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PRODUCTION OF REACTIVE ALUMINA FROM DOMESTIC SOURCES AND ITS USE IN ALUMINA-BASED SELF-FLOWING CASTABLE REFRACTORIES

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Abstract: High-quality alumina raw materials allow corundum-based brick and monolithics to perform to the full potential of alumina as a refractory material. Dense packing of the matrix to a submicron range and reduction of water demand of castables can be facilitated by a new family of multimodal reactive alumina. Dispersing aluminas ensure uniform mixing of dispersion and setting adjustment additives. In this study, fine reactive alumina powder production was investigated using Bayer gibbsite as a starting material. Experimental studies consist of two steps; in the first step, the soda content was reduced by means of boric acid and distilled water and then the powders obtained optimum conditions were ground in an attritor ball mill using distilled water for 8 hours. In the second step, physical characteristics such as rheological behaviours, bulk density, open porosity and thermal shock resistance, bending and compressive strength and fracture toughness in accordance with ASTM E399 standard were determined. Finally, K_{IC} values of the refractory samples which were prepared with the reactive alumina produced from Seydişehir gibbsite were higher than that of the refractory mixture containing commercial reactive alumina obtained from a refractory company.

Keywords: Seydişehir gibbsite, Reactive alumina, Self-flowing castable refractories, Fracture toughness

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1. Introduction

Castable refractories are classified as conventional castables (CCs) (CaO>2.5%), low cement castables (LCCs) (2.5%>CaO>1.0%), ultra-low cement castables (ULCCs) (1.0%>CaO>0.2%) and cement free castables (CFCs) (CaO<0.2%) according to their lime content by The American Society for Testing Materials (ASTM). In recent years, traditional high cement castable refractories have been replaced by low cement and ultra-low cement castable refractories. Nevertheless, several placement issues that arose during application led to modifications in the rheology of LCCs and ULCCs systems as well as the development of self-flowing castable (SFC) materials. After mixed, these can be applied without the necessity of external energy (Lee et al. 2001). Meanwhile, in LCCs and ULCCs refractory mixtures, besides a binder such as calcium aluminate cement, refractory aggregates such as tabular alumina, alumina spinel, fine-grained matrix components such as calcined alumina, reactive alumina or microsilica, and dispersing materials contribute to the development of high performance (Buhr and Laurich 2000; Lee et al. 2001). Moreover, alumina is a significant refractory material with exceptional high temperature resistance, thermal shock resistance, and corrosion resistance. It can be used as a furnace lining in a variety of sectors, including cement, glass, ceramics, petrochemicals, iron and steel, and glass and ceramics (Lee et al. 2001; Madono 1999). Alumina has various polymorphs such as α, γ, θ, κ, and η, of which the most thermodynamically stable phase is α-alumina, known as corundum (Lee et al. 2013; Zhu et al. 2020). α-alumina is frequently used in industrial ceramics, as well as in high strength materials, sapphire crystal growth (Akselrod and Bruni 2012), electronics and semiconductors (Fu et al. 2012). Because of this versatility, α-alumina synthesis is of great interest. Traditionally, α-alumina is obtained by the Bayer process and its conversion is completed between 1000-1400 °C (Chang et al. 2009; Xie et al. 2003). The hydrate (gibbsite) produced in the raw material calcined by the Bayer process contains 0.5% Na_2O, which is retained in the gibbsite structure. The soda content, which reduce the green density, can be removed by hydrate precipitation, water or acid leaching, or reaction by adding volatile chemicals such as boric acid. Also the use of alumina in this industry has been severely constrained because of the detrimental impact that these minute but significant levels of soda have on the refractory materials made from it (Gürel and Altun 2009; Lee et al. 2013).

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The performance of castable refractories depends not only on their refractoriness, but also on their physical properties such as density, porosity and durability. Physical properties play a critical role in the desired amount of water in castable mixes. 1% increase in water content causes an increase in apparent porosity of dried and fired refractory by 3% and severely reduces slag strength (Buhr and Laurich 2000).

Additionally, in order to fully utilize the optimized particle size distribution, achieve the lowest water consumption, and provide the appropriate rheological behaviour, all matrix components must be evenly dispersed while mixing with water in low cement castables. Phosphates, such as sodium-tripolyphosphate (STPP), sodium-hexametaphosphate (SHMP), and combinations of them, are conventional dispersion agents. The most recent generation of effective dispersing additives are dispersing aluminas. They combine enhanced dispersion activity with the ability to direct castables' setting behaviour to satisfy specific needs. It is advised that the castable have a total of 1% by weight of dispersing aluminas. Dispersing aluminas have a number of benefits over conventional phosphate-based deflocculating systems, including: (i) Higher mechanical strength and abrasion resistance due to a lower water demand, (ii) Controlling working time has almost no effect on the initiation of setting (iii) Castables have a longer shelf life due to their resistance to aging (Schnabel et al. 2014).

The aim of this study is to produce reactive alumina from Seydişehir gibbsite, to use this reactive alumina in SFC refractories, characterization and to compare it's fracture toughness with the refractory mixture containing commercial reactive alumina obtained from a refractory brick company. Thus, the usability of reactive alumina obtained from domestic sources in castable refractory products is evaluated in detail.

2. Materials and Methods

2.1. Production of Reactive Alumina

Gibbsite [$Al(OH)_3$], a commercially available powder used in this work, was produced by the Seydişehir Aluminum Company (Türkiye). The chemical composition of this gibbsite is as listed in Table 1. Additionally, boric acid (Etibor, 56.3% B_2O_3) was used to remove Na_2O. Gibbsite, 1.5 % by weight boric acid and distilled water were mixed until homogeneous, then dried at 100°C and sieved through a 1mm sieve. It was then calcined for 1 hour at 1250 °C with a heating rate of 25 °C/min. The calcined powders were ground for 8 hours in an attritor mill with 3mm alumina balls. Reactive alumina was obtained after milling, following another wash with distilled water and drying. Shimadzu brand 6000 model XRD device and scanning electron microscope (JEOL 6360 LV model, SEM) were used to characterize the obtained powders.

2.2. Optimization of SFC Binder Matrix System

ADS-1 and FS10, which has retarding qualities, provided by the Almatis and BASF firm respectively, were chosen as dispersants. ADS-1 contains 80% Al_2O_3, 0.10% Na_2O, 0.80% B_2O_3 and 1.80% CaO. FS 10 is a polymeric dispersant for improved refractory used. Both recommended for microsilica-free refractory materials containing CAC. Additionally, ADW-1 (80% Al_2O_3, 0.10% Na_2O, 0.03% B_2O_3 and 1.80% CaO), which has accelerating properties from Almatis firm was added after selecting the appropriate dispersant. During this experiment, the self-flow values for each castable composition were measured using the ASTM C 1446-99 standard. Accordingly, the secondary diameter was measured after one minute after the composition was cast into a conventional cone with an upper and lower diameter of 100 mm and 70 mm, respectively. For dispersant-free and added dispersants compositions, the following equation 1 was used to measure the self-flow value (SFV):

$$Self\ flow\ value\ (\%) = \frac{(d_2 - d_1)}{d_1} x100 \qquad (1)$$

where

d_2= the secondary average diameter after removal of cone

d_1= the initial diameter (100mm)

Table 1. The chemical composition of Seydişehir gibbsite

Product	Seydişehir Gibbsite*
Chemical composition (%)	Typical
Al_2O_3	65.10
Na_2O	0.325
Fe_2O_3	0.011
SiO_2	0.015
Particle size	<40µm

*Seydişehir Aluminum Company

2.3. Preparation of SFC Refractories Mix and Samples

The reactive alumina produced was added at a rate of 5 wt. % and 3wt. % dispersant to the high alumina, low cement castable refractory mix not containing reactive alumina, which was supplied from a commercial company. The refractory batches were then shaped using the slip casting technique in accordance with ASTM C862-02, after being mechanically mixed for 8 minutes with the addition of 5.5 weight percent water. The samples waited 24 h at about 20 °C, demolded and then air dried 24 hours at ambient temperature. The initial heating velocity was 10 °C/hour up to 110°C followed by 180 °C/hour up to 1000°C and 300°C/hour to the sintering temperature (1500°C). Soaking time was 5 hours. Two kinds (with reactive alumina produced and commercial reactive alumina) of refractory castables were then combined to create batches of SFC refractory to test the fracture toughness (K_{IC}). The samples were formed in accordance with ASTM E399 requirements by casting in molds that contain razor blades on half-heights.

2.4. Characterization of SFC Samples

Several tests were performed on the samples that were obtained after drying and sintering. The samples were boiled in water for 4 hours in accordance with ASTM C20-00 before being kept in water for 12 hours to calculate water absorption, apparent porosity, and bulk density values using the Archimedes' method. In accordance with ASTM C133-97, cold modulus of rupture (3-point bending strength) at room temperature and cold compression strength tests with a loading speed of 12MPa/min were performed in a Shimadzu Universal Tester on prismatic specimens of 25x25x152 mm with and without water absorption test. Fracture toughness was measured in accordance with the ASTM E399 standard using a Shimadzu Autograpfh AG-IS model 100kN mechanical test instrument at a loading speed of 0.05mm/min, and the results were compared. The fracture toughness was calculated based on the following equation 2:

$$K_Q = \frac{P_Q.L}{t\sqrt{b^3}}.Y_4 \tag{2}$$

where P_Q is the load applied to the notched bar, L is the span, l is the depth of the notch, t is the thickness of the specimen, b is the width of the specimen ([0.45.b ≤ l ≤ 0.55.b]; [L=4.b]; [t=b/2]) and Y_4 is the geometric function of the ratio l/b for the three-point flexure and can be expressed by the following equation 3 (ASTM E399):

$$Y_4 = 3{,}494.\left[1 - 3{,}396.\left(\frac{l}{b}\right) + 5{,}839.\left(\frac{l}{b}\right)^2\right] \tag{3}$$

3. Results and Discussion

3.1. Production of Reactive Alumina

Figure 1(a) shows the XRD pattern of the manufactured reactive alumina. With the addition of 1.5 wt. % boric acid, it is observed that about all of the Seydişehir gibbsite is transformed to alpha alumina (α-Al_2O_3). However, a trace of aluminum borate [$Al_{20}B_4O_{36}$ (PDF 802301)] was discovered. Gürel et al., (Gürel and Altun 2009) reported that gibbsite was completely converted to α-alumina at 1250 °C with the addition of 2 wt. % of H_3BO_3. However, the addition of 2 wt. % boric acid for Na_2O removal may be high and it has been suggested that it may cause more aluminum borate formation. SEM image of the reactive alumina produced was given in Fig 1(b) In accordance with the image, the particle size of the obtained powder is approximately minus 1µm.

3.2. Optimization of SFC Binder Matrix with Self Flow Values of the Compositions

One of the most crucial factors in determining how well self-flowing castables perform is self-flowing value. The effect of dispersant addition on the self-flowing values of the high alumina, low cement castable refractory mix with reactive alumina produced is shown in Figure 2. It can be seen the self-flow value increased in the dispersant added batch. Dispersing aluminas exhibit strong attraction forces due to their high specific surface area. Previous findings indicate that the self-flowing values of the self-flow castable composition are between 80 and 110% (Otroj et al. 2010; Silva et al. 2012). As seen in Figure 2, among the values calculated according to equation 1, the batch of dispersant-free (0%) showed only 70% flow value. After adding 1% FS10 dispersant, the flow was calculated as 90%. The best flow amount was obtained from ADS1 dispersant as 110% with 1% dispersant. After selecting ADS1 as the appropriate dispersant, ADW1 dispersant was also added to accelerate drying.

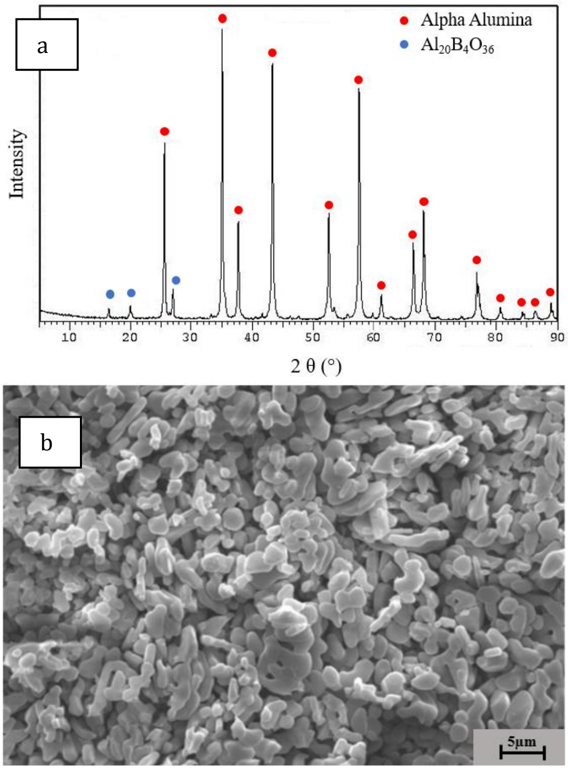

Figure 1. (a) XRD pattern (b) SEM micrograph of reactive alumina.

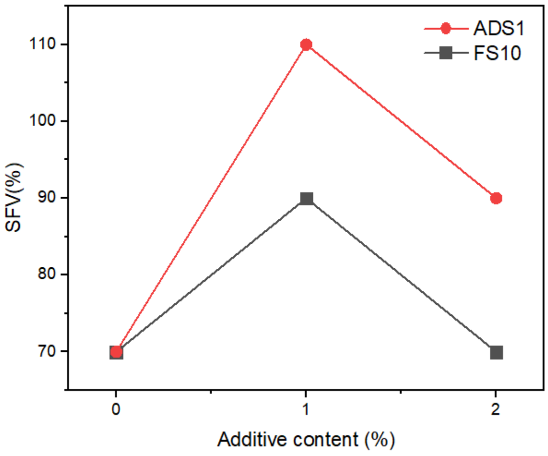

Figure 2. Self flow values as a function of dispersant content.

3.3. Water Absorption Tests

Figure 3(a) and 3(b) show the heat treated and tested samples. Figure 4(a) shows the results of the temperature-dependent water absorption test. As a result, the sample sintered at 1000°C exhibited the maximum water absorption rate.

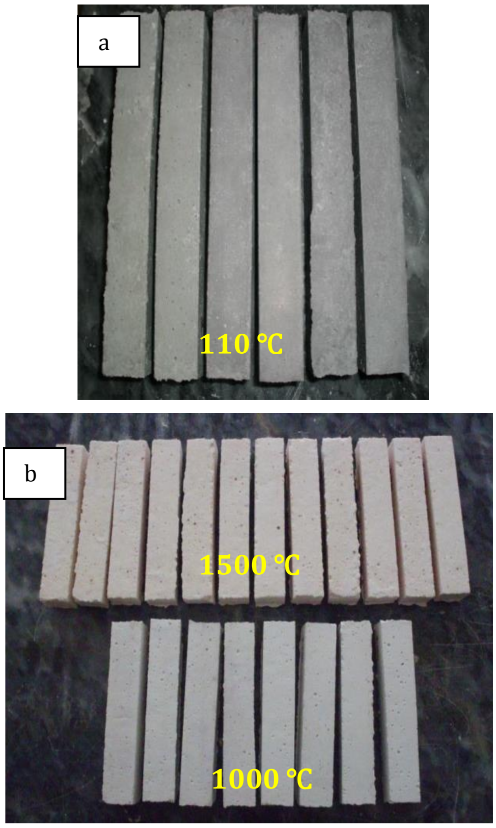

Figure 3. Photograph of (a) dried samples at 110°C (b) sintered samples at 1000°C and 1500°C.

The condensation behaviour of castable refractories as a function of temperature is shown in Figure 4(b). Hereunder, the bulk density of SFC refractory dried at 110 °C was 3.41g/cm³, and it decreased to 3.21g/cm³ in the sample sintered at 1000°C. After the refractory sample was sintered at 1500°C for 5 hours, the bulk density was calculated as 3.25g/cm³, and a slight increase was observed as a result. During the heat treatment of SFC refractories, porosity develops due to the internal evaporation of water, resulting in a drop in bulk density and an increase in apparent porosity (19.46 %) compared to the sample dried at 110°C following sintering at 1000°C. A high apparent porosity value in the castable sample sintered at 1000°C suggests that the pores formed by the evaporation of water were unable to be removed. The decrease in apparent porosity with increasing sintering temperature (1500°C) is attributed to the metastable liquid in the castable transforming into mullite and condensation (Göğtaş et al. 2010). According to a study involving alumina-based castable refractories, the apparent porosity value at 110°C is approximately 12 %, which is in good agreement with the results we obtained (Luz et al. 2018).

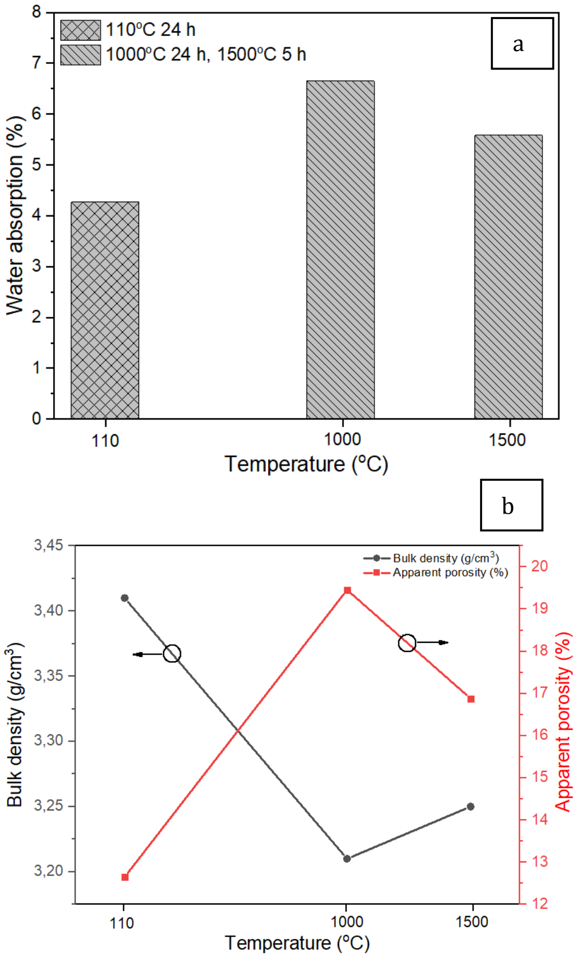

Figure 4. The effect of drying and firing temperature on the refractory's (a) water absorbtion and (b) bulk density.

3.4. Cold Modulus of Rupture (CMOR-3 Point Bending Strength) and Cold Compressive Strength (CCS)

Figure 5(a) shows the cold modulus of rupture (3 point bending strength) graph of the sintered samples. To analyse the behaviour of the samples before and after water absorption tests were applied and compared. The results are shown on the graph. Consequently, the highest flexural strength was obtained from the sample sintered at 1500°C after water absorption test and is approximately 16 MPa. The cold compressive strength of the samples heat treated at various temperatures, before and after water absorption tests, is shown in Figure 5(b). Accordingly, the sample sintered at 1500 °C and subjected to the water absorption test yielded the greatest cold compressive strength value, which was 173.13 MPa. The results of the three-point bending strength and cold compressive strength tests show that the samples that were subjected to the water absorption test had higher strength values. It was believed that the hydration of a minor quantity of unreacted calcium aluminate cement in the raw material contributed to the higher bending and compression strengths of with water-absorbed samples compared to without water-absorbed samples. Cement's interaction with water initiates hydration, which is followed by an exothermic reaction. Hydration is affected by the ratio of water to cement, curing conditions, and presence of impurities. Stable hydration products consisting of the first sintered mineralogical phases and their crystal structures often emerge within three to six months at room temperature or within the first 24 hours if curing is conducted at a higher temperature. When heated above 21°C, metastable hydrates transform into stable compounds (Lee et al. 2001; Ma and Brown 1999).

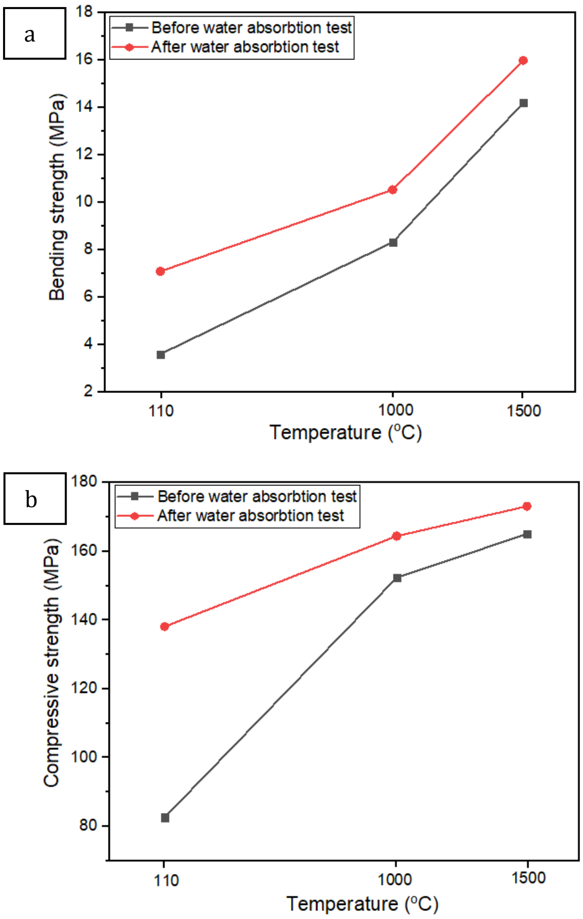

Figure 5. (a) 3 point bending and (b) compressive strength test results of the reactive alumina-added castable refractory mixture produced from Seydişehir gibbsite before and after water-absorption tests.

3.5. Fracture Toughness (K_{IC})

Figure 6 shows a graph that compares the results of an analysis of the fracture toughness of the reactive alumina-added castable refractory mixture made from Seydişehir gibbsite and the reactive alumina-added castable refractory material produced by a commercial company. As a result, the castable refractory sample containing reactive alumina produced from Seydişehir gibbsite had a higher fracture toughness value of 1.2 MPa.m$^{1/2}$. The castable refractory sample containing commercial reactive alumina from a commercial company has a K_{IC} value of 0.85 MPa.m$^{1/2}$.Typically, conventional castables have a K_{IC} in the range of 0.2-1.5 MPa.m$^{1/2}$ (Gogtas et al. 2014). The values obtained from both samples are within the range of values given for conventional castables in comparison to the findings of this study, but it is understood that the castable refractory samples obtained by adding Seydişehir reactive alumina are 1.5 times tougher than that of the commercially available castable refractories.

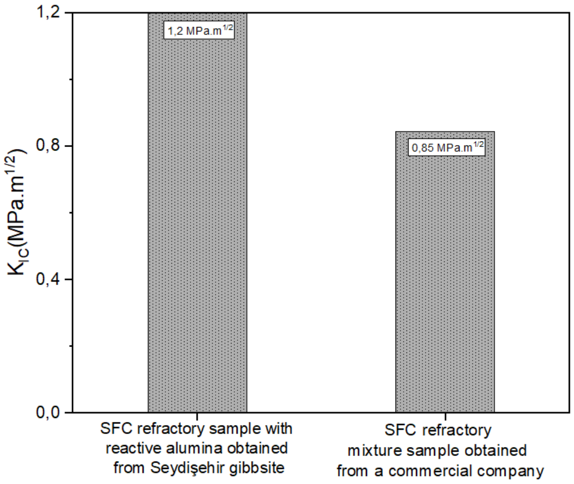

Figure 6. Fracture toughness comparison graph.

4. Conclusion

In this study, low sodium reactive alumina was produced from domestic raw material, Seydişehir/Türkiye gibbsite. This produced reactive alumina and various dispersants were added to the high alumina and low cement castable refractory mixture to optimize the binder matrix system. 110% self flow value was obtained by using 1% ADS1 dispersant. The samples shaped by casting according to the test standards were heat treated at 110°C for 24 hours, at 3°C/min at 1000°C for 24 hours and at 5°C/min at 1500°C for 5 hours. The samples obtained after heat treatment were systematically examined by applying water absorption, three-point bending strength and cold compressive strength tests. Also, the fracture toughness of the refractory mixture prepared with the reactive alumina produced from Seydişehir Gibbsite was compared with the refractory mixture containing commercial reactive alumina obtained from a refractory brick company. The best results were obtained from samples sintered at 1500°C. The apparent porosity, total water absorption rate, bulk density of the samples are 16.88 %, 5.59 % and 3.25 % respectively. The bending and compressive strengths of the samples are 16 MPa and 173.13 MPa respectively. The refractory mixture prepared with the reactive alumina produced from Seydişehir Gibbsite gave 1.5 times higher fracture toughness value than that of the refractory mixture containing commercial reactive alumina obtained from a refractory brick company. One of the parameters affecting the bulk density is the packing density of the aggregate mixture. The packing density of the aggregate mixture used in the experiments should be measured and an aggregate mixture that gives a higher packing density than this should be prepared. The second parameter is the degree of the reactive alumina used in the binder matrix. To increase this, sintering aid additives should be tried. With this study, it has been shown that domestic raw material resources can be used more efficiently and shed light on new studies to contribute to the economy. In future studies, the economic dimension should be investigated by cooperating with the industry.

Author Contributions

The percentage of the author(s) contributions is present below. All authors reviewed and approved final version of the manuscript.

%	H.S.C.T	C.B.E.A
C	50	50
D	100	
S		100
DCP	100	
DAI	100	
L	50	50
W	50	50
CR	50	50
SR	50	50
PM	50	50
FA	50	50

C=Concept, D= design, S= supervision, DCP= data collection and/or processing, DAI= data analysis and/or interpretation, L= literature search, W= writing, CR= critical review, SR= submission and revision, PM= project management, FA= funding acquisition.

Conflict of Interest

The authors declared that there is no conflict of interest. Also the authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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