively the same as for W. At 850 °C the intensity of quartz's peaks is decreased as the peaks of clinopyroxene increase, in all formulations tested. For firing at 900 °C, Fig. 6, quartz's peaks are further decreased as the intensity of clinopyroxene peak gets higher. At this temperature gehlenite's peaks are not present in bodies with BW. As the BW content increases, from 5 wt.% to 15 wt.%, the ratio of clinopyroxene to quartz peaks increases. At 950 °C the XRD analysis for W15 showed a strong background interference, corroborating the increased formation of amorphous phase.

SEM observations on polished surfaces revealed for the case of W a typical microstructure with elongated pores and clearly distinguished grains. No sign of liquid phase formation is evident for sintering at 800 °C. For 5 wt.% BW, the above described morphology is slightly altered and vitrified, yet highly porous, areas appear in the matrix. In Fig. 7(a) an assemblage of quartz, K-feldspars, calcite relics, Ca-rich microsites, and dehydroxylated chlorite grains (according to EDX analysis) is depicted for W15. For sintering at 850 °C, all bodies remain highly porous; however, densified regions appear in both bodies with WB. At 900 °C, Fig. 7(b), these regions are more compact demonstrating mainly closed pores. Quartz grains, as arrows point out and feldspars are enclosed in these formations. In terms of porosity, it remains interconnected and appears higher, for both W5 and W15, compared to W. For W5 and sintering at 950 °C, Fig. 7(c), the degree of vitrification is advanced. Nonetheless, porosity remains high and is still interconnected. For 15 wt.% BW and the same sintering temperature, Fig. 7(d), the microstructure is

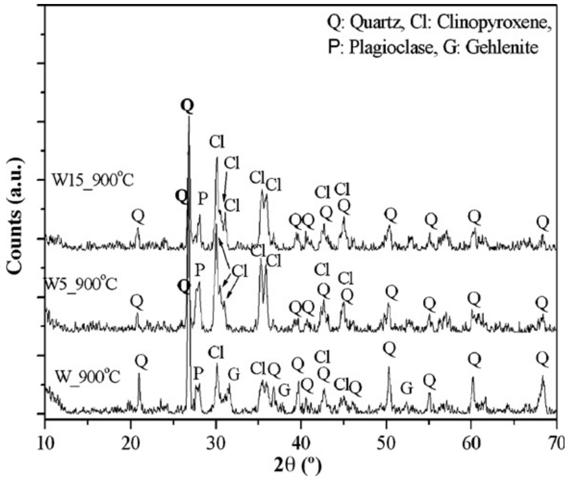

Fig. 6. XRD spectra of the samples W, W5 and W15, fired at 900 °C.

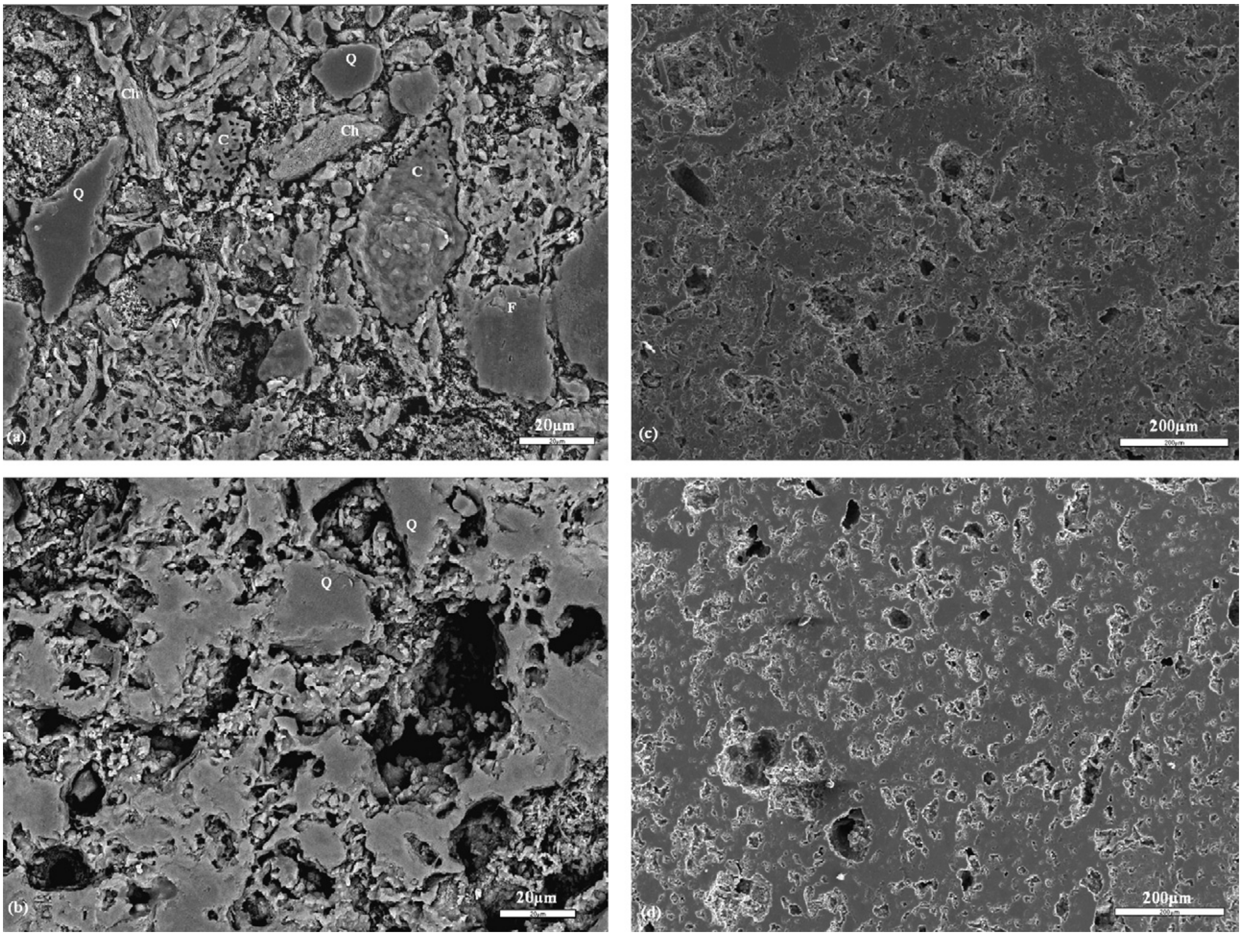

Fig. 7. (a) Back/ed, W15, 800 °C. Q: quartz, C: calcite, calcium-rich, Ch: dehydroxylated chlorite, F: K-Feldspar, V: vitrified area, (b) back/ed, W15, 900 °C. Arrows point quartz grains. (c) Sec., W5, 950 °C, (d) sec., W15, 950 °C. Back/ed: backscattered electrons image, sec. secondary electrons image. All polished surfaces.

highly glassy, in line with XRD results. Porosity remains high, yet closed pores are widespread in the glassy matrix and the large ones remaining are rounded. Interlinked and open porosity is still present.

4. Conclusions

The addition of BW in the clay body mixture W, results in the formation of increased amount of liquid phase during sintering. Shrinkage on sintering initiates at a lower temperature and the overall value is similar. The final mineralogical assemblage is comparable to W, but the ratio of clinopyroxenes to quartz increases as BW content raises and gehlenite is not detected for >900 °C.

In terms of physical–mechanical properties, for 5 wt.% BW addition and sintering in the range 900–950 °C, the end bodies present comparable water absorption and bending strength, with respect to the reference formulation. For 15 wt.% BW and sintering <950 °C, the bodies presented higher water absorption and reduced bending strength and bulk density, mainly due to the great amount of carbonates in BW contributing in the formation of porosity. For sintering at 950 °C, an extended amount of liquid phase was formed, drastically reducing open porosity, but also associated with the deformation of the final samples. Possibly, a decreased soaking period than the one followed in this work (4 h) will prevent warpage.

As a general remark, the use of BW in heavy clay production is feasible, ‘‘as-is’’, in small percentages whereas higher additions may necessitate the optimization of the sintering profile or a pre-calcination step for BW.

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