

IMPROVING HYDRATION RESISTANCE OF MAGNESIA-DOLOMA REFRACTORIES BY IRON OXIDE ADDITION

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Abstract: There have been lots of studies to control the poor hydration resistance of dolomite refractories; one of the most effective solutions has been the addition of magnesia to doloma. Using a co-clinker of magnesia-doloma as a starting material would provide more homogeneity in the properties of the product and has been published recently. On the other hand, addition of iron oxide to doloma has been found to increase the hydration resistance. In this paper, the effect of iron oxide addition on hydration phase analysis and microstructure of two different magnesia- doloma samples, one with CaO content of 25 wt% and the other one with that of 35 wt% has been investigated. Ten samples were prepared by pressing followed by firing at 1750 °C for 3hrs. Results showed that the hydration resistance of the samples improved by decreasing the CaO content, because CaO is much more prone to hydration comparing to MgO. Besides, 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.

Keywords: Magnesia-doloma, Iron oxide, CaO content, Hydration resistance.

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 $\text{CaMg}(\text{CO}_3)_2$ 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 magnesia-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; Ayg ül Yeprem has studied the effect of iron oxide addition to doloma and mentioned

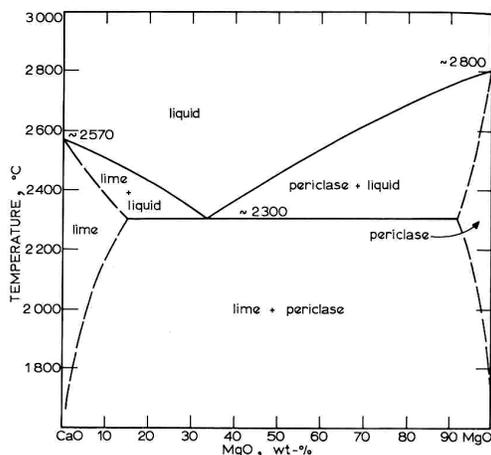


Fig. 1. The MgO- CaO system [3].

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_2O_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 Table1.

Table1. Chemical analyses of magnesia and doloma

(wt%)	Magnesia	Doloma
MgO	97.45	40.12
CaO	0.65	58.1
Fe₂O₃	0.3	0.35
Al₂O₃	0.15	0.25
SiO₂	1.05	0.6

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 μ m) 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].

Table2. Composition of the samples

Calcium Oxide (wt%) Iron Oxide (wt%)	25	35
0	C25	C35
2	C25-2	C35-2
4	C25-4	C35-4
6	C25-6	C35-6

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 C₃S, C₂F and C₄AF 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 doloma leads to formation of compounds which

have low melting points such as C₄AF (C = CaO, A=Al₂O₃, F=Fe₂O₃) and C₂F[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 C₄AF 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 C₂F (2CaO.Fe₂O₃) and in samples with that of 35 wt% (Fig. 3), the trace of C₄AF (4CaO.Al₂O₃.Fe₂O₃) 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 C₂F to decrease. FeO is completely soluble in MgO (the solid solution is called magnesio-wustite), but it has not been proved that Fe₂O₃ forms solid solution with MgO below 1000°C. In the normal atmosphere, which was the environment of the samples in this research, solubility of Fe₂O₃ in MgO has been found to be 10% at 1200 °C and 35% at 1400 °C [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 C₄AF which can be due to very low amount of alumina impurity that makes the amount of C₄AF 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

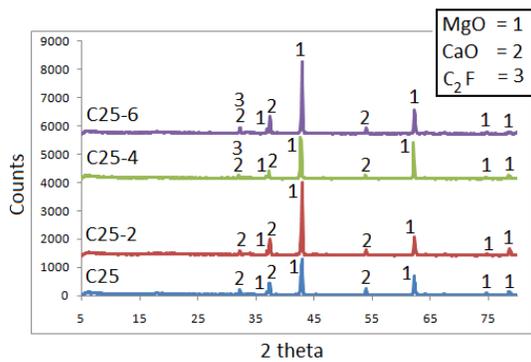


Fig. 2. XRD patterns of magnesia-doloma samples with CaO content of 25 wt% fired at 1750°C for 3 hrs.

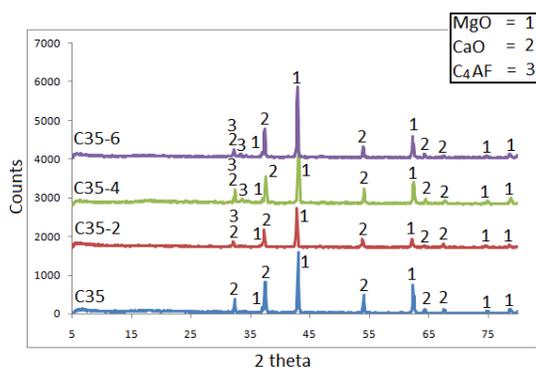


Fig. 3. XRD patterns of magnesia-doloma samples with CaO content of 35 wt% fired at 1750 °C for 3 hrs.

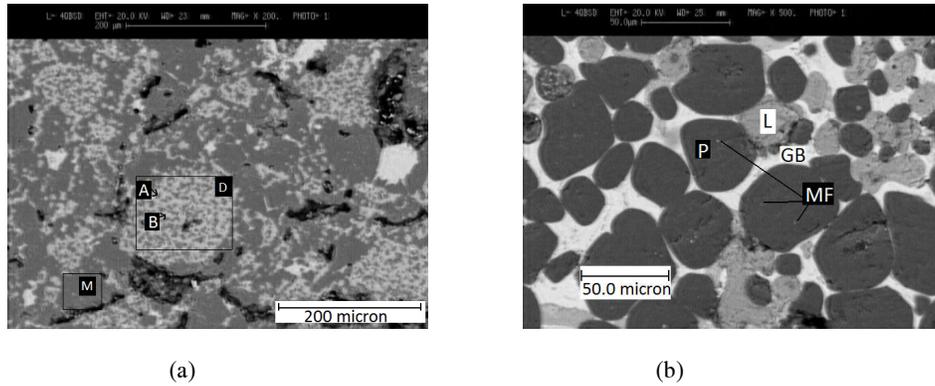


Fig. 4. SEM images of the samples: (a) C25 and (b) C25-6, fired at 1750°C for 3 hrs, with magnifications of 200 and 500, respectively.

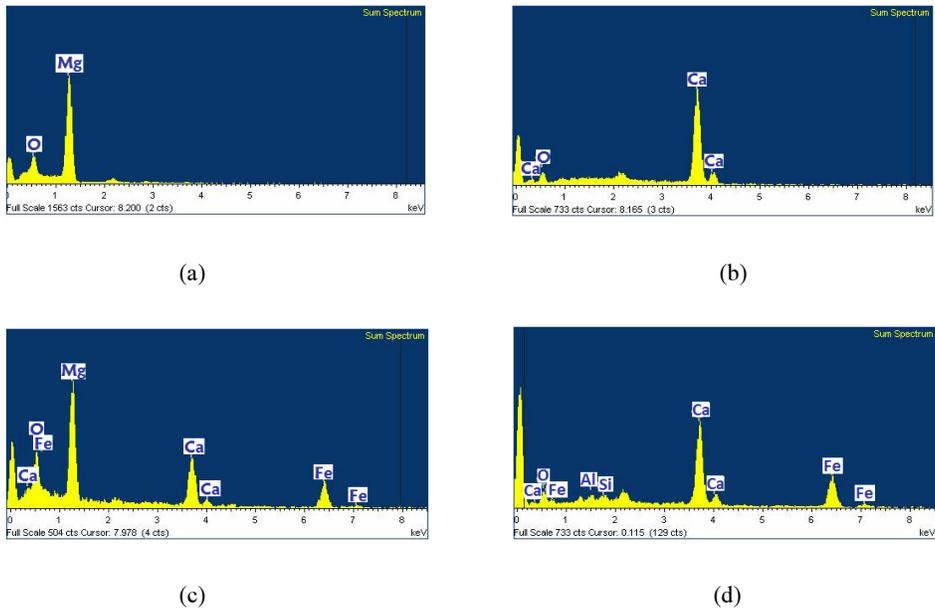


Fig. 5. EDS analyses of Fig. 4-b: (a) region P (periclase grain), (b) region L (Lime grain), (c) region MF (Magnesioferrite precipitates) (d) region GB (grain boundaries)

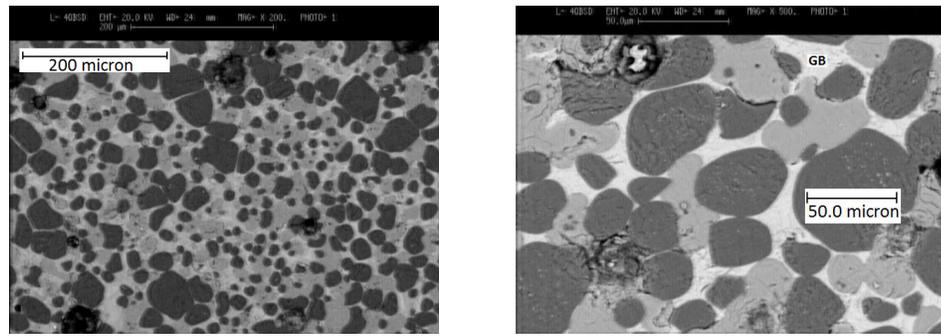
Fig.4 and those of samples with CaO content of 35 wt% can be seen in Fig.6. EDS analyses of different components of Fig. 4-b are presented in Fig.5 and that of Fig.6-b is shown in Fig. 7.

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 weight such as C_2F , 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 magnesio ferrite, 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



(a)

(b)

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.

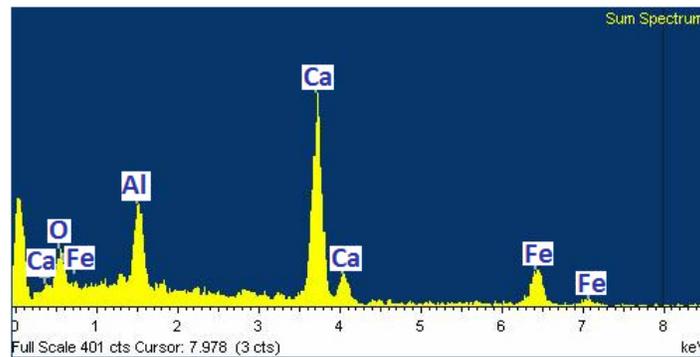


Fig. 7. EDS analyses of region GB (grain boundaries) in Fig. 6-b.

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 aluminoferrite (C_4AF) 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

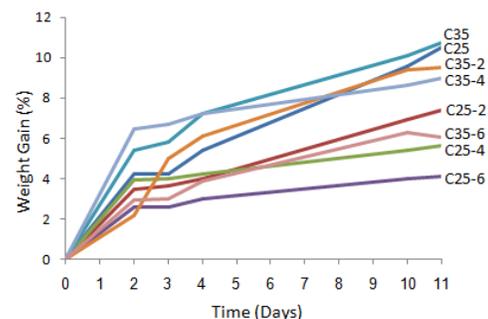


Fig. 8. Relationship between weight gain (%) from hydration and hydration duration (days) (conditions: 70% humidity and 110 °C)

that the hydration resistance of Magnesita-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_2F in samples with CaO content of 25 wt% and C_4AF in samples with that of 35 wt%) are formed in the grain boundaries. Dicalcium ferrite (C_2F) and calcium alumino ferrite (C_4AF) with melting temperatures lower than 1450 °C 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_2F and C_4AF 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_2F is less prone to hydration rather than C_4AF [19] and regarding less amount of CaO content, C25-n samples are more hydration resistant.

4. CONCLUSIONS

- Hydration resistance of Magnesita-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_2F , but by increasing the amount of CaO, in samples with CaO content of 35 wt%, C_4AF was formed. C_2F and C_4AF 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

1. Yeprem, H., "Effect of iron oxide addition on the hydration resistance and bulk density of doloma", Journal of the European Ceramic Society, 2007, 27, 1651-1655.
2. Chester, J. H., "Refractories, Production and Properties", The Metals Society, 1983.
3. Roth, R., Negas, T. and Cook, L., "Phase Diagrams for Ceramists", The American Ceramic Society, 1981.
4. Nandi, D. N., "Handbook on Refractories, Tata McGraw-Hill Publishing Company Limited", New Delhi, 1987.
5. Chen, M., Jin, A., Wang, N. and Yu, J., "Synthesis of Hydration-resistant CaO Refractory by Addition of MgO", Dev. Chem. Eng. Mineral Process., 2006, 14(3/4), pp. 409-416.
6. Hadian, A. M., "Development of Dolomite Based Refractories", Proceedings of Tehran International Conference on Refractoris, Iran, 2004, 589-593.
7. Hadian, A. M. and Nazari, B., "Influence of Magnesita Addition on Hydration of Iranian Dolomite", IJMSE, 2010, Vol 7, No. 3.
8. Routschka, G., "Pocket Manual Refractory Materials: Basics", Structures, Properties, Vulkan-Verl. Publication, 2004.
9. Molinari, T. and Neuböck, R., "Innovative Refractory Solutions for the Stainless Steel Industry", RHI Bulletin, 2005.

10. Othman, A. G. M., Abou El-Maaty, M. A. and Serry, M. A., "Hydration-resistant lime refractories from Egyptian limestone and ilmenite raw materials", *Ceramics International*, 2001, 27, 801–807.
11. Ghosh, A., Bhattacharya, T. K., Maiti, S., Mukherjee, B., Tripathi, H. S. and Das, S. K., "Densification and properties of lime with V_2O_5 additions", *Ceramics International*, 2004, 30, 2117–2120.
12. Chen, M., Lu, C. and Yu, J., "Improvement in performance of MgO–CaO refractories by addition of nano-sized ZrO_2 ", *Journal of the European Ceramic Society*, 2007, 27, 4633–4638.
13. KashaniNia, F., Sarpoolaky, H., NaghiZadeh, R., Bagheri, A. R. and ZamaniPour, M., "The Effect of composition on Properties and Microstructure of Magnesia-Doloma Refractories", *Proceedings of 7th Iranian Ceramic Congress, Iran, Shiraz, 2009*.
14. KashaniNia, F., Sarpoolaky, H., NaghiZadeh, R., Bagheri, A. R. and ZamaniPour, M., "The Effect of Iron Oxide Addition on Properties and Microstructure of Magnesia-Doloma Refractories", *Proceedings of 15th International Metallurgy & Materials Congress, Turkey, Istanbul, 2010*.
15. Khlebnikova, I. Yu., Zhukovskaya, A. E. and Selivanova, A. N., "Methods for Determining Hydration Resistance of Refractories, Refractories and industrial Ceramics", 2007, Vol. 48, No. 2.
16. Searle, A. B. and Grimshaw, R. W., "The Chemistry and Physics of Clays and other Ceramic Materials", Ernest Benn Limited, London, 1960.
17. Suvorov, S. A., Nazmiev, M. I., Polovinkina, R. S. and Maryasev, I. G., "Water-Resistant Lime-Magnesian Clinker", *Refractories and industrial Ceramics*, 2006, Vol. 47, No. 5.
18. Chen, M., Wang, N., Yu, J. and Yamaguchi, A., "Effect of porosity on carbonation and hydration resistance of CaO materials", *Journal of the European Ceramic Society*, 2007, 27, 1953–1959.
19. Muzhen, S., Yimin, C., Liping, S., Jun' an, D. and Xiaoxin, L., "The Application of Thermal Analysis and Conduction Calorimetry on the Formation and Hydration of Calcium Aluminoferrite", *Journal of Thermal Analysis*, 1992, Vol. 38, 2147 -2155