1. INTRODUCTION

The MgO-CaO system (Fig.1) is remarkable for the high liquidus and solidus temperatures over the complete range 100% MgO-100% CaO, as the eutectic for the CaO-MgO binary system occurs at 2370 °C [1-2].

Dolomite is the double carbonate of calcium and magnesium, having the formula CaMg(CO\(_3\))\(_2\) and the average ratio of Ca:Mg ranges between 1.5 and 1.7. Doloma, produced from the dolomite, consists of a phase mixture of lime (CaO) and periclase (MgO) [1,4]. Doloma has long been regarded as an attractive potential refractory for applications in metallurgical industries because of its global abundant sources, as well as its advantages of high melting temperature and inhibition against deep infiltration by the reaction of CaO with acidic slag. However, the application of doloma as a refractory has always been restricted by the drawback of poor hydration resistance [5]. Some studies have been carried out on magnesia-doloma refractories in order to decrease the amount of CaO content to develop the performance of doloma refractories. According to these studies, a composition in the range of 60-80% MgO and CaO may lead to approximately desirable properties [6-8]. Different ways have been proposed to produce magnesia-doloma refractories. A new approach is using sintered and fused co-clinker of magnesia and doloma as a starting material for the magnesium-doloma refractories which would lead to more homogenous products with more desirable properties [6,9]. Another approach has been focused on addition of different additives to lime and doloma; Aygül Yeprem has studied the effect of iron oxide addition to doloma and mentioned
in his article that iron oxide addition increases the resistance against the hydration which is the biggest disadvantage of doloma. Besides, iron oxide addition results in increasing the density [1]. Othman et al added ilmenite to lime and claimed that the hydration resistance of lime increased [10]. Gosh and colleagues tested the effect of V$_2$O$_5$ addition on the hydration resistance of lime and reported that the hydration resistance increased [11]. Min Chen et al studied the effect of ZrO$_2$ addition on the properties of refractories in MgO-CaO system. They claimed that the addition of ZrO$_2$ can lead the hydration resistance of MgO-CaO refractories to increase [12]. But limited researches have been done on studying the effect of additives on the properties of magnesia-doloma refractories. The effect of addition of iron oxide on the properties of magnesia-doloma with CaO content of 25 wt% has been studied in the previous researches of the authors [13,14]. In the current research, in collaboration with Iranian Refractories Procurement and Production Co., two base compositions of Magnesia-doloma with CaO content of 25 and 35 wt% have been chosen and the effect of addition of different amount of iron oxide on properties of magnesia-doloma samples such as phase content, microstructure and hydration resistance has been investigated.

2. EXPERIMENTAL PROCEDURE

Chemical analyses of the starting materials are shown in Table 1.

<table>
<thead>
<tr>
<th>Composition of the samples</th>
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<tbody>
<tr>
<td>Calcium Oxide (wt%)</td>
</tr>
<tr>
<td>Iron Oxide (wt%)</td>
</tr>
<tr>
<td>0</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>4</td>
</tr>
</tbody>
</table>

Table 1. Chemical analyses of magnesia and doloma

<table>
<thead>
<tr>
<th>(wt%)</th>
<th>Magnesia</th>
<th>Doloma</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>97.45</td>
<td>40.12</td>
</tr>
<tr>
<td>CaO</td>
<td>0.65</td>
<td>58.1</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>0.3</td>
<td>0.35</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>0.15</td>
<td>0.25</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>1.05</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Two compositions with different CaO contents (25 & 35 wt %) were adopted and then by addition of different amounts of iron oxide, ten batches were prepared according to table 2. They were mixed, pressed and fired for 3 hours at 1750°C.

Samples were kept in kerosene to be away from the moisture and were polished with that to protect against hydration. Phase composition of the samples was determined by the XRD technique (Jeol-8030, Cu K$_\alpha$, 25 kV) and microstructure was investigated by using a scanning electron microscopy (SEM, Cambridge, S360) attached with an EDS unit. The hydration resistance was determined as following: each sample was powdered to gain a particle size finer than sieve no.40 (425 µm) and after weighing, placed in a Petri dish in a climate room with 70% humidity in 110°C. The samples then were weighed different times to 11 days [2].
3. RESULTS AND DISCUSSION

3.1. Phase Studies

Phase analyses of magnesia-doloma samples with 25 wt% of CaO are shown in fig. 2 and those of the samples with 35 wt% of CaO can be seen in fig. 3.

It can be seen that MgO and CaO didn't have any interactions with each other, confirmed by their phase diagram (Fig. 1) [5]. Regarding the impurities of the starting materials, other than lime and periclase, we expected to see peaks for C<sub>3</sub>S, C<sub>2</sub>F and C<sub>4</sub>AF phases in all patterns [8], but the iron and silicon impurities of the samples were too little to be detected via XRD technique. It has been reported that iron oxide addition to dolomia leads to formation of compounds which have low melting points such as C<sub>4</sub>AF (C = CaO, A=Al<sub>2</sub>O<sub>3</sub>, F=Fe<sub>2</sub>O<sub>3</sub>) and C<sub>2</sub>F[1]. Searle and Grimsha also claimed in their article that in their previous studies of stabilizing dolomite when iron oxide was added it usually formed C<sub>4</sub>AF and when the effects of this phase at high temperatures were analyzed, liquid phase increased with increasing the temperature [16].

In this research, samples with CaO content of 25 wt% (Fig. 2), the trace of C<sub>2</sub>F (2CaO.Fe<sub>2</sub>O<sub>3</sub>) and in samples with that of 35 wt% (Fig. 3), the trace of C<sub>4</sub>AF (4CaO.Al<sub>2</sub>O<sub>3</sub>.Fe<sub>2</sub>O<sub>3</sub>) have been detected. For C2F only one identification peak is marked which can be due to its three identification peaks with maximum intensity which are close to each other and may have overlapped. Moreover, some amount of iron oxide may have been solved in periclase or reacted with that, which reduces the amount of iron oxide reacting with lime and so caused the amount of C<sub>2</sub>F to decrease. FeO is completely soluble in MgO (the solid solution is called magnesiowustite), but it has not been proved that Fe<sub>2</sub>O<sub>3</sub> forms solid solution with MgO below 1000ºC. In the normal atmosphere, which was the environment of the samples in this research, solubility of Fe<sub>2</sub>O<sub>3</sub> in MgO has been found to be 10% at 1200 ºC and 35% at 1400 ºC [1] and magnesio ferrite precipitates during cooling to room temperature which its amount has been lower to be detected via XRD technique, but it can be seen in SEM images as the bright spots. While Fe ions diffuse into periclase grains and form solid solution, the inner crystal energy changes by developing thin inclusions and also lead the lattice parameter to increase. This provides the growth of periclase (MgO) grains and facilitates the sintering by increasing the recrystallization ability [1].

Also there can be seen only one identification peak for C<sub>4</sub>AF which can be due to very low amount of alumina impurity that makes the amount of C<sub>4</sub>AF lower than can be detected via XRD technique.

3.2. Microstructure Studies

Microstructure images of the Magnesia-doloma samples with CaO content of 25 wt% are shown in
Fig. 4 and those of samples with CaO content of 35 wt% can be seen in Fig. 6. EDS analyses of different components of Fig. 4-b are presented in Fig. 5 and that of Fig. 6-b is shown in Fig. 7.

In Fig. 4-a, microstructure of sample C25 can be seen with magnification of 200. It shows clearly how doloma (region D) and magnesia (region M) grains are located next to each other. It can be seen that magnesia grains have covered doloma grains and so have limited their exposure to the moisture. The phase indicated with A (dark phase in the doloma grain) declares periclase and the one indicated with B (bright phase in the doloma grain) declares lime.

Microstructure of sample C25-6 has been shown with magnification of 500 in Fig. 4-b. The bright grain boundaries declare the presence of phases with higher atomic weigh such as C$_2$F, which have capsulated the CaO and MgO grains.

Fig. 5 shows the EDS analyses of different components of sample C25-6. According to Fig. 5-a, dark grey regions in Fig. 4-b show periclase grains and white little spots on them show precipitates of magnesioferrite, as shown in Fig. 5-c. Bright grey regions in Fig. 4-b indicate lime grains considering Fig. 5-b and Fig. 5-d shows that
Ca, Fe, Si, Al and O exist in the grain boundaries which have covered CaO and MgO and restrict their exposure to the moisture.

In Fig. 6-a, microstructure of sample C35 with magnification of 200 has been presented and Fig. 6-b shows that of sample C35-6 with magnification of 500. The EDS analyses of region GB (grain boundaries) in sample C35-6 can be seen in Fig. 7. Like GB region in sample C25-6, Ca, Fe, Si, Al and O exist in the grain boundaries and have covered the MgO and CaO grains. It can be said that the sharper Al-peak in Fig. 7 (rather than that of Fig. 5-d) shows the possibility of calcium alumino ferrite (C₄AF) formation in sample C35-6.

3.3 Hydration Test

Results of the hydration test are given in Fig. 8. It can be seen that the percentage of weight gain and so the hydration resistance of the samples has improved by increasing the additional iron oxide content. We can also see

![Fig. 6. SEM images of the samples: (a) C35 and (b) C35-6, fired at 1750°C for 3 hrs, with magnifications of 200 and 500, respectively.](image1)

![Fig. 7. EDS analyses of region GB (grain boundaries) in Fig. 6-b.](image2)

![Fig. 8. Relationship between weight gain (%) from hydration and hydration duration (days) (conditions: 70% humidity and 110 °C).](image3)
that the hydration resistance of Magnesia-doloma samples with CaO content of 25 wt% is better comparing to those with 35 wt% of CaO due to their lower lime content, because CaO is much more prone to hydration comparing to MgO.

Refractories based on periclase (magnesium oxide) and bearing calcium oxide can undergo hydration in a warm humid atmosphere. In this case the powder grains break, the material is pulverized, and the articles crack [17]. Several methods have been tested to control this phenomenon, including methods through which CaO and MgO grains are covered by phases grow in the grain boundaries and those through which the porosity of the system decreases; all methods lead the accession of CaO and MgO to the moisture to decrease [1,5,7,9-12,17,18].

In this research, formation of iron oxide included phases was detected by increasing the amount of additional iron oxide. According to the results achieved in phase and microstructure analyses, the phases containing iron oxide (C$_2$F in samples with CaO content of 25 wt% and C$_4$AF in samples with that of 35 wt%) are formed in the grain boundaries. Dicalcium ferrite (C$_2$F) and calcium alumino ferrite (C$_4$AF) with melting temperatures lower than 1450 ºC and better hydration resistances rather than CaO[3,19], can hinder the hydration process by covering the CaO grains and so can improve the hydration resistance. Moreover, regarding their low melting points, C$_2$F and C$_4$AF both are liquid at the firing temperature of the samples and so can promote the sintering. As a result, the porosity content of the samples would decrease and so does the exposure of the grains to the moisture; so, the hydration resistance would increase. Furthermore, C$_2$F is less prone to hydration rather than C$_4$AF[19] and regarding less amount of CaO content, C25-n samples are more hydration resistant.

4. CONCLUSIONS

- Hydration resistance of Magnesia-doloma improved by addition of iron oxide.
- Iron oxide addition lead to the formation of iron-containing phases which increased the hydration resistance of the samples both by capsulating the CaO and MgO grains and by promoting the liquid phase sintering.
- Iron oxide addition in samples with CaO content of 25 wt% caused the formation of C$_2$F, but by increasing the amount of CaO, in samples with CaO content of 35 wt%, C$_4$AF was formed. C$_2$F and C$_4$AF Both are low melt phases and also have more resistance against hydration comparing to CaO.
- Hydration resistance of the samples with CaO content of 25 wt% was more than that of the samples with CaO content of 35 wt% because CaO is much more prone to hydration comparing to MgO; but they didn't differ too much and so each can be used according to the conditions.

REFERENCES