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Effect of Nano-Sized Fe_2O_3 on Microstructure and Hydration Resistance of MgO-CaO Refractories

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Abstract

In this work the effect of Nano-sized Fe_2O_3 on microstructure and hydration resistance of MgO-CaO refractories with 35 wt% CaO was investigated. MgO-CaO refractories with 35 wt% CaO content was prepared by using dolomite and magnesite calcined as starting materials and Nano-sized Fe_2O_3 (2,4, 6 and 8 wt%) as an additive. Samples were pressed into briquettes at a pressure of 90 MPa. Briquettes after drying at 110 ^oC for 24 hours were sintered at 1650 ^oC for 3 hours. Hydration resistance was measured at 25 ^oC in 95% relative humidity through the weight gain after 72 hours. According to the results, it is observed that when the amount of Nano-sized Fe_2O_3 added increased to 8 wt% the bulk density increased to 3.14 gr/cm^3 and apparent porosity decreased to 8.20%. For the sample without addition, the mass gain after 72 hours was 1.76, which sharply decreased to 1.27 with increasing the amount of Nano-sized Fe_2O_3. With the addition of Nano-sized Fe_2O_3, bulk density and hydration resistance of the samples increased while apparent porosity decreased. Densification of MgO-CaO refractories was promoted to increase of Nano-sized Fe_2O_3 content. Nano-sized Fe_2O_3 addition led to formation of low melting phases such as C_2F ($2CaO.Fe_2O_3$), CF ($CaO.Fe_2O_3$) and C_3A ($3CaO.Al_2O_3$). The formation of this low melting point phases surrounding the CaO and MgO grain and grain boundaries and promoted densification of MgO-CaO refractories. The nature of Nano-sized Fe_2O_3 promoting densification is increasing the liquid phase sintering.

Keywords: *Hydration resistance, Densification, Refractory, Nano-sized Fe_2O_3.*

1. INTRODUCTION

MgO-CaO refractories are considered as one type of chrome-free refractories that are suitable for substituting the MgO-Cr_2O_3 refractories [1]. MgO-CaO refractories have been widely used in cement rotary kilns and steel ladles for their high melting point, excellent thermal shock resistance, and good resistance to basic slags and clinker [1]. Furthermore, MgO-CaO refractories are beneficial for removing inclusions from molten steel, thus they have been considered to be one of the effective refractory types for processing clean steel products [2]. In recent years, with increasing the demands of molten steel purity, the awareness of environmental protection and resource shortage have grown and MgO-CaO materials have been become one of the attractive steel making refractories because of their low cost and high ore sources [3]. However the application of MgO-CaO refractories has been limited by their poor hydration resistance [2-6]. MgO-CaO materials are susceptible to hydration because the free lime in them can react easily with water, volume expansion of the resultant can cause severe damage to materials [7]. The hydration resistance of free lime materials can be improved by treating them in a CO_2 atmosphere which leads to the formation of the dense layer on the surface of CaO [8]. Further improvement may be made by adding metal oxides such as CuO, Fe_2O_3, SiO_2 and V_2O_5 [9], to react with lime to form a low-point phase or by adding ZrO_2 [4] to form high- melting stable compounds with CaO. However, the liquids formed may significantly reduce their refractoriness and slag resistance of refractories [4, 8, and 9]. The hydration resistance of MgO-CaO refractories can also be improved by surface carbonation and phosphate coating [8]. It has been reported that the addition of Fe_2O_3 can appreciably improve the properties of the MgO-CaO refractories, but it causes the reduction in refractoriness of MgO-CaO system [6]. Therefore, it is important to decrease the amount of Fe_2O_3 for the purpose to improve the properties of the MgO-CaO refractories. Nanotechnology has been introduced to refractories in recent years. It has been reported that the performance of the refractories appreciably improved for the well dispersion of Nano-sized particles in the microstructure and reaction activity [4]. The purpose of this work is to study the effect of Nano-sized Fe_2O_3 addition on hydration resistance of MgO-CaO refractories so as to confirm the possibility to improve the hydration resistance with less Fe_2O_3 addition by Nanotechnology.

2. EXPERIMENTAL PROCEDURE

The starting materials used were dolomite of Zefreh region and magnesite of Birjand region in Iran with (CaO/MgO=7/15), which chemical compositions were as shown in Table 1. Initially dolomite and magnesite were crushed in 0.2-1 mm. Dolomite and magnesite were calcined at 1000 ^{o}C for 3 hours. Batches were prepared by mixing the powdered doloma and magnesia with 0, 2, 4, 6 and 8 wt%.

Nano-sized Fe_2O_3 with 68 nm size (Characterizes of Nano-Fe_2O_3 is shown in table 2) in a pot mill for 2 hours. Subsequently, the batch was mixed with 5 wt%. Resin phenolic as binder and pressed at 90 MPa. The pellets were dried at 110 ^{o}C for 24 hours. Finally, the samples were fired at a temperature of 1650 ^{o}C in an electrically operated program controlled muffle furnace with 3 ^{o}C soaking at peak temperature. The sintered samples were characterized by bulk density, apparent porosity and hydration resistance measurement, microstructure, and phase composition analysis. Bulk density and apparent porosity were measured by Archimedes principle using kerosene as an immersion medium under vacuum.

The hydration resistance of the samples was measured on the size fraction of 5±10 BS mesh. The atmosphere of the chamber was maintained at 25^{o}C and 95% relative humidity for 72 hours. The percentage of weight gain before and after hydration was the measure of hydration resistance (Equation 1). The microstructure was analyzed by scanning electron microscopy (SEM 20 kv).

***Table1**. Chemical analysis of magnesia and doloma*

Oxide	magnesia (wt%)	doloma (wt%)
MgO	93.2	37.2
CaO	2.7	57.7
TiO_2	0.2	0.2
MnO	0.45	0.18
Fe_2O_3	0.6	0.6
Al_2O_3	1.6	2.8
SiO_2	0.8	0.7
L.O.I	0.3	0.44

Equation: 1

Hydration Resistance (%) = $\frac{M2-M1}{M1} * 100$

M_2= weight gain after hydration test.

$M_{1=}$ weight gain before hydration test.

***Table:* 2**. *Characterizes of Nano-Fe_2O_3*

Average particle size (nm)	Specific surface area (m^2/g)	Density (gr/cm^3)	Impurity (%)
68	159±18	0.15	99.9>

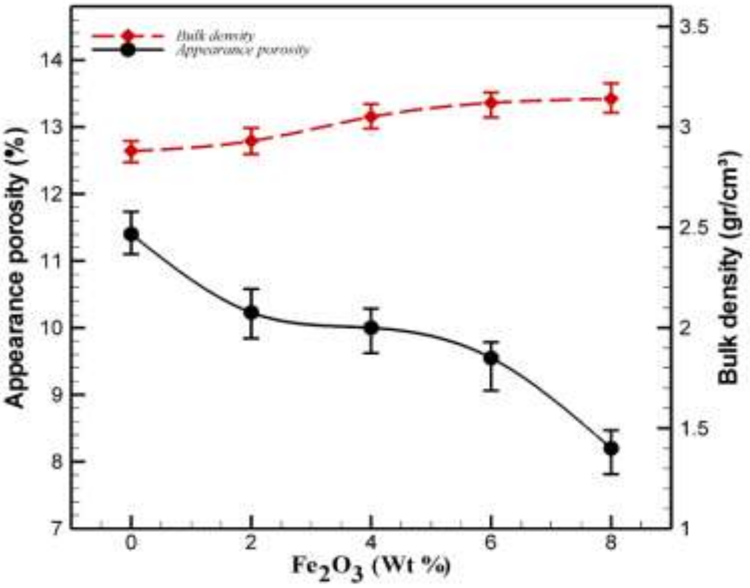

Figure1. *Effect of Nano-sized Fe_2O_3 on densification of MgO-CaO refractories.*

Phase composition was determined by X-ray powder diffraction (XRD, Cu target, 40 kv).

3. RESULTS AND DISCUSSION

3.1. Densification:

Figure. 1 shows the effect of Nano-sized Fe_2O_3 addition on the bulk density and apparent porosity of the samples sintered at 1650 ^oC for 3 hours. It is observed that the bulk density increased gradually and the apparent porosity decreased with the addition of Nano-sized Fe_2O_3. When the amount of Nano-sized Fe_2O_3 increased to 8 wt% the bulk density increased to 3.14 gr/cm^3 and apparent porosity decreased to 8.20%. This result indicates that adding Nano-sized Fe_2O_3 promoted the sintering and densification of MgO-CaO refractory. The additive Nano-sized Fe_2O_3 helps the sintering of CaO-MgO materials from the formation of liquid phases and facilitates the mass transfer through it.

3.2. Phase Composition and Microstructure:

Figures. 2-4 show the XRD patterns of samples without addition, with 2% and 8% Nano-sized Fe_2O_3. In the sample without addition, MgO and CaO were the main crystalline phases. Simultaneously, in the sample with 2% and 8% Nano-sized Fe_2O_3, MgO, CaO, C_2F ($2CaO.Fe_2O_3$), $Ca_3Al_2O_6$ ($3CaO.Al_2O_3$) and CAF were the main crystalline phases. CaO reacted with Nano-sized Fe_2O_3 and formed, C_2F

($2CaO.Fe_2O_3$), $Ca_3Al_2O_6$ ($3CaO.Al_2O_3$), and CAF with low melting point which are the source of glassy phase in the microstructure. The presence of Nano-sized Fe_2O_3 in MgO-CaO forms liquid above 1400 °C at grain boundary and promotes sintering [6]. Increasing additive content helps to generate more liquid phases between grains. Therefore, wet ability of grain increases and results in grain growth through solution and precipitation. The amount of glassy phases increases with increasing the additive concentration.

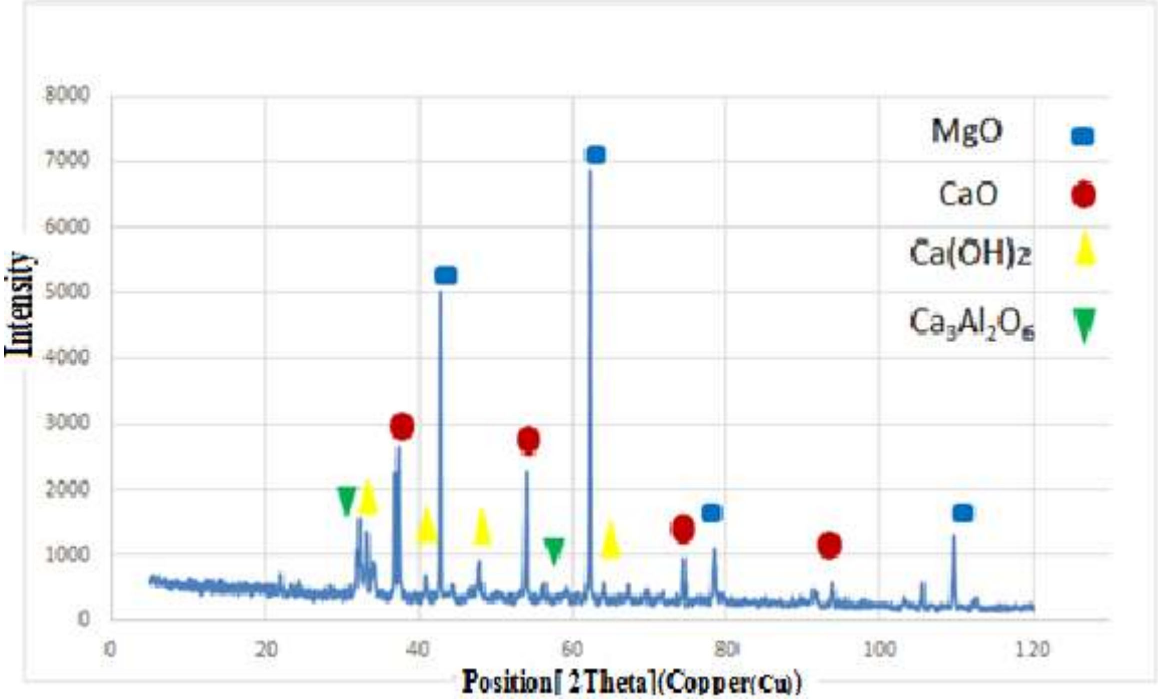

Figure2. *XRD pattern of MgO-CaO refractories without addition.*

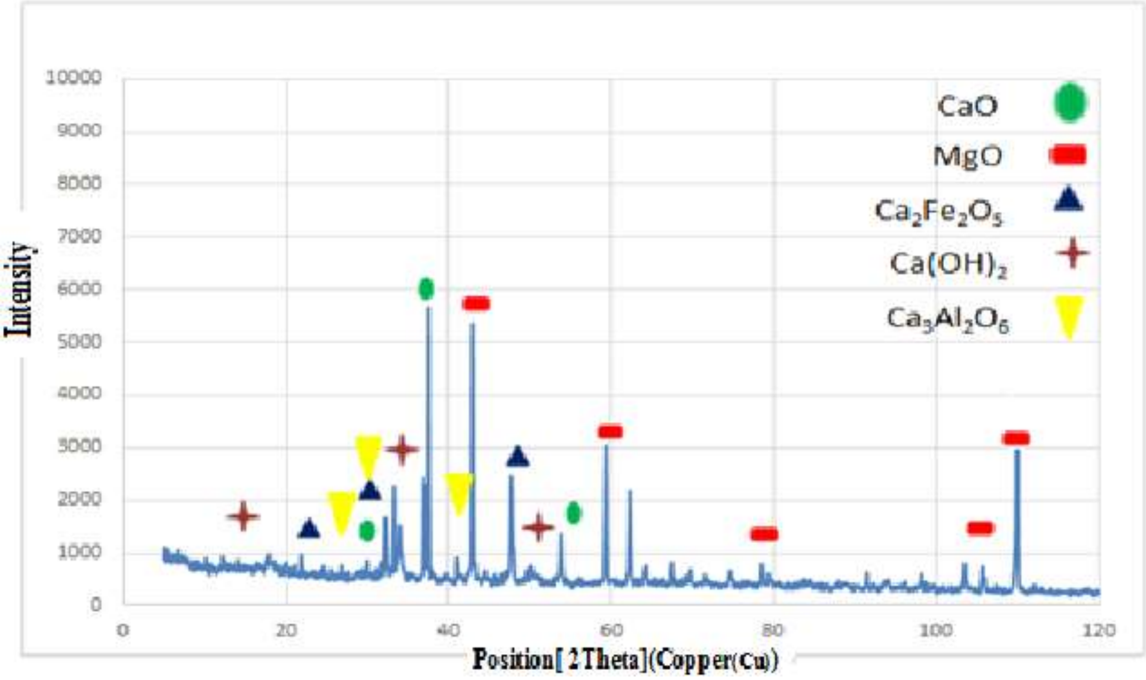

Figure3. *XRD pattern of MgO-CaO refractories with 2% Nano-sized* Fe_2O_3 *addition.*

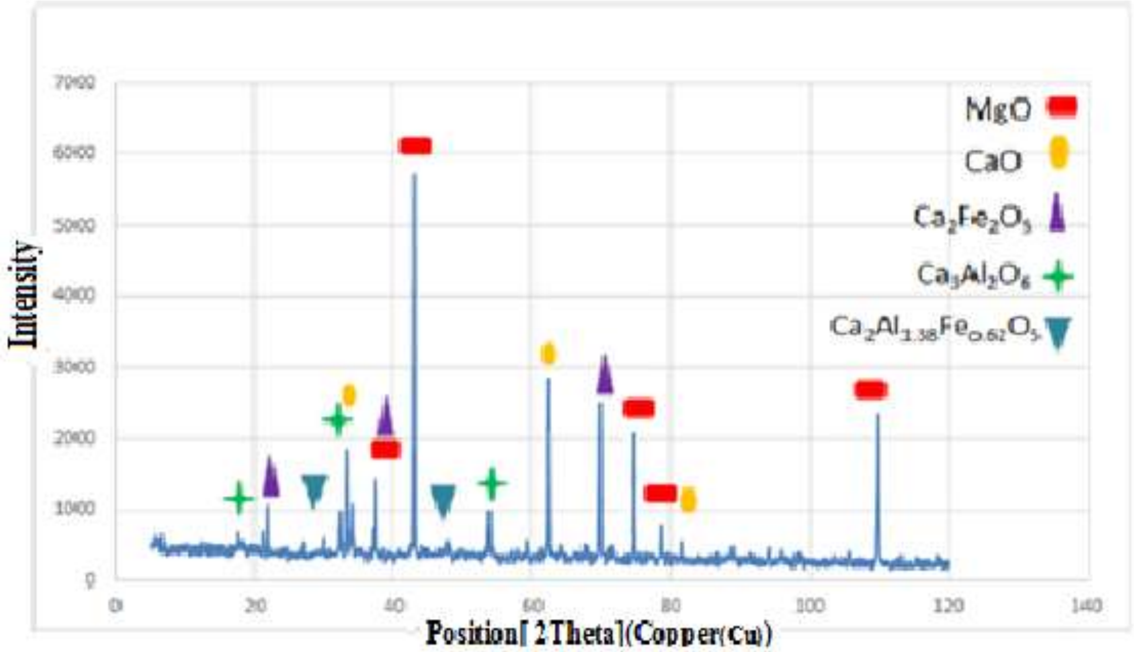

Figure4. *XRD pattern of MgO-CaO refractories with 8% Nano-sized Fe_2O_3 addition.*

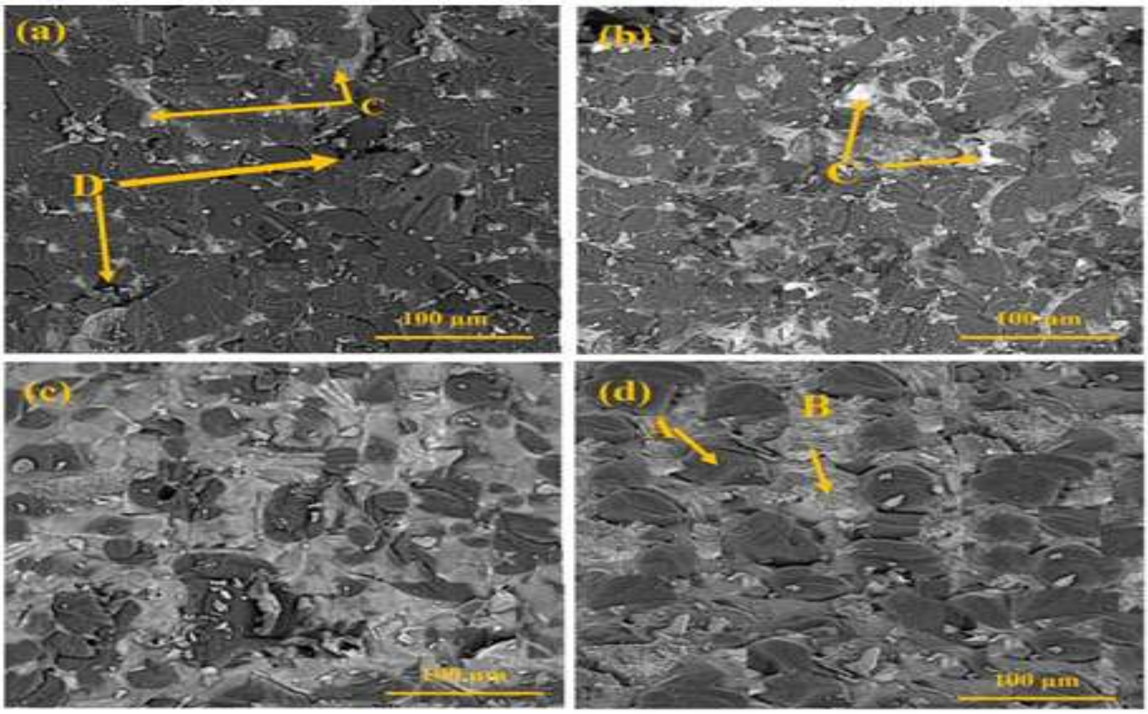

Figure5. *SEM images of fractured surfaces of the samples with various Nano-sized Fe_2O_3 addition: (a) without Fe_2O_3, (b) 2% Fe_2O_3, (c) 4% Fe_2O_3 and (d) 8 wt%.*

$$Fe_2O_3 \xrightarrow{3CaO} 2\,Fe^{o}_{Ca} + V''_{Ca} + 3O_O \qquad \text{Equation: 2}$$

$$Fe_2O_3 \xrightarrow{3MgO} 2\,Fe^{o}_{Mg} + V''_{Mg} + 3O_O \qquad \text{Equation: 3}$$

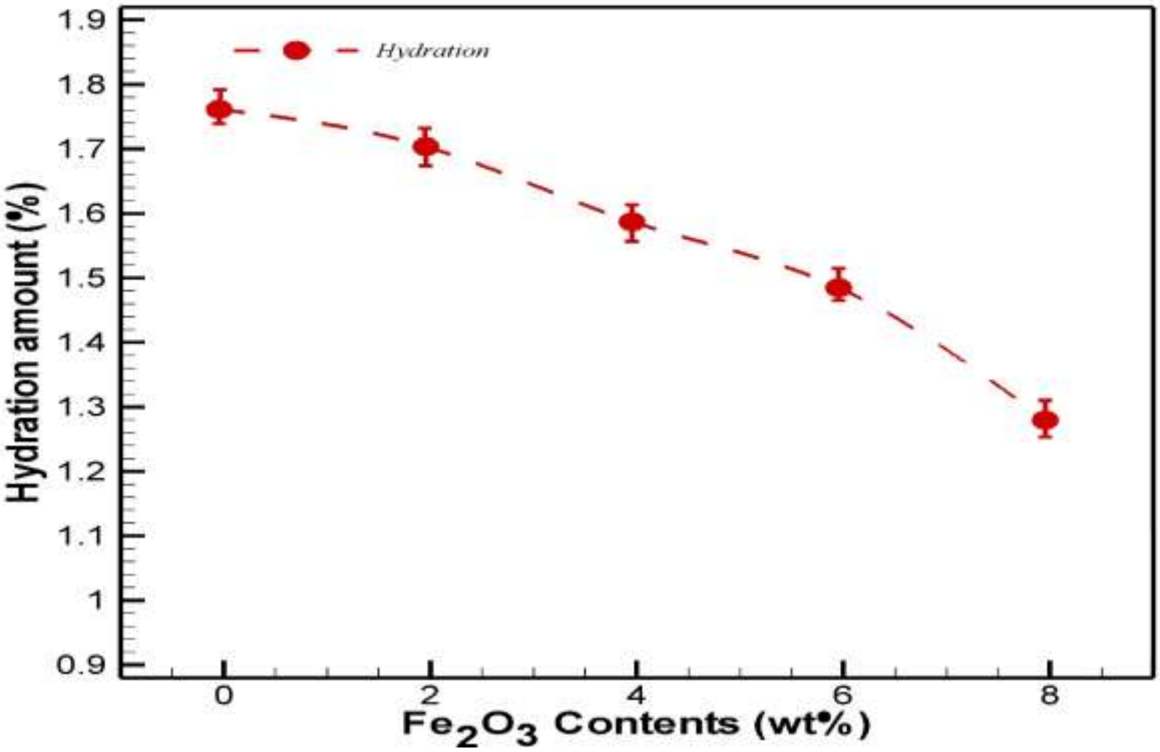

Figure6. *Effect of Nano-sized Fe_2O_3 addition on improvement of slaking resistance of samples.*

Figure5 shows the typical microstructure of the fractured surfaces of samples with various amounts of Nano-sized Fe_2O_3. In the sample without addition, due to impurities in the starting materials, some low melting point phases were observed at grain boundaries and triple point besides MgO (dark gray) and CaO (light gray) grain (Fig. 5(a)). EDX analyses (Table 3) do not show the phases but the elements. So XRD and EDX results confirm the presence of Some low melting point phase formed by reaction of CaO (in doloma) with impurities of Al_2O_3, Fe_2O_3, SiO_2 to generate calcium aluminate, calcium silicate, calcium ferrite, calcium ferrite aluminate, etc. MgO (dark gray), CaO (light gray), and low melting phases (white) were observed in the microstructure (Fig. 5(b-d)). The grain size for the sample without additive is 4.5 µm and pores are present in the intergranular and intragranular position. With increasing additive to 8wt% the grain size has increased to 15 µm. However, the pores area is widely distributed throughout the matrix. The microstructure of sintered MgO-CaO with 8wt% shows that the grain growth takes place substantially in the presence of additive. The pores are present only in the intergranular position. Also, glassy phases uniformly distributed between CaO and MgO grain.

3.3. Hydration Resistance

Figure. 6 shows the effect of Nano-sized Fe_2O_3 addition on hydration resistance of MgO-CaO samples. It can be observed that the mass gain of MgO-CaO refractories decreased appreciably with Nano-sized Fe_2O_3 addition. For sample without addition, the mass gain after 72 hours was 1.76, which sharply decreased with increasing the amount of Nano-sized Fe_2O_3. Increase in the amount of additive reduces the weight gain due to more grain growth and lower grain boundary and porosity. The degree of hydration is related to the chemioabsorption of water on the grain boundary surface. Hence, the grain surface area reduces along with grain growth, which is ultimately responsible for improving hydration resistance.

It is known that the hydration resistance of materials that contains CaO, both rich-CaO and rich-MgO materials, is strongly dependent on the content of free CaO in materials and its microstructure [4].

***Table: 3.** EDX analyses of 1) A, 2) B, and 3) C point.*

Element	Point A (Wt%)	Point B (Wt%)	Point C (Wt%)
O	22.42	38.20	69.35
Mg	-	61.65	1.56
Si	-	-	2.96
Ca	57.19	-	15.15
Fe	19.8	-	1.7
Al	-	-	9.1
Au	0.59	0.24	0.18

When Nano-sized Fe_2O_3 was added, the promotion of the hydration resistance of the refractories is considered due to the following reasons:

First, the promotion of densification by adding of Nano-sized Fe_2O_3 decreased the porosity of the refractories and thus its reaction specificity area decreased while the refractories were exposed to a humid environment.

Second, with increasing the addition of Nano-sized Fe_2O_3, the content of free CaO in refractories decreased further and thus the slaking resistance of refractories improved**.**

Third, it is well-known that the slaking reaction always begins from the sites with crystal defect. Thus, the grain boundaries, especially the triple points, are the poor slaking resistance sites**.** When Nano-sized Fe_2O_3 was added, some low melting point phases such as C_2F, CAF, and $Ca_3Al_2O_6$ formed predominately located at grain boundaries and the triple point of CaO and MgO grains thus promotion on the hydration resistance of the refractories. During sintering (at 1650 ℃) and cooling process, Nano-sized Fe_2O_3 enters MgO and CaO crystal and causes MgO and CaO vacancy (Equation 2 and 3).

Though the use of Nano-sized Fe_2O_3 increases cation vacancy and enhances diffusion, so improves the link between particles and decreases amount of porosity in samples. Decreasing this area improve the hydration resistance of samples.

4. CONCLUSION

The present work studies the effect of Nano-sized Fe_2O_3 addition on microstructure and hydration resistance of MgO-CaO refractories with 35 wt% CaO. It could be concluded as follows:

- The densification of MgO-CaO refractories improved by the addition of Nano-sized Fe_2O_3 at 1650 ^{o}C due to the formation of some low melting phases such as C_2F, CAF and $Ca_3Al_2O_6$ and promoted the densification through the liquid phase sintering.
- Sintering in the present of additive causes lower porosity and higher grain size for CaO and MgO grains.
- The hydration resistance of MgO-CaO refractories appreciably improved by the addition of Nano-sized Fe_2O_3 due to its effect on decreasing the content of free CaO in the refractories, promotion of densification as well as modification of microstructure.
- The Nano-sized Fe_2O_3 addition was more effective owing to its higher activity.

Addition of Nano-sized Fe_2O_3 improved hydration resistance of MgO-CaO refractories with less Fe_2O_3 addition by taking advantage of nanotechnology.

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