INFLUENCE OF MAGNESIA ADDITION ON HYDRATION OF IRANIAN DOLOMITE

M. Hadian* and B. Nazari
* *hadian@ut.ac.ir*
Received: January 2010 **Accepted: May 2010**

School of Metallurgy and Materials, Faculty of Engineering, University of Tehran, Tehran, Iran.

Abstract: *Dolomite refractories have a good production potential in Iran due to the existence of high-quality dolomite ore in many regions of the country, particularly in Isfahan and Hamedan. The basic problem associated with the production and use of this type of refractories is inherent tendency to hydration of calcined dolomite. One of the methods to overcome this problem is to increase the amount of magnesia in doloma. This study focuses on the use of Iranian dolomite to produce magnesia –doloma (mag-dol) refractory with high resistance to hydration and corrosion. It was found that addition of 20wt% magnesite to dolomite would result in capsulating of CaO by MgO that protects doloma from further hydration.*

Keywords: *Dolomite, Magnesite, Mag-dol, Refractory, Hydration, Corrosion.*

1. INTRODUCTION

Dolomite refractories are among basic products which their raw materials consists of either fused or sintered doloma. Normally, these refractories have 60wt% calcium oxide and 40wt% magnesium oxide in their composition. Some impurities such as SiO_2, Al_2O_3, Fe_2O_3 , and ZrO_2 in form of calcium or magnesium compounds are found in these materials [1].

The main application of dolomite refractories is in steel making, cement and lime industries [2, 3]. Calcined dolomite is highly prone to hydration. This inherent property limits the storage time and transportation of this type of refractory materials. To stabilize doloma against hydration many research works have been done and variety of methods has been applied, but most of these methods somehow alerts such properties as refractoriness and corrosion resistance of dolomite refractories or causes environmental problems. One of the most effective methods to stabilize doloma is addition of magnesia to doloma. The product is called magnesite-dolomite (mag-dol) refractory. At the moment this product is being used so please specify the success of using and also the situation needed to be described. The amount of magnesia in these products ranges between 50-80 wt%. The high percent of magnesia improves such properties as resistance to hydration [4] and corrosion by slag [5], cold and hot crush strength and also resistance to abrasion [6]. Some methods have been used to produce mag-dol refractories; the most important one is the use of mixture of sintered magnesia and doloma. Another method is to partially hydrate doloma to reduce the percentage of CaO in it. Another new method is the application of calcined mixture of dolomite and magnesia via two-stage calcinations process [7].

In Iran high quality dolomite is found in many regions. Most of the mines are open mines and do not need any ore dressing process. The most important dolomite mines in Iran are located in Isfahan, Hamedan, Kerman, Zanjan and Azarbayjan provinces.

The purpose of this research work is to study the use of Iranian dolomite and magnesite to produce mag-dol refractory via two-stage calcinations process.

2. EXPERIMENTAL

The raw materials used consisted of dolomite and magnesite from Isfahan and Birjand mines respectively. The chemical analysis and physical properties of these materials before and after calcinations process is shown in Table 1. In order to maintain the effect of particle size distribution, particles having 0 - 1 mm diameter were selected and divided into three different ranges, 0-0.2 mm, 0.2 - 0.6 mm and 0.6 - 1 mm.

Using Anderiasin's method, proper amount of

each rang was calculated in order to obtain optimum particle packing (Table 2). To prepare starting clinker by two-stage calcinations method. Mixture of dolomite and magnesite having 20, 40 and 60wt% magnesite were prepared. The particle size of magnesite was between 0 - 0.2 mm. The mixtures were then uniaxially pressed into cylindrical samples having 3 cm diameter.

The samples were then calcined for 3 hrs at different temperatures mainly 1100, 1200, 1300 and 1400 °C. It was found that a temperature range between 1200-13000 °C is suitable for the calcinations process. According to Table 3, mixtures of 20, 40 and 60wt% magnesite in dolomite with 6% moisture prepared and uniaxially pressed into samples having about 1 kg weight. The samples were then calcined at 1250°C for 3 hrs. The calcined samples were then crushed and sized as the starting clinker.

In order to study the effect of calcinations process, two types of samples were prepared; the first type was made of calcined clinker and the second type was prepared sing a mixture of sintered doloma and magnesia. To prevent samples from hydration, they were kept in an oven at 110°C. All the samples were then fired at 1600°C for 4 hrs. After firing, samples were tested for microstructural examinations, density measurement, crush strength and resistance to hydration. The hydration tests were done according to Paul's method [8].

3. RESULTS AND DISCUSSION

3.1. Microstructural Examinations

Figure 1 illustrates a SEM image of the

Table 1. Chemical analysis and physical properties of raw materials

Dolomite											
MgO (%)	CaO (%)	Fe_2O_3 (%)	Al_2O_3 (%)	SiO_2 (%)	Na_2O (%)	P_2O_5 (%)	K_2O (%)	SO_3 (%)	MnO (%)	L.O.I (%)	
22.10	31.86	0.45	0.14	0.35	<0.01	0.01	<0.01	<0.02	<0.03	46.92	Dolomite
38.87	60.02	0.85	0.26	0.66	<0.02	0.02	<0.02	<0.03	<0.04	-	Calcined Dolomite
Water absorbsion: 0.66%				apparent porosity=1.87%						Density=2.82gr/cm^3	
Magnesite											
MgO	CaO	Fe_2O_3	Al_2O_3	SiO_2	L.O.I						
45.69	1.72	0.28	0.06	0.78	51.31	Magnesite					
93.83	3.53	0.58	0.13	1.60	-	Calcined Magnesite					
Water absorbsion: 2.16%			apparent porosity=6.04%			Density=2.79gr/cm^3					

Table 2. Particle size distribution of starting materials

(0.0.2)	(0.2-0.63)	(0.63-1)	Particle size range (mm)
32	40	28	Ratio of mixture

Table 3. The ratio of magnesite and dolomite in starting mixtures

Particle size range			Code of samples
(0-0.2mm)	(0.2-0.63mm)	(0.63-1mm)	
%32D	%40D	%28D	D
%20M+%12D	%40D	%28D	D-20M
%32M	%8M+%32D	%28D	D-40M
%32M	%28M+%12D	%28D	D-60M
%32M	%40M	%28M	M

Table 4. Chemical analysis of starting mixtures after calcinations

CaO (%)	MgO (%)	Fe_2O_3 (%)	Al_2O_3 (%)	SiO_2 (%)	Starting mixture	Code of sample
3.53	93.84	0.58	0.13	1.6	Magnesite	M
26.21	71.22	0.68	0.18	1.23	Dolomite+60% Magnesite	D-60M
37.43	60.25	0.74	0.2	1.04	Dolomite+4% Magnesite	D-40M
55.08	49.03	0.79	0.23	0.85	Dolomite+20% Magnesite	D-20M
60.02	37.87	0.85	0.26	0.66	Dolomite	D

starting clinker containing 40 wt% magnesite which calcined for 3 hrs at 1300°C. From the figure, it can be seen that there is no bonding between the doloma and magnesia particles. This indicates that the calcinations temperature is not high enough for bond formation at the doloma/magnesia interface. The XRD pattern of the same sample is shown in Figure 2. The pattern indicates the lack of formation of low melting temperature oxide phases in this sample.

Figure 2 illustrates an electron microscope image of a fired sample at 1500°C. This sample was prepared using a starting clinker containing 60wt% magnesite in its composition. From the figure, remarkable porosity exists between the magnesia and doloma grains. This finding is in a good agreement with the density measurement results given in Figure 7. Comparing the SEM micrograph shown in Figure 3 which belongs to a sample with the same composition but higher firing temperature (1600°C) with this

Micrograph (Fig. 2) shows the considerable effect of firing temperature in porosity reduction in this system.

Figure 4 shows the interface between the doloma and the magnesia grains. This image was taken from the sample containing 60wt% magnesia and 40wt% doloma in its composition and fired at 1600°C. The figure shows a good bond formation between the magnesia and doloma grains which have a positive effect on the strength of the sample. Figures 5 and 6 show optical microscopy images of the samples having 20 and 60wt% magnesite. The figures indicate that microstructure of the samples consists of doloma grain being surrounded by honeycomb-shape network of magnesia. This network is thicker in the sample with higher amount of magnesia (Fig. 5). The sample has also more porosity. However, in the sample with 20wt%

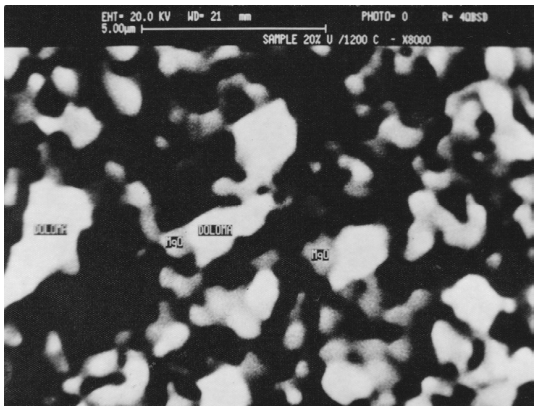

Fig.1. SEM micrograph of the starting clinker containing 40wt% magnesite in it.

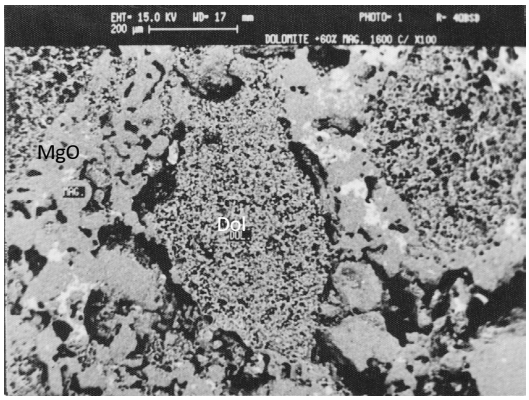

Fig. 3. SEM micrograph of a fired sample at 1600°C containing 60wt% magnesite.

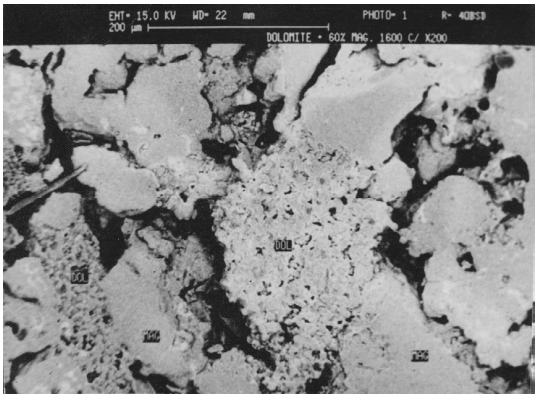

Fig. 2. SEM micrograph of a fired sample at 1500°C containing 60wt% magnesite.

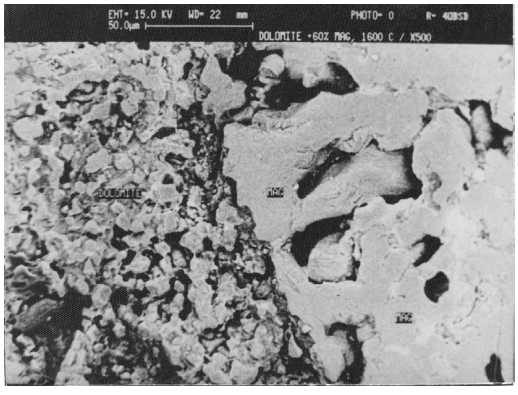

Fig. 4. Doloma/magnesia interface in the sample shown in Fig. 3.

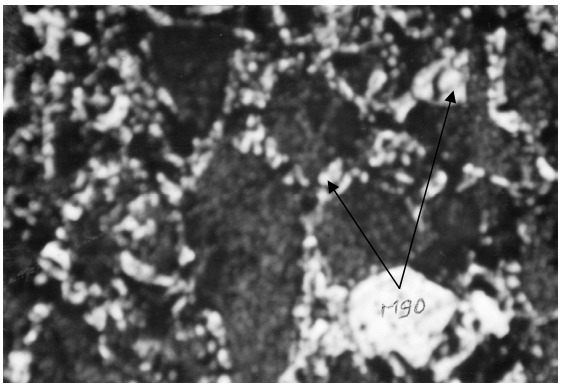

Fig. 5. Optical microscopy image of a mag-dol sample having 60wt% magnesite.

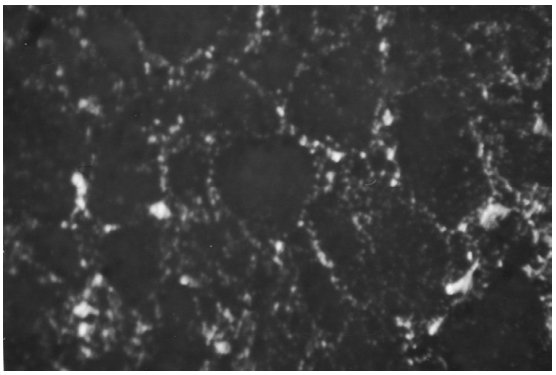

Fig. 6. Optical microscopy image of a mag-dol sample having 20wt% magnesite.(x1000)

magnesite (Fig. 6) the network's wall is thinner and contains less porosity.

3.2. Density Measurement

The results of density measurement test of the samples shown in Figure 7. To have a more accurate result, five samples were selected for each measurement. The figure shows that by increasing amount of magnesite in starting clinker the porosity increases and consequently density decreases in all the samples. it also shows that the density of the samples which have been prepared by two stage calcinations process is significantly higher than that of the samples being made by using a mixture of sintered doloma and magneia. It was found that by increasing the firing temperature the density increases in the samples prepared from calcined clinker. This behavior was not observed in the samples having more dolomite in their starting clinker. This can be due to first: higher melting temperature and less impurity content of magnesite do not allow for a full sintering at the firing temperature. And second: the activity of calcined magnesia is lower than that of calcined doloma due to partial sintering of magnesia during calcinations process. Therefore, sintering of the samples having more doloma will be more completed under the processing conditions.

3.3. Resistance to Hydration

The results of resistance to hydration test of the samples made of calcined clinker are shown in Figure 8. The figure shows that by increasing magnesite from 20wt% to higher values the resistance to hydration decreases, while the samples with 20wt% magnesite has the highest resistance value. This behavior can be described

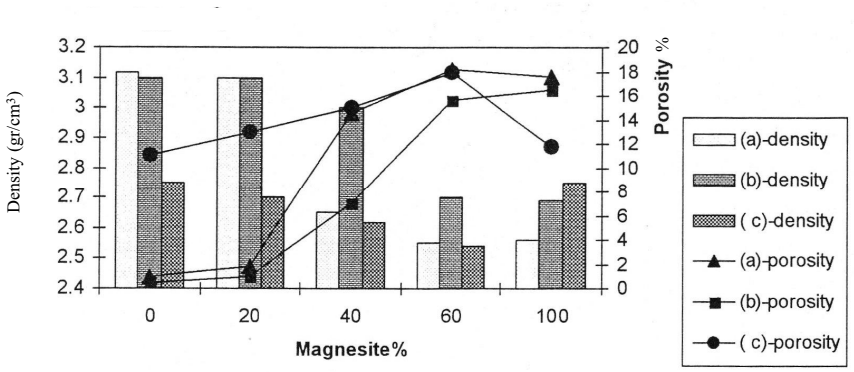

Fig. 7. Density and porosity of different samples vs. the amount of magnesite. (a) calcined clinker of magnesite and dolomite (fired at 1500°C), (b) calcined clinker of magnesite and dolomite (fired at 1600°C), and (c) sintered doloma and magnesia (fired at 1600°C).

by looking at the microstructure of the samples given in Figures 4 and 5 in which as was stated previously the doloma grains are surrounded by magnesia grains resulting in increased resistance to hydration.

Figure 7 shows SEM micrograph of a mag-dol sample with 20wt% magnesite and Figure 8 illustrates a dolomite sample with no excess magnesite. As can be seen from Fig. 7 the microstructure consists of magnesia matrix surrounding calcia grains. However, in dolomite sample (Fig. 8) the dominant phase is calcia, which is more prone to hydration.

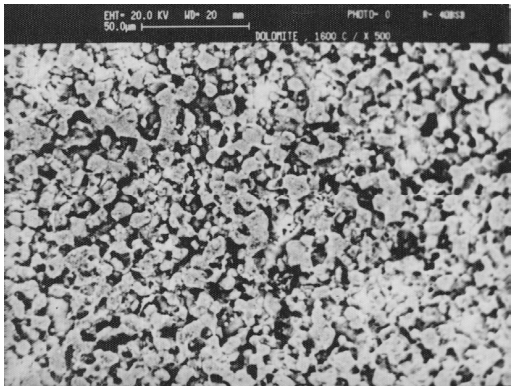

Fig. 10. SEM micrograph of a mag-dol sample with 20wt% magnesite.

4. CONCLUSIONS

From the results of this study it can concluded that:

1. By increasing the percentage of magnesia in doloma the hydration resistance of doloma refractories increases remarkably.
2. The two stag calcinations process can be applied successfully for production of mag-dol refractories.
3. The main reason for the increase in hydration resistance in mag-dol refractories is the change in microstructure from a matrix in which CaO is predominant phase to a matrix in which MgO is the major phase.
4. The CaO phase in mag-dol refractories is surrounded by MgO phase which also enhances hydration resistance of this type of refractories compare to doloma refractories.

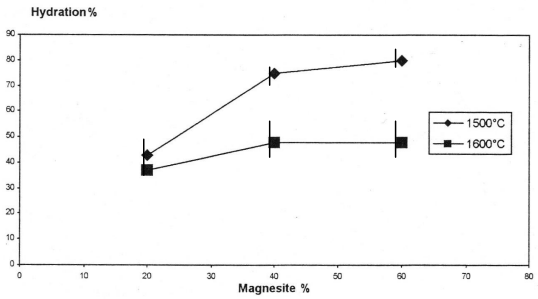

Fig. 8. Resistance to hydration vs. the amount of magnesite.

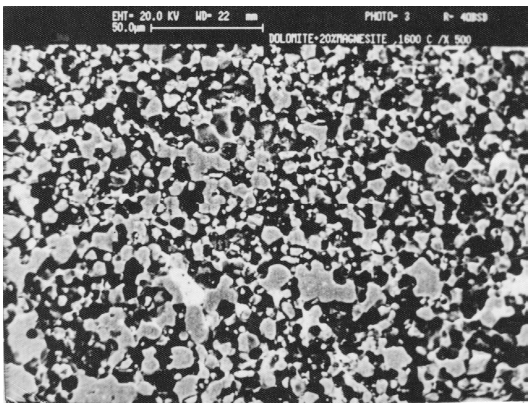

Fig. 9. SEM micrograph of a mag-dol sample with 20wt% magnesite.

REFERNCES

1. Routschka, G., "Refractory Materials" , Translated to persian by B. Mirhadi, IUST publication, 1999.
2. Degaviva, T., Cichida, S. and Otatani, T. " Development of CaO-MgO Refractories and their Effects on Refining Mechanism of Extremely Clean steel" , Proceedings of 2nd International Conference on Refractory, Tokyo , 1987, 842-856.
3. Fleisher, J. and Prange, R. "Application of Dolomite and Magnesite Refractories for Converters and Stel making Process" , Interceram Special Issue , 1981, 11-14.
4. Spencer, F. " Basic Refractory Raw Materials"

, Meeting of the Refractory Materials Section, London, 9-10 November, 1971, 23-25.
5. Delmann, W. and Zednicek, W. "Experimental Results of Ladle with Magnesite Products and Bricks Made of Magdol-co- Clinker", Interceram Special Issue, 1998, 365-379.
6. Maoqiang, Li. and Messing, G. L. "Study of Thermal Decomposition of Alkaline Earth Carbonates and Surface area of Product Oxides", Proceedings of International Symposium on Refractories Raw Materials and High Performance Refractory Products, 1988 244-254.
7. Lynch, A. J. "Mineral Crushing and Grinding Circuits" , Vol. 1, 4th ed., 1989.
8. Paul, T. Cash, "Hydration Rate for Dead Burned Dolomite" , Ceramic Bulletin, Vol. 61, No. 7 ,1982.