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Corrosion Resistance and Some Physical Performance of Basic Refractories Made from Natural Calcitic-Brucite Ore

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Anahtar Kelimeler
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Abstract
Dolomitic refractories are widely used in iron and steel, refractory, glass and soda industries. In this study, the usability of basic refractories produced from calcitic-brucite [CB; $CaCO_3.Mg(OH)_2$] raw materials, which may be an alternative to dolomitic refractory raw materials, was investigated. The CB raw material was pre-treated for 6 hours at 1500°C and then particle size classification was made. The sintered CB raw material was doped with graphite, ceramic powder and metallic powder to form CB1, CB2 and CB3 recipes, respectively. These three mixtures were then uniaxially pressed with 1500 kg/cm^2 pressure in the 50x10 cm rectangular shape and tempered at 300°C. Porosity, bulk density, compressive strength and corrosion measurements were carried out to tempered samples. It was found that CB can be utilized in basic refractory production, addition of ceramic and metallic powders improves physical and mechanical properties, and the best corrosion performance was achieved with CB3 sample.

Doğal Kalsitik-Brusit Cevherinden Yapılan Bazik Refrakterlerin Korozyon Direnci ve Bazı Fiziksel Performansları

Özet
Dolomitik refrakterler demir-çelik, refrakter, cam ve soda endüstrilerinde yaygın olarak kullanılmaktadır. Bu çalışmada dolomitik refrakterlere alternatif olabilecek, kalsitik-brusit [CB; $CaCO_3.Mg(OH)_2$] hammaddelerden üretilmiş bazik refrakterlerin kullanılabilirliği araştırılmıştır. CB hammaddesi 1500°C'de 6 saat ön işleme tabi tutulmuş ve ardından parçacık boyut sınıflandırması yapılmıştır. Sinterlenmiş CB hammaddesi sırasıyla grafit, seramik tozu ve metalik toz ile katkılandırılarak CB1, CB2 ve CB3 reçeteleri oluşturulmuştur. Bu üç karışım daha sonra 1500 kg/cm^2 basınçla tek eksenli olarak preslenmiş, 50x10 cm boyutlarında dikdörtgen şeklinde numuneler hazırlanmış ve 300°C'de temperlenmiştir. Temperlenmiş numunelerde gözeneklilik, kütlesel yoğunluk, basınç dayanımı ve korozyon ölçümleri yapılmıştır. CB'nin bazik refrakter üretiminde kullanılabileceği, seramik ve metalik tozların eklenmesinin fiziksel ve mekanik özellikleri iyileştirdiği ve en iyi korozyon performansının CB3 numunesi ile elde edildiği görülmüştür.

1. INTRODUCTION

Physical, chemical and mineralogical properties of raw materials used for refractory production takes great importance affecting the final properties of refractory products. For this reason, search for alternative raw materials having superior characteristics is of interest since many times, especially these days. Besides that, an increase in demand for basic refractories subjected to continuously growing iron-steel industry is so essential that dolomitic refractories by using dolomite raw material having low impurity content are significant.[1,2]

Dolomite that is composed of calcium carbonate ($CaCO_3$) and magnesium carbonate ($MgCO_3$) is very critical raw material for basic refractory classes.[2] This material decomposes at appropriate temperatures, and unstable free lime (CaO) and periclase (MgO) constituents occur accordingly.[3] After heat treatment at elevated temperatures, sintered doloma, which is so important to iron-steel industry and having high thermomechanical properties, is obtained.[4] Additionally, several sintering aids like iron (III) oxide (Fe_2O_3) is added into raw material in order to overcome instability of materials during sintering stage. Thanks to the sintering aid impurity Fe_2O_3, some essential phases like C4AF, C2S and C3S can be obtained.[5,6] Thus, the more stable structure and the higher density values are attained with the help of sintering temperature, time and Fe_2O_3 content.[7-9]

Brucite mineral [Mg $(OH)_2$], on the other hand, occurs at regions where Mg^{2+} ion-rich groundwaters deposit under proper circumstances.[8] At the same time, these waters are very rich in terms of Ca^{2+} ion concentration, and therefore calcium-based minerals are included either by impurity or basic mineral constituent inside brucite. Additionally, Al_2O_3 and SiO_2 oxides are contained as negligible constituents. The final properties of products are affected not only by chemical or mineralogical characteristics of starting raw materials, but also by shaping, heat treatment as well as binders used.

In addition, dolomitic bricks, which are synthetically produced in the last years, contain dolomite (less contaminate) and the results are better than natural dolomite.[10] The technical properties can be improved owing to the constitutions of the contents of CaO and MgO, according to some literature findings.[8] Since the calcitic-brucite mines around Afyon Region ($CaCO_3.Mg(OH)_2$) are similar to dolomite mines as a chemically and contain very little contamination. Therefore, we consider that these ores may be used in the dolomite refractory industry as an alternative candidate.

For above mentioned reasons, the aim of this study is to investigate the usability of calcitic-brucite raw materials from Afyon region to manufacture basic refractory with calcitic-brucite raw materials by adding metallic and ceramic powder as additives.

2. MATERIALS & METHODS

2.1 Materials

In the present work, we aimed at utilizing natural calcitic-brucite ore to produce dolomitic refractories within the context of alternative raw material usage. CB material was supplied from Afyonkarahisar region/Turkey. Particle size fraction was performed by crushing and grinding process. The classified particles were then dried in oven at the temperature of 105 °C for 2 hours. After that, XRF analysis (Table 1) for chemical analysis of CB was performed via S8 Tiger, Bruker. XRD analysis (Fig. 1) for phase identification was carried out via RINT2000, Rigaku by using Cu K_α as radiation source in the range of 10-70 degrees with 2 degrees per minute speed. DTA-TG analysis (Fig. 2) were done by Setaram Setsys Evo device in nitrogen atmosphere and 5°C per minute heating speed. Lastly, SEM analysis (Fig. 3) for microstructure observation was applied via 1430, Leo device by coating samples with carbon.

Table 1: Chemical analysis of CB raw material.

Constituents	Wt%
SiO_2	0,09
Al_2O_3	0,09
CaO	35,40
MgO	23,38
SO_3	0,04
K_2O	0,03
LOI	40,97
Total	100,00

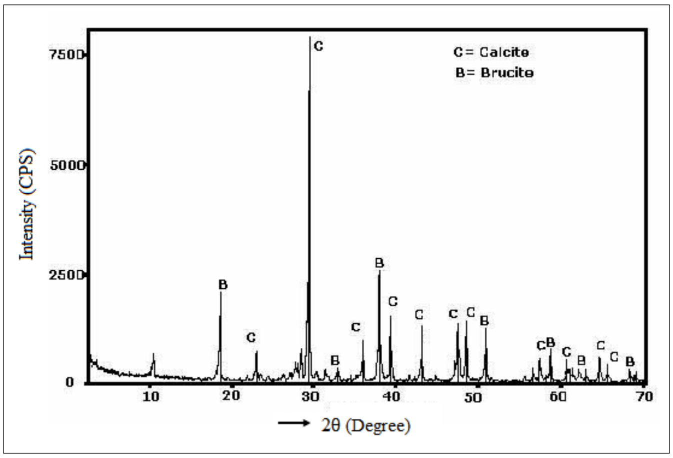


Figure 1: Mineralogical phases of CB raw material.

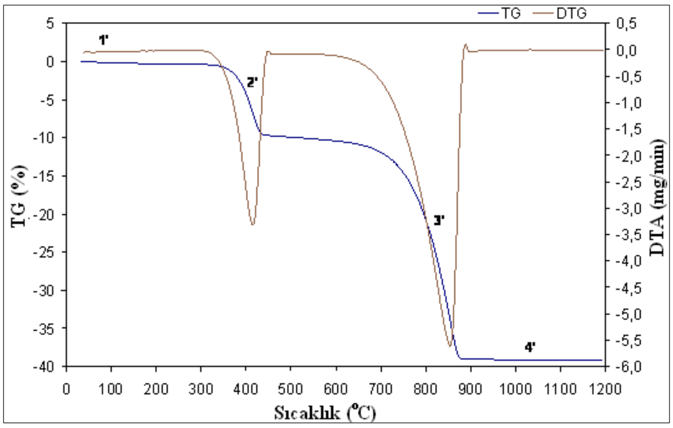


Figure 2: DTA-TG analysis of CB raw material.

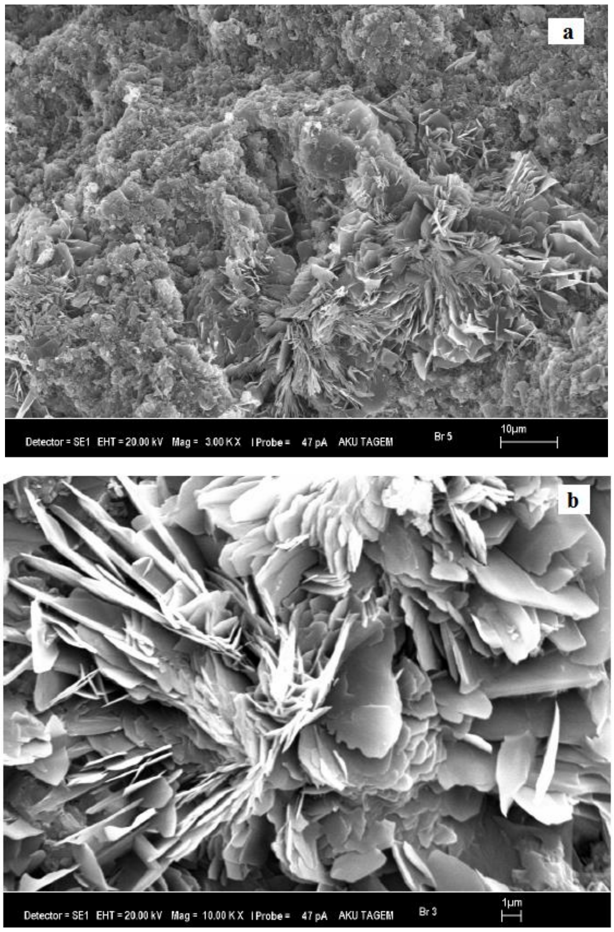


Figure 3: SEM images of calcitic-brucite (a) and brucite (b) crystals.

After completion of raw material characterization, 0.5 % iron scale (98% Fe_2O_3) in 45µm particle size was added into CB and was mixed up together with ethyl alcohol in rotary mixer for half an hour, and lastly mixture was dried in oven at 110 °C till all moisture moves off. Next, mixture was sintered at 1550 °C for 6 hours in magnesite crucible. The sintered calcitic brucite was classified as four different fractions as 2-4 mm, 1-2 mm, 0.09-1 mm and <0.09 mm. Later on, graphite, resin and hexamin tetramin were added up with including differing amounts of ceramic and metallic powders. Table 2 shows the recipe of prepared mixture in weight percentages. The recipe shown in Table 2 is coded as CB1 while 10% ceramic powder added is coded as CB2 and 10% metallic powder as CB3.

Table 2: Recipe of CB1 sample.

Ingredient	Wt%
CB (2 – 4 mm)	21
CB (1 – 2 mm)	30
CB (0,09 – 1 mm)	20
CB (<0,09 mm)	19
Graphite	10
Novalak	5
Resin	7
Hexamin Tetramine	0,3
Total	100,00

2.2 Sample Preparation

Determined amounts of each recipe constituents were precisely weighed and mixed up. Then, three rectangular shaped samples for each code in the dimensions of 50x10 cm was obtained by applying 1500 kg/cm^2 uniaxial pressure. All samples was heated up to 300°C with 1°C/min, and holded for 2 hours, and then cooled down to 200°C with 1°C/min and holded for 10 hours. XRD and SEM analysis results of these samples are given in Fig. 4 and Fig. 5, respectively.

2.3. Measurements

Compressive strength measurement was done in accordance with ASTM C 830-93 and DIN51065-1 standards while TS 4898 standard was applied to figure out appearant porosity and bulk density of samples. It is essential to mention that samples were coated with parafin in order to not wet sample surface before Arcihmedes' principle. Life test was performed to samples to see moisture characteristics. Every 2 days-weighing cycle was done to show up stability of samples and the unstability time period was found out. Corrosion test was carried out to reveal resistance against steel slag attacks. The chemical analysis of slag supplied from Kardemir Inc. was shown in Table 3. 4 grams of slag was put onto samples and heated up to 1300 °C and waited for 48 hours. The corrosion resistance of samples were determined by SEM-EDX analysis.

Table 3: Chemical composition of steel slag.

Constituent	Wt%
SiO_2	11,08
Al_2O_3	1,22
Fe_2O_3	37,67
CaO	41,97
MgO	4,06
SO_3	0,36
K_2O	0,03
Na_2O	0,04
Cr_2O_3	0,098
Loss on ignition (LOI)	3,46
Total	99,988

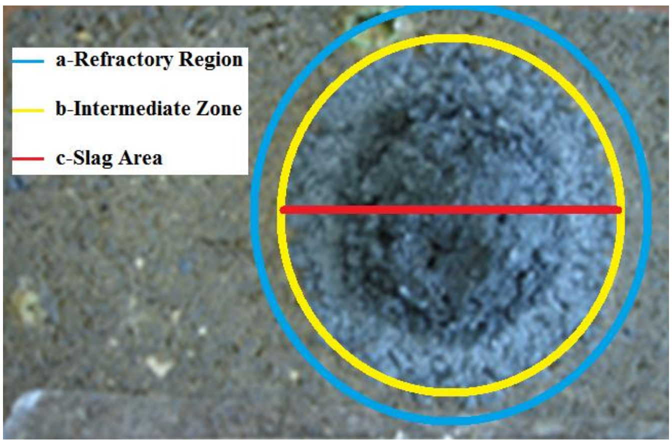


Figure 4: Images captured after corrosion test and three main areas of corroded sample.

Distribution of steel slag on refractory samples in terms of area was captured and calculated via SEM and EDX analysis. Fig. 5 shows captured images of samples. For area calculation, fifty diameter measurements around slag was done and average value was used. As a result of this test, distribution and wetting ratio of slag on refractory which is an indicator of corrosion resistance was determined. Afterwards, SEM images and EDX analysis were taken from refractory region (non-wetted), intermediate zone, and slag area (Fig. 4).

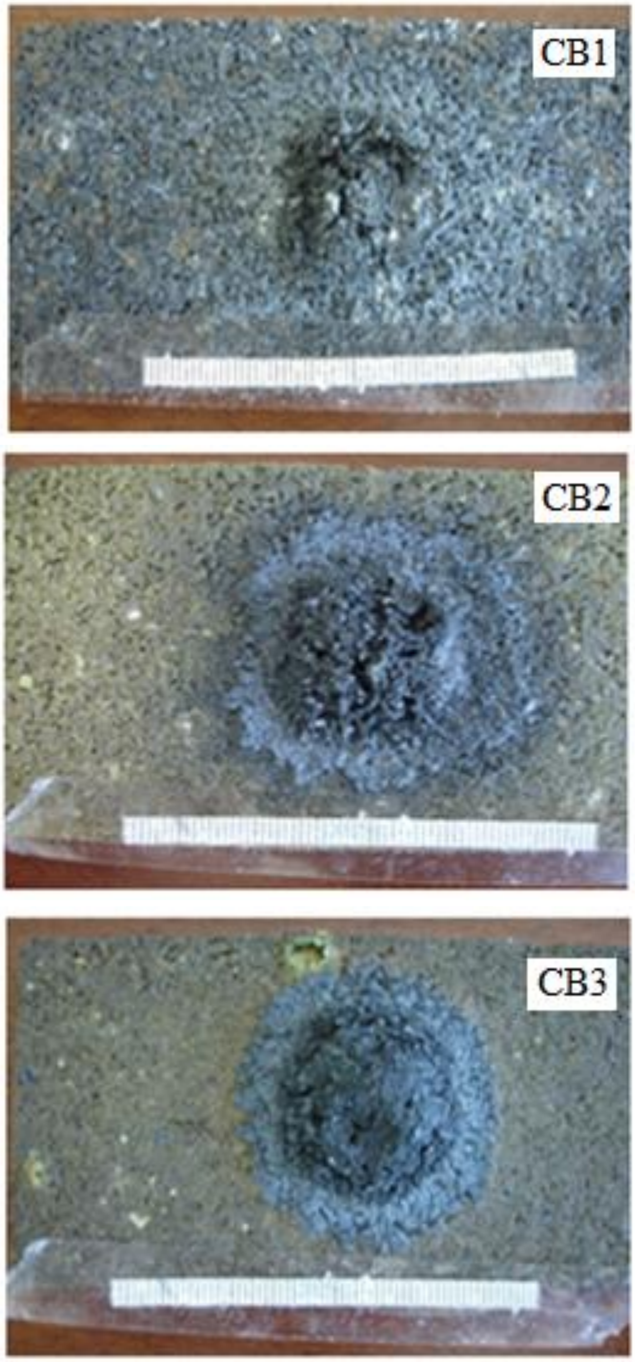


Figure 5. Images captured after corrosion test (from up to down CB1, CB2 and CB3, respectively)

3. RESULTS AND DISCUSSION

XRF analysis of CB raw material listed in Table 1. shows that mainly CaO and MgO oxides are included while Al_2O_3 and SiO_2 oxides are lower than 0,1%. As already mentioned in previous study that Al_2O_3 should not exceed 0,2% whereas SiO_2 should be lower than 0,1% for dolomitic refractory production. Besides, CB material is so pure in terms of iron (III) oxide amount that it is not observed inside.

XRD analysis of CB raw material given in Fig. 1 shows that calcite (C) and brucite (B) are the main phases irrespective of very lower intensity of others which can be attributed to impurities, which is also parallel to the chemical analysis results.

DTA-TG analysis of CB raw material presented in Fig. 2 reveals that there are 3 main endothermic peaks at 66°C, 417°C and 817°C which can be linked to physical water removal, hydroxyl ions of brucite removal and carbonate decomposition of calcite, respectively. When it comes to TG graph, it is well seen that 38,99% weight loss occurs.

SEM microstructure images of CB raw material shown in Fig. 3 point outs the calcite (a) and lamellar brucite (b). As seen, brucite crystals are dispersed inside calcite crystals.

Similar to dolomitic refractories, calcite brucite is sintered so as to achieve stable structure ensuring to moisture resistance. Several additives for having more stability are included such as iron oxide[5] or zircon[11,12]. The main reason behind including additives is to bind CaO and MgO oxides. However, semi-stable situation should be obtained for basic refractories because CaO and MgO oxides will come together with Fe_2O_3 along with melting process of metals in iron-steel production, and the highest stability of refractory against moisture attacks will be achieved.[8]

XRD analysis and SEM images after sintering of calcitic brucite are presented in Fig. 6 and Fig. 7, respectively. The highest peak intensities belong to CaO and MgO phases while very low intensities relating to the C3S and C4AF can also be observed. Besides that, angular structure relates to CaO crystals whereas lamellar ones are MgO crystals in SEM images.

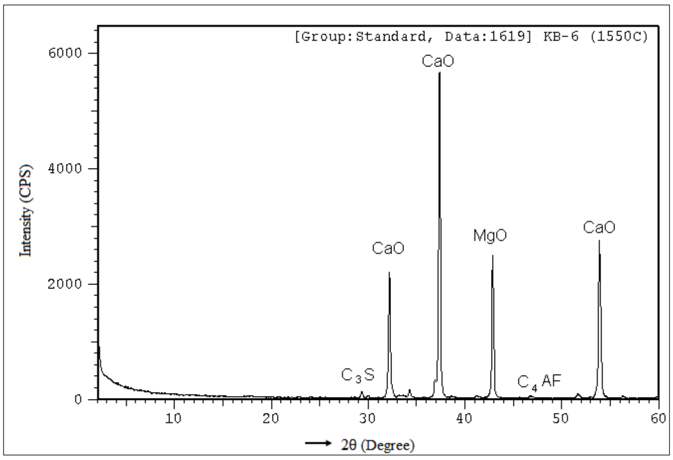


Figure 6. XRD analysis of sintered CB raw material.

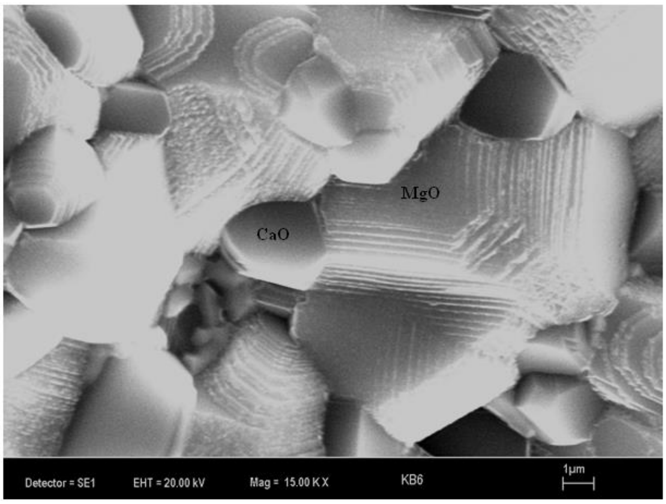


Figure 7. SEM images of sintered CB raw material.

After presenting results with regards to CB raw material and sintered CB, Fig. 8 shows XRD results of mixtures which is already coded as CB1, CB2 and CB3. In general aspect, main phases are as follows : lime (CaO), periklase (MgO), carbon (C), portlandite [$Ca(OH)_2$], calcium silicate (C_3S) and larnite (C_2S).

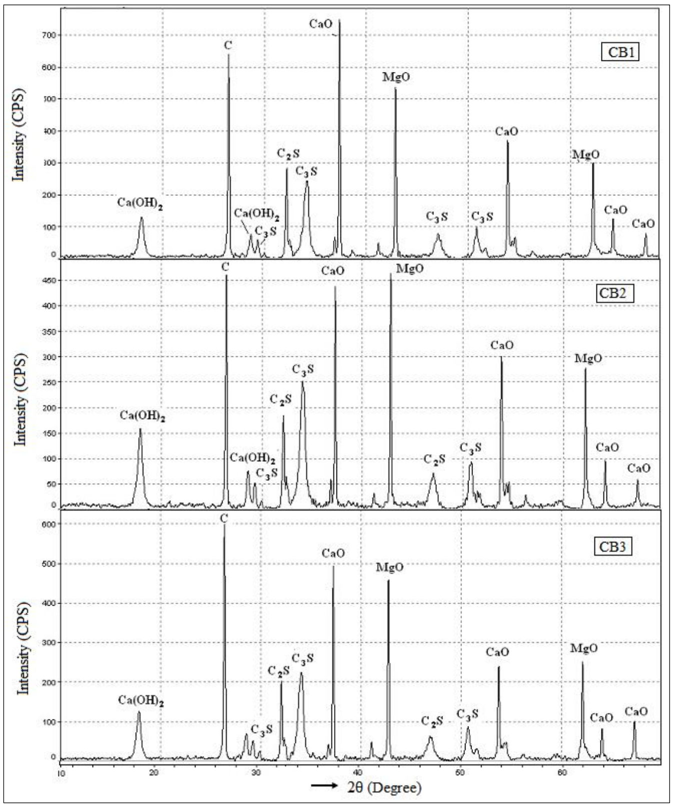


Figure 8. XRD analysis of CB mixtures.

As shown in Fig. 9, CB1 sample have CaO and MgO oxides and graphite particles are located between those. In the SEM image of ceramic powder added CB2 sample large and round alumina silicate ceramic particles are observed (Fig. 10). These particles come from ceramic powder additive since EDX analysis appearently shows the results. Fig. 11 shows the SEM image of metallic powder added CB3 sample rounded metallic particles are seen and EDX analysis of CB2, CB3 are given in Table 4.

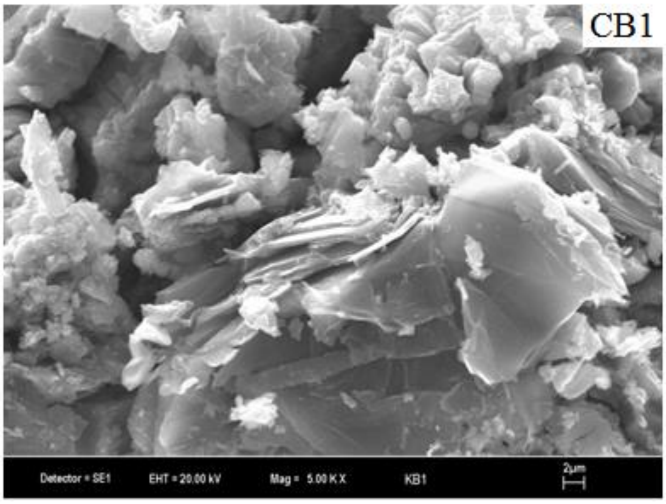


Figure 9. SEM analysis results of tempered CB1.

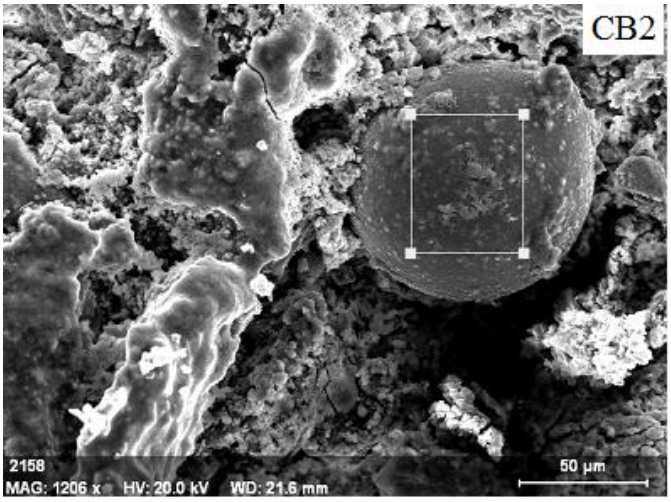


Figure 10. SEM analysis results of tempered CB2.

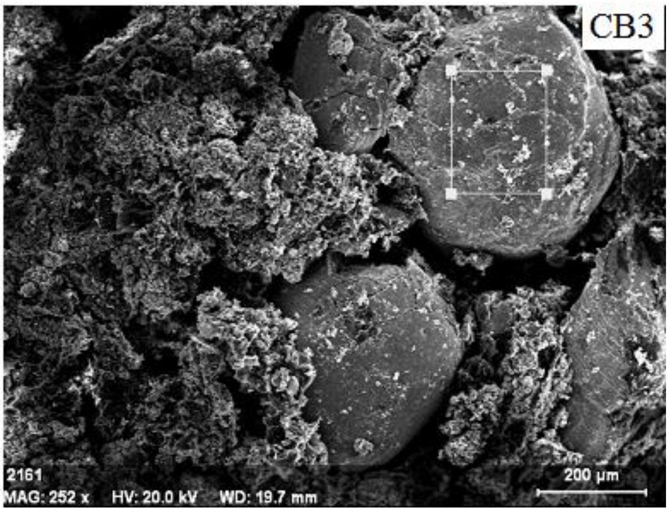


Figure 11. SEM analysis results of tempered CB3.

Table 4: EDX analysis result of CB2 and CB3.

	Element	% Weight	% Atom
CB2	O	55.21	68,94
	Al	20.21	14.89
	Si	18.15	12.91
	Ca	6.54	3.26
	Total	92.7	100
CB3	C	8.99	23.22
	O	17.72	34.36
	Mg	1.67	2.13
	Ca	2.34	1.81
	Fe	69.28	38.48
	Total	105.3	100

Life test on samples took 28 days. There is no change in material till the first 16 days, however fragmentation started to occur after 18th day. On the 26th day of life test, fragmentation ended up completely. It was concluded that there is no connection between life test and additives.

Bulk density, appearant porosity and compressive strength measurement results of three CB samples are given in Fig. 12. It is clearly indicated that additives improve physical and mechanical properties of refractories since CB2 and CB3 have greater bulk density and compressive strength and lower appearant porosity compared to non-added CB1 sample. On the one hand, CB3 shows best performance under compressive strength while ensuring lowest appearant porosity.

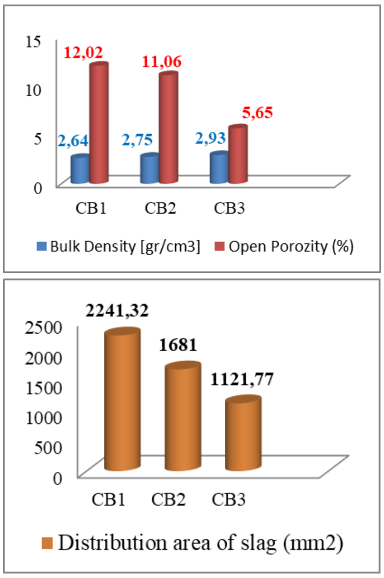


Figure 12. Bulk density, open porosity percentage and distrubution area of slag after the corrosion test.

Corrosion resistance of three different samples were determined with the help of adding steel slag. Since dolomitic refractories are commonly preferred by iron-steel industry corrosion resistance takes significant importance. During corrosion test liquid phase occurred as a result of slag moves along opened pores and grain boundaries. Corrosion takes place until oxides like CaO or MgO dissolve into liquid phase and saturation occurred.[13] Hence, there is a cloe tie between distribution area of slag and porosity percentage of refractory. Fig.12 presents bulk density, porosity percentage and distrubution area of slag values of three different samples after corrosion test completed. It is clearly found out that distribution area of slag decreases with decreasing porosity percentage. SEM images and EDX analysis representing three main areas of corroded samples, which present in Fig.4, are given in Fig. 14-18.

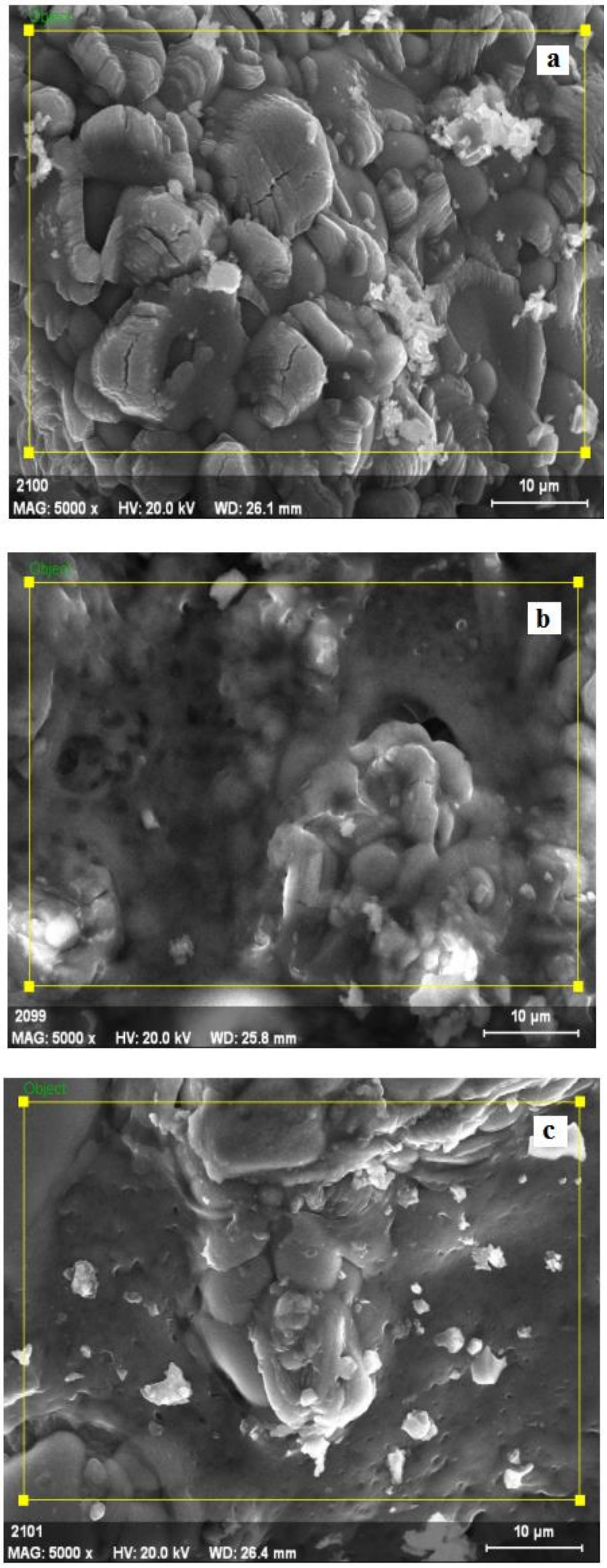
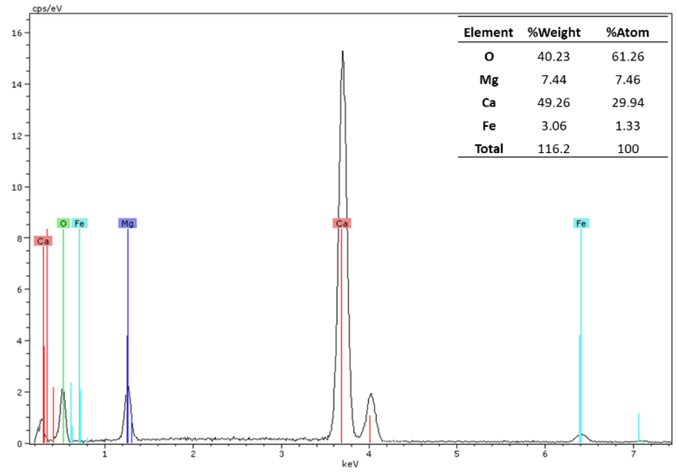
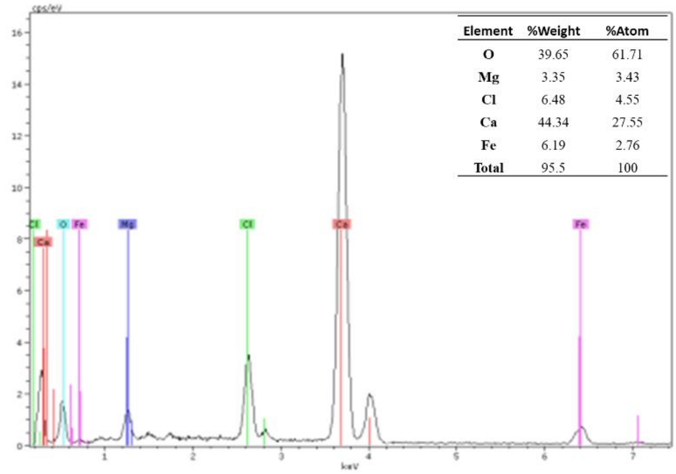


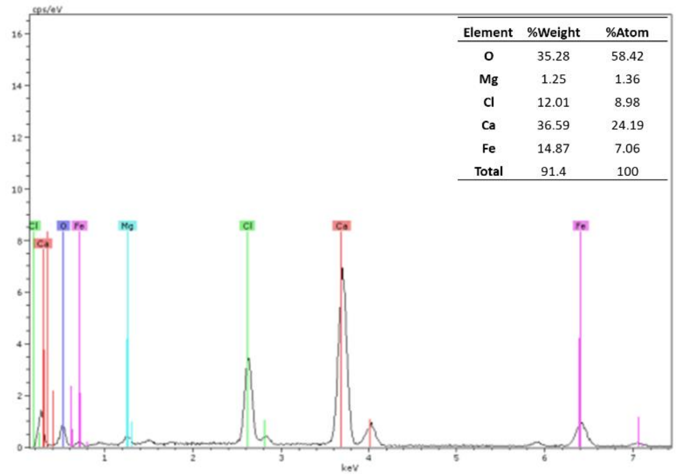
Figure 13. SEM images of CB2 sample from three main area, a) refractory region, b) intermediate zone, c) slag area.



(a) refractory region

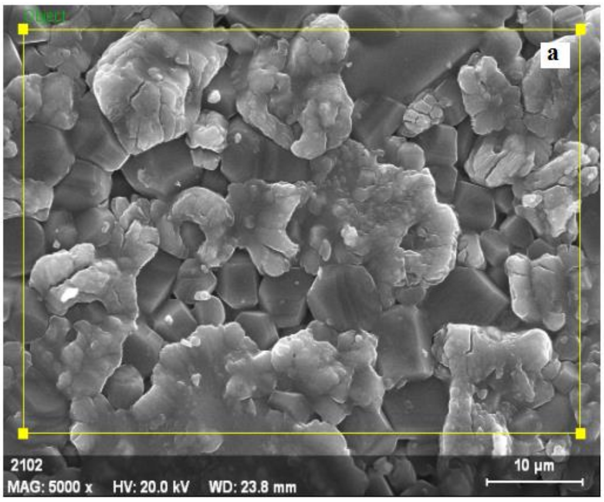


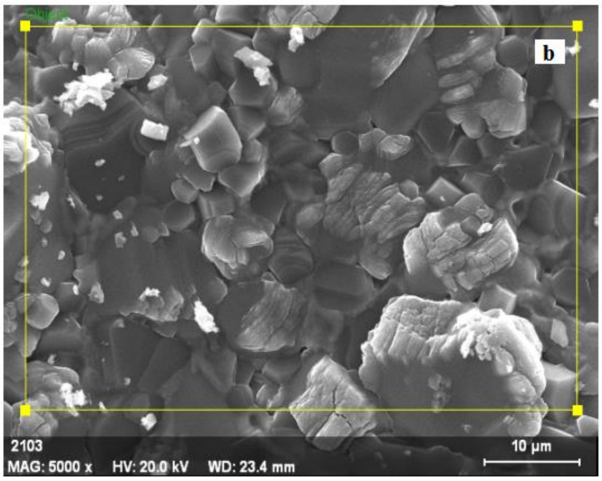
(b) intermediate zone



(c) slag area

Figure 14. EDX analysis of CB1 sample from three main area, a) refractory region, b) intermediate zone, c) slag area.





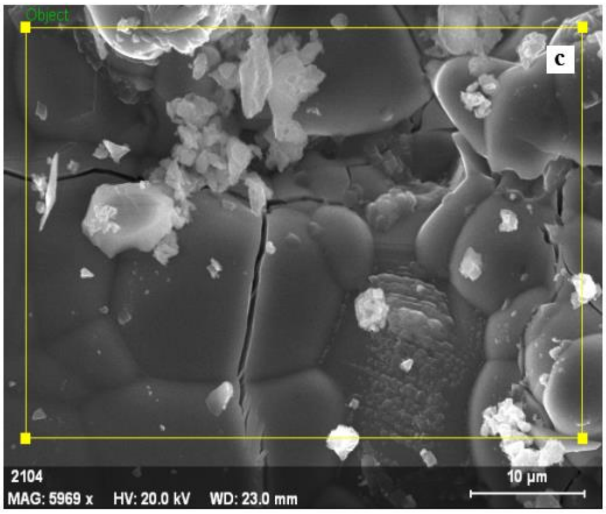
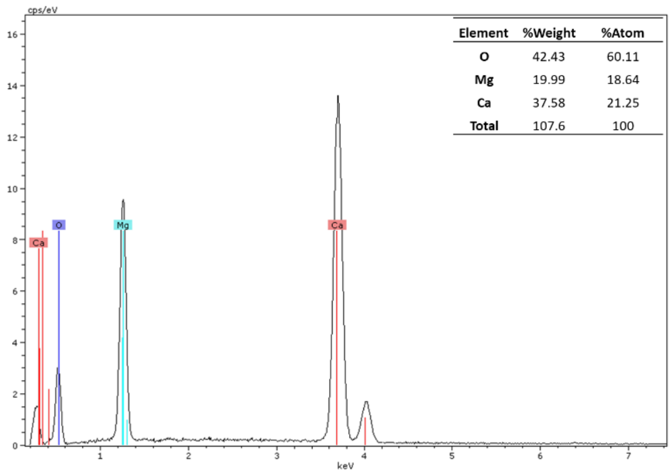
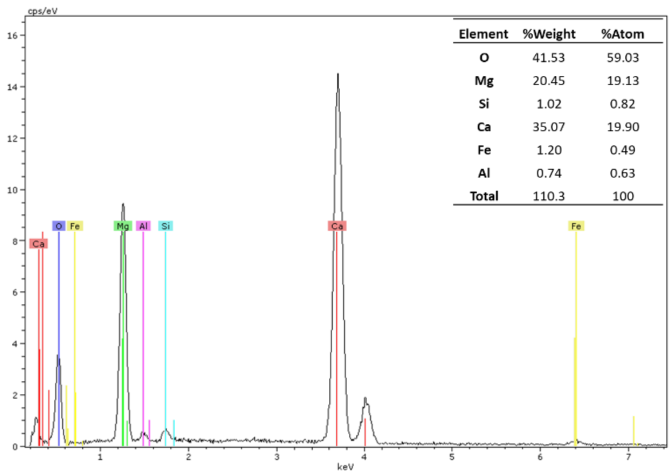


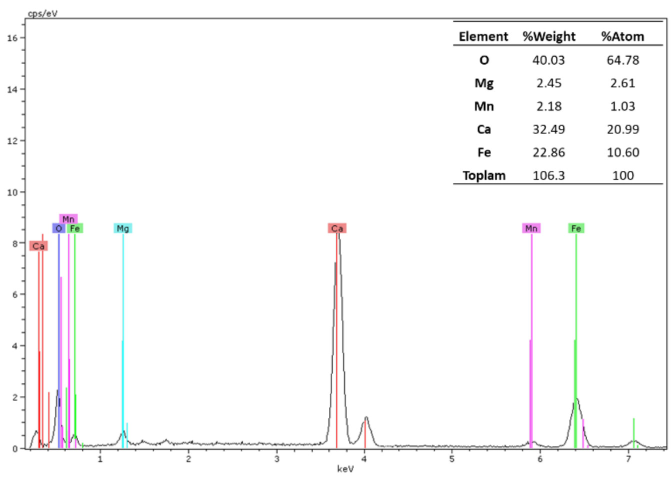
Figure **15.** SEM images of CB2 sample from three main area, a) refractory region, b) intermediate zone, c) slag area.



(a) refractory region

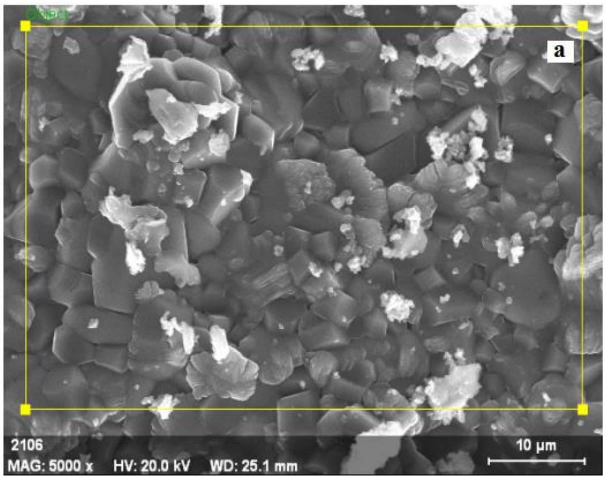


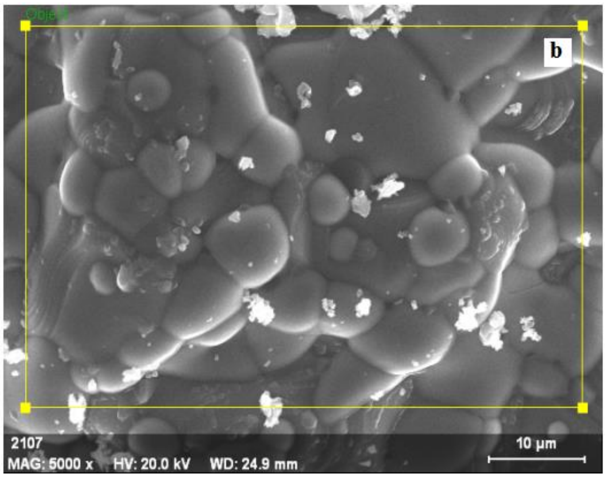
(b) intermediate zone



(c) slag area

Figure 16. EDX analysis of CB2 sample from three main area, a) refractory region, b) intermediate zone, c) slag area.





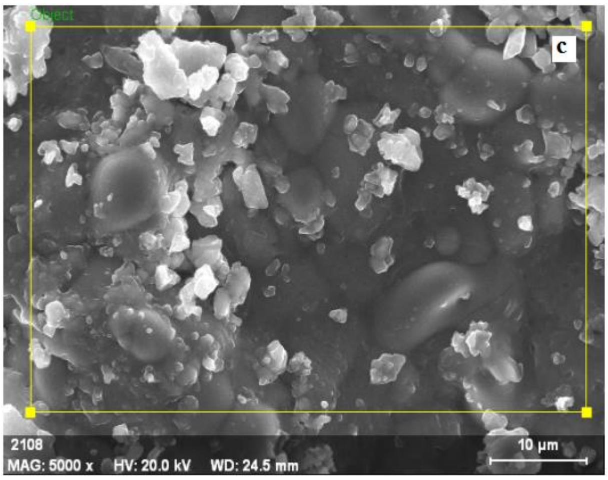
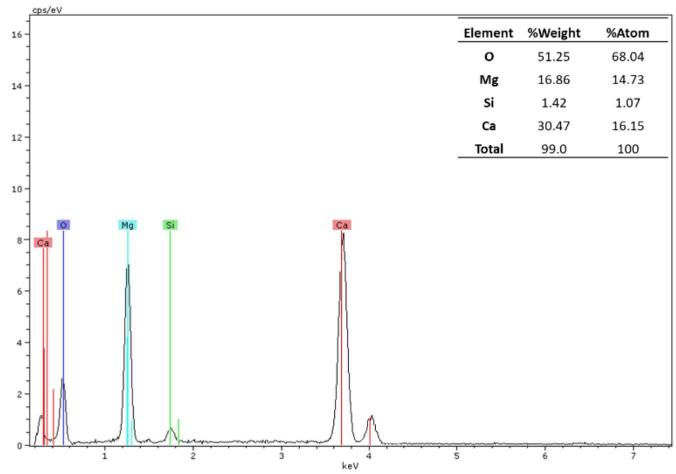
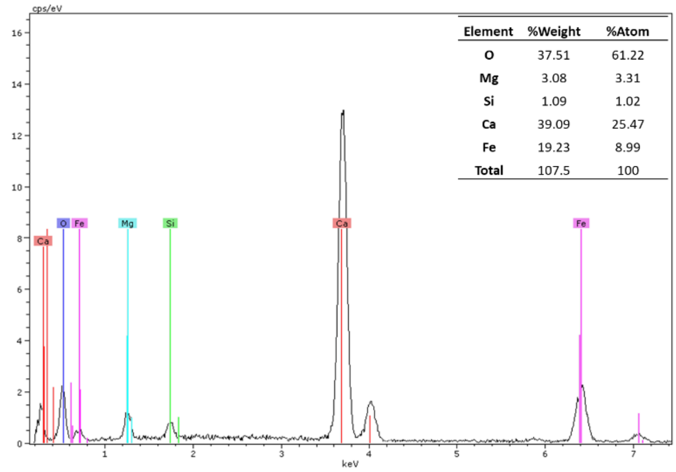


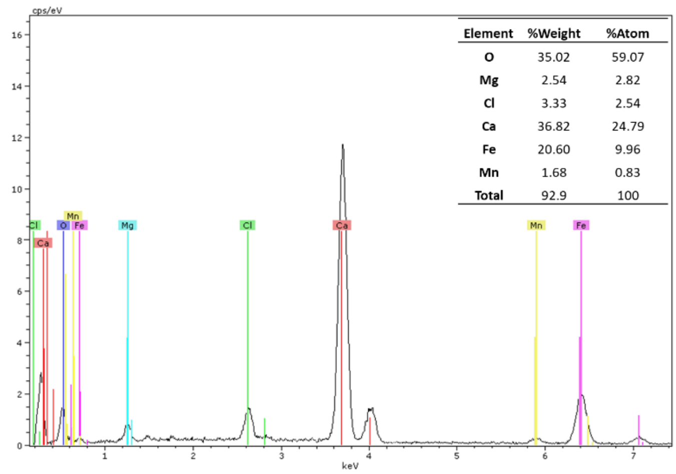
Figure 17. SEM images of CB3 sample from three main area, a) refractory region, b) intermediate zone, c) slag area.



(a) refractory region



(b) intermediate zone



(c) slag area

Figure 18. SEM images of CB3 sample from three main area, a) refractory region, b) intermediate zone, c) slag area..

4. CONCLUSIONS

The XRF analysis result of the Calcitic-Brucite raw material obtained from the Afyon region was shown in Table 1, and found to have a suitable purity for use in the refractory industry.

With the metallic powder addition to the calcitic-brucite, it has increased the density of the CB sample from 2.45 gr/cm^3 to 2.75 gr/cm^3 and improved performance against corrosion resistance. This results showed that the CB from Afyon region can be used in the production of dolomatic refractory.

It can be clearly deduced that additives improve both physical and mechanical properties of CB refractories. On the other hand, additives have no influence on life test of CB samples. All CB samples have 28 days-life without fragmentation completed. In addition, calcitic brucite raw material can be utilized for basic refractory production, and product performance can be increased by using the additives.

- Natural calcitic-brucite ore was used to produce dolomitic refractory.
- Graphite, ceramic powder, and metallic powder were separately used as dopants.
- The main crystal phases were lime, periclase, carbon, portlandite, calcium silicate, and larnite.
- Bulk density and compressive strength improved as dopants were introduced into the mixture.
- In the corrosion test, the distribution area of slag decreased with the decreasing porosity percentage.

Competing Interests

The authors declare no competing interests.

Author Contributions

Author T. Kavas conceived and supervised the project and evaluated the results. Authors R. Kurtuluş and A. Durğun conducted the experimental work and the characterization of the samples.

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