

Effect of binder type and other parameters in synthesis of magnesite chromite refractories from process waste

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Abstract

Recycling of the process waste in basic refractory production will not only make it possible to put the waste substances to use but also help to solve the problems of environmental pollution and storing. This paper is the first part of a study on using the magnesite and chromite dusts in refractory production, accumulated in -10^{-3} m and finer particle fraction as process waste at the Konya Chrome-Magnesite Plant. In this work, three different MgO and Cr₂O₃ compositions were studied. Magnesite ore is added to the mixture without any thermal process. The type and proportion of the bond to be used, particle size distribution of the magnesite and chromite ores and the influence of compaction pressure on the refractory properties were examined. Consequently the influence of the changes in the mixture composition and sintering temperature on refractory properties was studied. The results of the experiments revealed the optimum type and content of the bond as MgSO₄·7H₂O and 8%, and optimum pressing pressure of the materials containing raw magnesite at 250 MPa. It was observed that when the chromite content of the material composition increased from 10 to 28% and 50%, the cold crushing strength (CCS) of the material has decreased, yet its porosity (P%) increased. This improves when the sintering temperature increased from 1450 to 1550 °C and 1750 °C. The optimum sintering temperature was found at 1750 °C © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The magnesite ore is used in refractory production after being sintered, however, it is quite problematic to sinter it in the form of fine dusts in rotary furnaces. The use of unsintered magnesite ore in refractory production is not preferred because of the unfavorable effect of the CO₂ and moisture on refractory, which is present in the structure of the ore.¹

Chemically bonded refractory bricks are pressed with the addition of chemical bond in order to strengthen them. The chemical bonds are defined as such components which harden by chemical reactions above room temperature or below the temperature required for ceramic bond. The strength of the chemical bond decreases during the drying process since the bonds are impaired,

and the refractory gains ultimate strength during the firing process due to the change of the chemical bond to the ceramic bond. Sodium silicate, sulfide liquor (goulloc) and a small amount of argillaceous earth or bentonite are added to the chemically bonded refractories as chemical binder.² Magnesia bonds are obtained from caustic magnesite [Mg(OH)₂], they are magnesium chloride or magnesium sulfate solutions. Caustic magnesite is obtained by burning magnesite as well as a by-product in producing sulfate.

The hardening mechanism of magnesia bonds is still not fully understood. It is assumed that the refractory hardens due to the flocculation of colloidal Mg(OH)₂. During the sintering process, the formation of secondary crystals, in addition to the formation of magnesium oxychloride, causes the strengthening of structure of the magnesite–chromite refractories. In addition to the above reactions, no other reaction occurs in the bond other than the removal of SO₂ and Cl₂ at high temperatures. The only process is the crystallization of periclase and the reaction of aggregate material.^{3,4}

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Today, many of the refractories contain either sulfate bond obtained from ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) salts or sulfate bond obtained by addition of sulfuric acid in the refractory mixture. This bond is not formed immediately; and its formation depends on the progress of the convenient alteration process of the refractory heated between 60 and 100 °C. Many of the studies have shown that the bond formed is basically magnesium oxychloride and magnesium oxysulphates.^{2,5–7}

In magnesite–chrome refractories, when the chromite component in the mixture is predominantly made of fine particles, the formation of periclase–chromite–spinel direct bond is enhanced. Besides, as the size of the chromite particle increases the sintering temperature rises up to about 2000 °C. Previous studies suggested to grind the chromite finer in order to decrease the sintering temperature below 1900 °C.^{6,7,8}

Increase in the content of chromite in the mixture decreases its ability to density, which is related to the poor sintering tendency of the chromium oxide.⁹ When the temperature is increased the tendency of the chromium oxide to crystallize increases.¹⁰

The sintering rate depends on the sintering temperature, particles size distribution and impurities. Hence, the diffusion interval and sintering time can be influenced.¹¹

2. Experimental studies

2.1. Materials and compositions

Magnesite and chromite ores from regions of Central Anatolia were used in the experimental studies as raw materials. The chemical compositions and particle size analyses of these ores are indicated in Tables 1 and 2.

The C/S mole ratio was calculated at 0.472 in the data obtained from the chemical analysis. The value $\text{C/S} < 1$ indicates that the sinter magnesite to be obtained after the sintering will contain forsterite and periclase phases

Table 1
The particle size analysis of the magnesite and chromite ores

Sieve (μm)	+ 1000	+ 500	+ 250	+ 100	+ 63	–63
Magnesite (%)	10.80	34.70	20.80	19.10	3.40	11.20
Chromite (%)	11.40	25.60	27.1	22.80	5.63	7.80

Table 2
The results of the chemical analysis of the magnesite and chromite ores

Composition (%)	MgO	Al ₂ O ₃	Cr ₂ O ₃	Fe ₂ O ₃	SiO ₂	CaO	L.O.I
Magnesite (%)	47.73	0.05	–	0.27	1.43	0.63	49.89
Chromite (%)	18.02	13.51	48.58	15.87	2.66	0.63	0.73

with a high melting point. In addition, the sintered product may contain small quantities of merwinite (C_3MS_2) and Monticellite (CMS).¹²

The percentage of mixture used in the experiments are; 90% magnesite + 10% chromite, 72% magnesite + 28% chromite, 50% magnesite + 50% chromite, respectively, as shown in Table 3.

2.2. Preparation of samples

The mixtures were prepared by using the ores whose particle size distribution was given in Table 1, and the properties of the refractory obtained with this mixture were compared with those obtained by sieving magnesite ore to -10^{-3} m and chromite ore to $-63 \cdot 10^{-6}$ m. The binders of MgSO_4 solution ($\rho_{\text{MgSO}_4 \cdot 7\text{H}_2\text{O}} = 1.28 \text{ kg/m}^3$), prepared from $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ concentration of which was specified at 19.87%, and alternatively the sulfide liquor ($\rho_{\text{sulfide liquor}} = 3.329 \text{ kg/m}^3$) waste of paper industry were added to the mixtures prepared for both particle distributions at the proportions of 4, 6, 8 and 10%.^{13–16}

In order to specify the optimum pressing pressure, a range of pressures from 120 to 300 MPa was studied.

3. Results and discussion

3.1. Effects of particle size distribution, type of bond and compaction pressure

3.1.1. Type of bond

In the first stage of the experimental study, the mixture prepared by using the material of the original particle size and the alternative binders was pressed under the pressure of 99 MPa and sintered at 1450 °C.

In Fig. 1, the products in which MgSO_4 solution was used as the bond, the experimental cold crushing strength (CCS) values were found to be higher than for the sulfide liquor bond, and the apparent porosity values were found to be lower. It was assumed that sulfide liquor, due to their organic contents left behind voids in the refractory after sintering at 1450 °C, and therefore the resulting porosity was higher compared with those in which the MgSO_4 solution was used as the binder. On the other hand, MgSO_4 was completely decomposed at 900–1100 °C by releasing MgO, SO_2 or SO_3 .^{4,17,18}

In the experiments in which content of MgSO_4 solution of 27 °Be was increased as 4, 6, 8 and 10%, the

Table 3
Number of mixture

Mixture no.	1	2	3
Magnesite (%)	90	72	50
Chromite (%)	10	28	50

properties were found to be optimized in the refractories in which 8% bond was used. When the X-ray diffraction diagram of this sample was examined, periclase, M_2S phases, $MgCr_2O_4$ and MAC ($MgO-Al_2O_3-Cr_2O_3$) spinel structures were found to exist. On the other hand, in the refractories in which 8% sulfide liquor was used as the bond, MAC and $MgCr_2O_4$ spinel structures and CMS plus forsterite (M_2S) were found in addition to the periclase structure.

3.1.2. Particle size distribution

The earlier study was repeated with finer particle sizes of each component. The composition of 90% magnesite (-10^{-3} m) and 10% chromite ($-63 \cdot 10^{-6}$ m) with $MgSO_4$ solution and sulfide liquor solution were prepared with addition of 4, 6, 8 and 10% bond and fired at 1450 °C. The results obtained from these experiments are given in Fig. 2.

It was observed that the CCS increased and the porosity decreased in the samples prepared with finer particle size distribution. In this case the $MgSO_4$ solution of 8% was again found to be the most suitable bond type and quantity. The X-ray diffraction analysis of the refractories having both particle size distributions indicated presence of periclase, $MgCr_2O_4$ spinel, CMS and forsterite (M_2S) phases.

3.1.3. Compaction pressure

In order to study the effects of the compaction pressure on the properties of the products and to specify the optimum pressure, the mixtures with fine average particle size distribution were pressed prepared between the

range of 120–300 MPa. The variation of density with consolidation pressure for the samples including raw magnesite and chromite content of 10% are given in Table 4. The samples were sintered at varying temperatures of 1450, 1550 and 1750 °C, and the porosity and CCS values were measured. The effect of the compaction pressure on the CCS values and the porosities, for

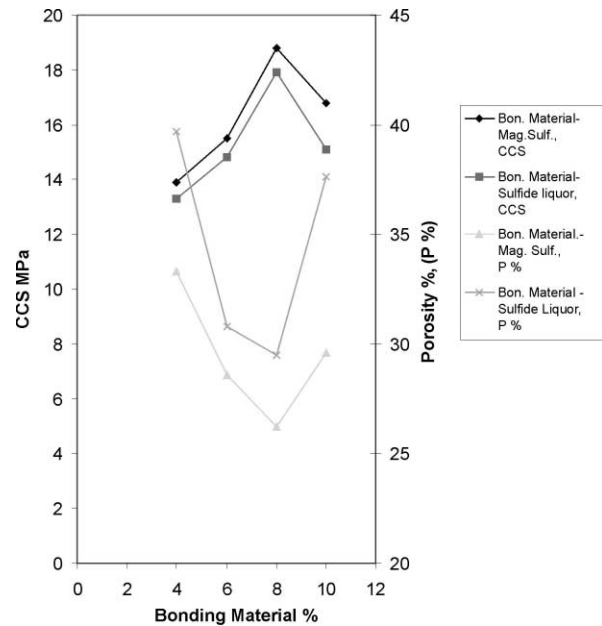


Fig. 2. Change in the values of the porosity percentage and cold crushing strength (CCS) of the refractories in which particle size distribution was made fine by the type and amount of bond.

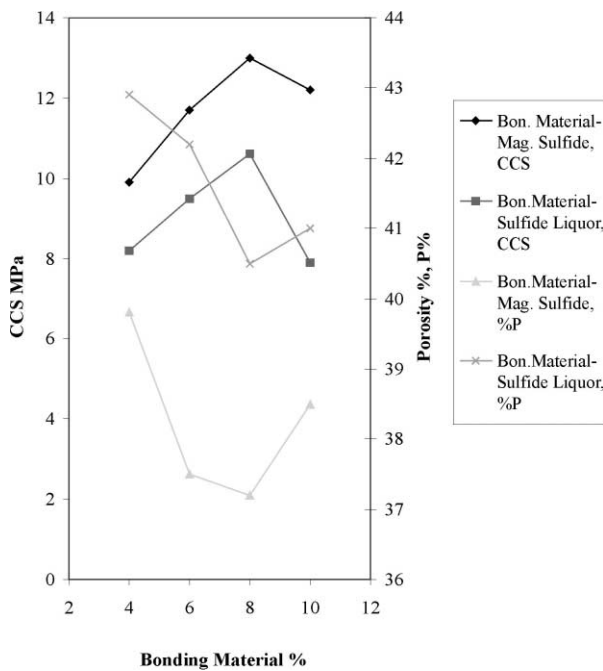


Fig. 1. Change in the type and amount of bonds and in the values of the porosity percentage and cold crushing strength (CCS).

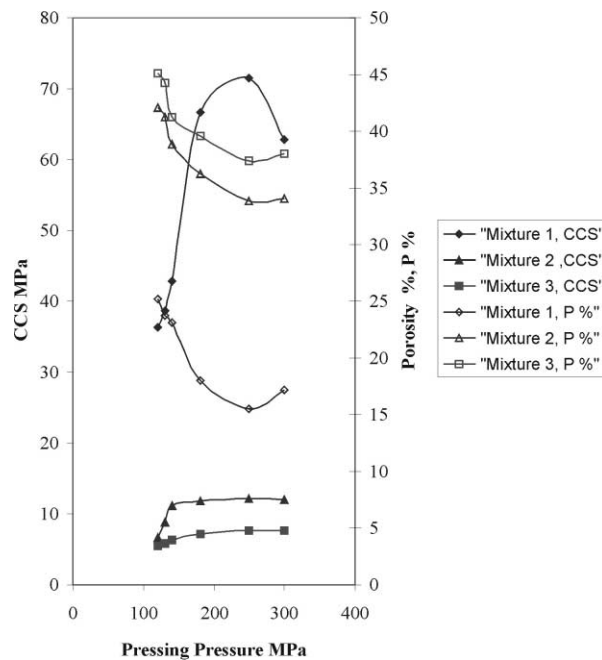


Fig. 3. Change in the values of the pressing pressure, porosity percentage and cold crushing strength (CCS) of the samples in (-10^{-3} m) magnesite and ($-63 \cdot 10^{-6}$ m) chromite particle sintered at 1750 °C.

Table 4

Changes in the pressing pressure and densities of the materials containing raw magnesite

P(MPa)	ρ (kg/m ³)
	90% Magnesite (-10^{-3} m)
	10% Chromite ($-63 \cdot 10^{-6}$ m) 8% MgSO ₄
120	2.44
130	2.45
140	2.48
180	2.50
250	2.54
300	2.54

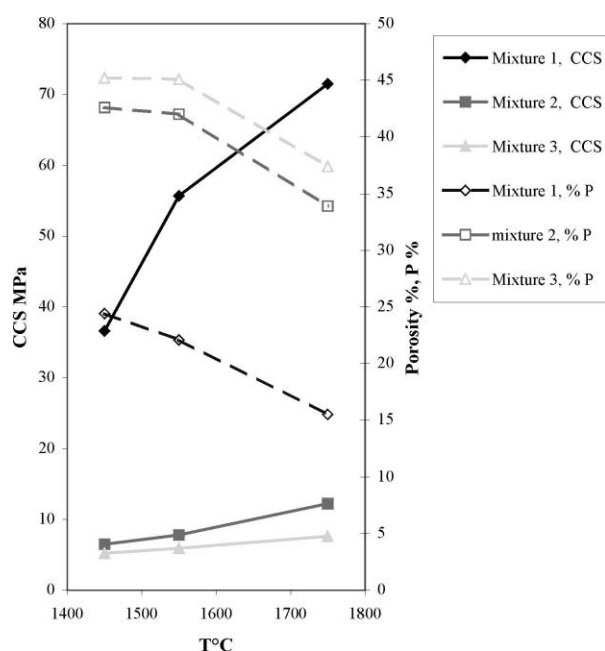


Fig. 4. Change in the sintering temperature, porosity percentage and cold crushing strength (CCS) of the refractories in which particle size distribution was made fine by the composition.

the samples sintered at the optimum sintering temperature of 1750 °C is shown in Fig. 3.

It can be seen from the figure that 300 MPa of compaction pressure resulted in high density in the samples containing raw magnesite, whereas the analyses of sintered product revealed that the samples pressed at 250 MPa showed higher CCS and lower porosity compared with those pressed at 300 MPa. This can presumably be explained by the fact that the particles start to crumble into smaller pieces as the pressure increases over a certain limit and the original particle granulation is destroyed. Consequently, the pressure of 250 MPa was taken as the standard compaction pressure throughout the course of further experiments.

3.2. Effects of material composition and sintering temperature

The content of the chromite phase was changed as 10, 28 and 50% in the composition of the mixtures, and the effects of the material composition on refractory properties were studied. Formulations were prepared with the MgSO₄ solution as the bond from the material having the compositions stated earlier, and the refractories were compacted under 250 MPa pressure and sintered at 1450, 1550 and 1750 °C in order to investigate the effects of the sintering temperature.

The results obtained are given in Fig. 4. It can be seen from the figure that, as expected, the values of CCS and bulk density increase and porosity decreases as the sintering temperature rises. As the content of the chromite was changed from 10, to 28% and 50% in the composition of the mixtures, the values of CCS and bulk density was observed to decrease and porosity to increase.

4. Conclusions

1. The raw materials with (-10^{-3} m) magnesite and ($-63 \cdot 10^{-6}$ m) chromite particle sizes were observed to improve the properties of samples, when the binder composition of 8% MgSO₄·7H₂O was used. The optimum compaction pressure for the mixtures was found to be 250 MPa. Above this level, the properties started to deteriorate.
2. As the sintering temperature was increased as 1450, 1550, and 1750 °C, the porosity was observed to decrease and strength to increase. The sintering behavior was enhanced by decreasing the particle size distribution of the mixture.
3. As the chromite content of the mixture increased, the bulk density and strength was found to decrease resulting from increase in open porosity. This effect was considered to result from the inability of densification of the system with increasing chromite content.
4. The experimental results indicated that, as given in Fig. 4, the composition from process waste, with 10% chromite content and bonded with 8% MgSO₄·7H₂O binder, can be applied for the production of MgO–Cr₂O₃ refractory brick.¹⁹

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