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# Effect of $Fe_2O_3$ Additions on Sinterability of Konya Dolomite of Turkey

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**Abstract .** The sintering behaviour of dolomite extracted from a mine in the Konya-Sille-Ecmel region of Turkey was studied. Sintering tests were performed at different sintering temperatures (1600°C, 1650°C and 1700°C) and soaking times (2, 4, 6 hours) on powders which were either pure or contained selected amounts of iron scale of a thickness below 45 μm (98.66 wt% $Fe_2O_3$). The bulk density and the apparent porosity of the sintered products were examined which turned out to be dolomite (doloma), and the differences obtained under various sintering conditions were explored. The study revealed the following results: (1) The sintering temperature of the raw dolomite was decreased by the addition of iron oxide, which is attributed to the formation of liquid phase. (2) The newly formed phases were found to sintered granule surfaces very well, resulting in a smaller influenced area and a higher resistance to hydration. Thus, the study has shown that the addition of iron oxide at a level that is small enough to avoid corrosion results in a sintering process that can be carried out at distinctly lower temperatures and in less time. This behaviour may encourage the use of domestic doloma**.**

## Introduction

Doloma refractory obtained from the mineral dolomite ($CaMg(CO_3)_2$) consists of a phase mixture of lime (CaO) and periclase (MgO) in the theoretical ratio of approximately 60/40 wt% after calcination. The temperature at which the eutectic mixture of lime and magnesia starts to melt is 2370°C. According to literature [1], technical and economical dolomite must have the following properties: MgO > 18 wt%, CaO/MgO ratio < 1.6, impurity content ($SiO_2$, $Fe_2O_3$, $Al_2O_3$) between 0.5 wt% and 1.5 wt%, a grain size < 0.3 mm and a homogeneity as large as possible. The purity of dolomite refractory obtained from the mineral dolomite should not exceed 2 wt%, whereas the bulk density should lie above 3 g/cm$^3$, the apparent porosity should be less than 8%, and the grain size should be between 2 and 20 μm [2, 3].

Together with the developments in steel production technology, the widespread usage of basic refractories increases day by day. Recently, magnesium and chromium-magnesium refractories have been used more than dolomite refractory in steel production. However, besides the contribution of scrap iron and electricity, the refractory has a crucial role in steel production costs, and therefore the significance of long life and low cost of the refractory becomes important. Thus, the usage of dolomite refractory that provides not only metallurgical advantages also cheapness and high refractory property is ever expanding in modern steel production. So, cleaner steel production with respect to phosphor and sulphure is possible [4, 5]. Dolomite refractory used in Turkey is generally imported and domestic production is very recent. However, dolomite as a mineral is abundant in Turkey and can be easily produced by the open mining method [6].

Koval et al. [7] obtained dense doloma (about 95% of theoretical), when the total concentration of 0.5 wt% $Fe_2O_3$ is reached, but at high sintering temperature (> 1600°C). Consequently, $Fe_2O_3$ is often added as mill scale during commercial manufacturing processes. Doloma grades containing high $Fe_2O_3$ were found to be of good quality (2$^{nd}$ class) when dead-burned and was shown to partially balance lime in rotary furnaces by the iron dross additive [8]. On the other hand, it was

observed that doloma materials containing more than 2% $Fe_2O_3$ gave bricks of decreased slag corrosion resistance [9].

**Experimental**

The domestic dolomite[1] percentage, chemical analysis and grain size of raw dolomite extracted from the reserve were examined and checked to determine whether dolomite is suitable for refractory production. For chemical analysis a representative sample was taken from the deposit and crushed below 0.074 mm and were investigated using a proper scheme of wet silicate analysis. Table 1 shows the data of the chemical analysis of raw dolomite. X-ray diffractometer studies revealed that the raw material is dolomite with a purity of 99% (the rest is a very low fraction of calcite) (Fig.1). XRD analysis was carried out using a 08 Advance Bruker diffractometer operating CuKα radiation. It is observed that the mean value of grain size is 200 μm by taking a thin cross-section in the image analysis LEICA Q 550 CW optical microscope.

The raw dolomite was cleaned, crushed and finally sieved to 3-6 mm granule sizes. By adding 0.5 and 1.0 wt% from each of iron scale that are sieved below 45 μm, three groups of dolomite granules were prepared. The 13 prepared samples (300 g of each) were intimately wet-mixed[2] in a glass ball manually for half an hour. Prepared samples and pure experimental samples were dried at 110°C for two hours. Dried samples were single-stage fired[3] at 1600°C, 1650°C and 1700°C for 2, 4 and 6 hours at a rate of 10°C/min. An electric furnace equipped with Kanthal molybdenum disilicide heating elements was used[4]. At the end of each sintering cycle, the electric power was cut to zero in order to obtain natural cooling. Density, phase composition and microstructure of the sintered samples were determined experimentally. The variations of the densification of the doloma was traced using the Archimedes[5] technique. Optical microscopy was conducted on polished and etched specimens produced by mounting the sintered samples in a thermo–press device and subsequent grinding using SiC papers 320, 600, 1000 grit size. Final polishing was done with an automatic vibratory polishing machine using 9 and 3 μm diamond paste. Only the unmixed samples have been etched with pure acetic acid and it was decided that there was no necessity to etch the mixed samples. Microstructure of some selected dense samples was investigated using a JEOL JSM SEM of model 5410 LV equipped with an EDS unit of system 5480 IXRF. Solid-phase composition was qualitatively determined by XRD.

Table 1. Chemical analysis of raw dolomite

| Composition (wt%) | |
|---|---|
| MgO | 22.52 |
| $Al_2O_3$ | 0.15 |
| $Fe_2O_3$ | 0.04 |
| CaO | 29.46 |
| $SiO_2$ | 0.15 |
| LOI[6] | 47.68 |
| Total | 100 |

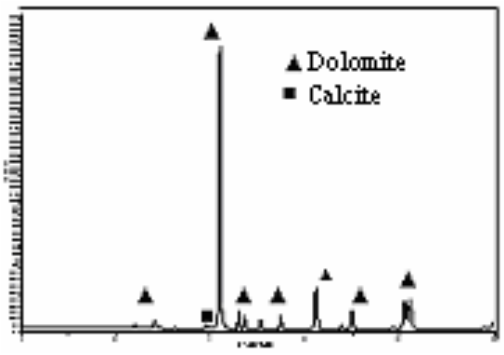


Fig 1. X-ray diffraction pattern of raw dolomite

[1] Konya Chrome-Magnesite Co., Konya, Turkey.
[2] Distilled water was used as binder.
[3] As a result of the pre-sinterisations it was observed that dolomite could easily be sinterised and two-stage firing [8] was not carried out due to economical reasons.
[4] Sorvall Heraeus Bodenlader and Nabertherm LHT4/R17.
[5] EN 993-1 and MPIF Standard 42 (immersion liquid ethyl alcohol.)
[6]

## Results and Discussion

### Densification

In Fig. 2, it is shown that full sinterisation did not occur and the $Fe_2O_3$ additive at 1600°C did not influence the process but, on the contrary, it was observed that with the $Fe_2O_3$ addition and sintering temperature the bulk density increased. Increases of the bulk density by the additive ratio is evidence of improved sinterisation, and at the same time it can be seen that the optimum sintering temperature decreased. It was observed that this increase only happened when the $Fe_2O_3$ content was between 0 and 0.5 wt% and decreasing when $Fe_2O_3$ between 0.5-1.0 wt%. Furthermore, it was observed that the influence of the additive on the density at 1650°C and 1700°C was almost the same.

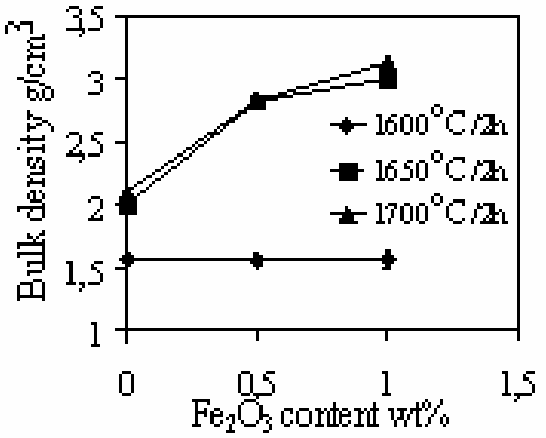


Figure 2. Densification curves of various dolomas.

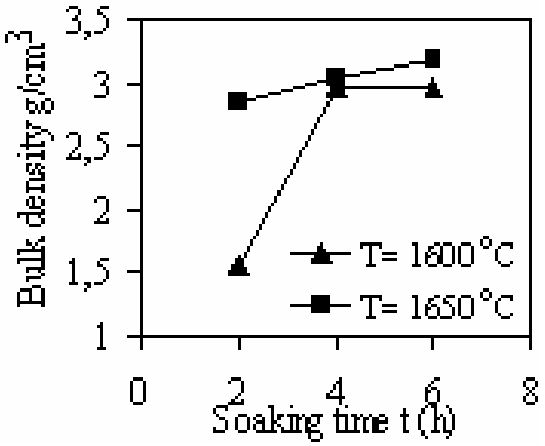


Figure 3. Effect of soaking time on the densification of dolomas containing 0.5 wt% $Fe_2O_3$.

### Effect of Soaking Time

In Fig.3, the effect of soaking time on the density is shown. It was observed that the density of the samples having 0.5 wt% $Fe_2O_3$ increased to 2.95 g/cm$^3$ after 4 hours at 1600°C, but remained at this insufficient level even after 6 hours. At 1650°C, on the other hand, the densification process developed much faster with soaking time, and especially after 6 hours a density level of 3.17 g/cm$^3$ was reached. Moreover, it was observed that the amount of liquid phase was (formed that is) sufficient for stimulating its role in densification at longer soaking time. On the contrary, higher liquid phase contents may tend to increase of the rate of discontinuous growth of periclase particles by a solution-precipitation mechanism on soaking. As a result of this, a higher fraction of closed pores is expected, thus inhibiting the percentage of densification at later stages [10].

### Phase Compositions and Microstructure of Dolomas

As a result of phase analysis based on XRD patterns and EDS, it was found that, at all three temperatures studied and after a soaking time of 2 hours, in the samples without additive the amount of free lime was very small and disappeared with longer soaking time and with the increase of the additives. Accordingly, it can be concluded that, with adequate temperature and soaking time, the addition of $Fe_2O_3$ may impede hydration. As for the other phases, especially periclase (MgO), it has been demonstrated previously that the presence of phases like $C_4AF$ (brownmillerite) and $C_2F$ is more pronounced in samples with additives, whereas $C_2S$–based phases are found in samples treated at low temperatures, and phases like $C_3S$ and $M_2S$ (forsterite) are more likely in samples at higher temperatures [11]. According to ceramic nomenclature, the abbreviations have the following meaning: C=CaO; A=$Al_2O_3$; F=$Fe_2O_3$; M=MgO; S=$SiO_2$.

In Fig.4, the XRD pattern of the sample containing 0.5 wt% $Fe_2O_3$ additive is shown after sintering at 1650°C for 4h which are thought to be to optimum conditions. It is known from previous studies that with the addition of dolomite $Fe_2O_3$ usually $C_4AF$ or $C_2F$ phases are formed and that with increasing temperature these phases both cause an increased rate of liquid phase formation and accelerated sinterisation [12,13]. Moreover, in the microstructure of the same sample in Fig.5, periclase (dark grey), CaO (light grey) and other phases with $C_4AF$ majority (white) are seen. Thus, it could be established that, with the influence of additive and soaking time, the formation of periclase increases. It should be noted that in dolomites the increase of the average size of the periclase particles increases the resistance to hydration [13].

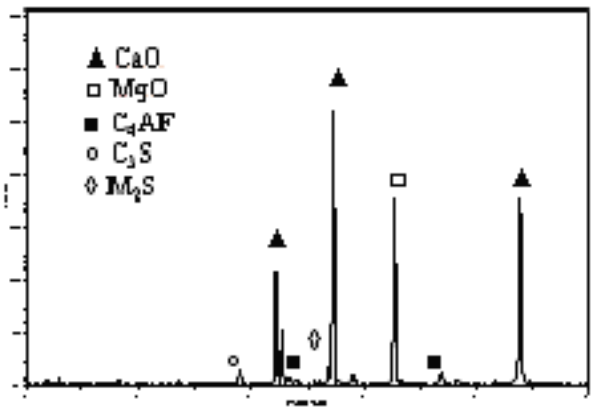


Figure 4. XRD pattern of doloma with 0.5 wt% $Fe_2O_3$

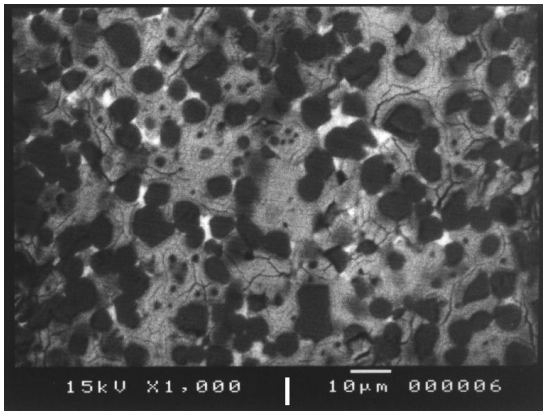


Figure 5. SEM micrograph of doloma

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