



The Effect of Nano-Additives on the Hydration Resistance of Materials Synthesized From the MgO-CaO System

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ABSTRACT

In this study, the effect of variety of Nano- additives doping on the hydration resistance of the MgO-CaO system was investigated. Samples were prepared from calcined dolomite and magnesite. Nano-additives that contained cations with various valences (trivalent and tetraivalent) used as a dopant. The bulk density, apparent porosity and hydration resistance were studied and evaluated. Also, phase analysis of samples was conducted by using X-ray diffraction (XRD) and the microstructure investigation was done by scanning electron microscopy (SEM). The use of both additives improved the hydration resistance. However, the important role of the higher-valence cation in improvement of the hydration resistance of MgO-CaO materials was revealed. This behavior is believed to be due to the formation of vacancies in solid solution of CaO or MgO with higher-valence cation. Zr^{4+} cation form a solid solution with CaO, which reduce the Ca^{2+} concentration and leads to the improved hydration resistance of the MgO-CaO system. Also trivalent cation led to the formation of some low melting phases such as C_2F ($2CaO.Fe_2O_3$), CF ($CaO.Fe_2O_3$), C_3A ($3CaO.Al_2O_3$). The formation of these low melting point phases surrounded the CaO and MgO grain, grain-boundaries and thus promoted densification and hydration resistance of the MgO-CaO system.

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1. INTRODUCTION

MgO-CaO refractories has long been regarded as an attractive potential refractories for applications in metallurgical industries because of the global abundant sources of dolomite and magnesite in world [1-6], as well as advantages such as of high melting temperature [7, 8], excellent resistance to alkalin slag [7-9], low vapor pressure [10], and thermodynamic stability in the presence of carbon [11]. However, the application of these refractories has always been restricted by the drawback of poor hydration resistance [1-10]. Therefore, studies on improving the hydration resistance of MgO-CaO refractories have been carried out since the 1940s, and especially in recent years with development of clean-steel refining, MgO-CaO refractories shows great advantage in dephosphorization and desulfurization [3-9]. This means that a study on the improvement hydration resistance of MgO-CaO

refractories is imperative [4-8]. Different ways have been propose to produce MgO-CaO refractories. A new approach is using sintered and fused co-clinker of magnesia and doloma as a starting material for the MgO-CaO refractories which would lead to more homogenous products with more desirable properties [11-13]. The hydration resistance of free lime materials can be improved by treating in a CO_2 atmosphere which leads to the formation of the dense layer on the surface of CaO and protect CaO grain from hydration [9]. Further, improvement may be made by adding metal oxides such as Fe_2O_3 [5-7], CuO [8], SiO_2 [5] and V_2O_5 [10], $FeTiO_3$ [3] to react with lime to forms some low melting point phase or by adding ZrO_2 [12] to form high-melting stable compounds with CaO. It has been reported that the addition of Fe_2O_3 can appreciably improve the properties of the MgO-CaO refractories, but it causes a reduction in refractoriness of MgO-CaO system [5-7]. Also, it has been reported that additions of ZrO_2 [5, 11] and TiO_2 [6] can improve the hydration resistance of MgO-CaO refractories by enhancing solid state sintering without sacrificing refractoriness via

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formation of hydration resistance solid solutions, but it led to the price of product appreciably rising. Therefore, it is important to decrease the amount of additives 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 was appreciably improved because of the high specific area and well dispersion of Nano-sized particles in the microstructure and reaction specific area [12]. The purpose of this work is to investigate and compare the effect of variety of Nano-additives on the hydration resistance of MgO–CaO system. Also, the microstructure changes through slaking test were studied with a consideration of crystalline phase's changes.

2. EXPERIMENTAL PROCEDURE

Materials from MgO–CaO system were synthesized using dolomite and magnesite that were calcined at 1000°C for 3hr (Table 1), mixed with Nano-additives (Table 2), pressed into high-density briquettes, and subsequently fired to temperature as high as 1650°C for 3hrs (Table 3). The Samples with 30 mm in diameter and 30 mm in thick were prepared by pressing, using a 150-ton hydraulic press, and then sintered in an electrical kiln for 3hr. The sintering temperature for samples was 1650°C. Also, hydration resistance test was conducted on samples with a grain size of 1-3 mm; this test involved placing the powders of samples in a chamber of constant temperature (25°C) and humidity (95%) for 72 hr. The percentage weight gains before and after hydration were the measures of hydration resistance (Equation (1)).

$$\text{Hydration Resistance (\%)} = \frac{M_2 - M_1}{M_1} * 100 \quad (1)$$

M_2 = weight gain after hydration test.

M_1 = weight gain before hydration test.

Microstructure was investigated by using a scanning electron microscopy (SEM, Cambridge, S360) attached with an EDS unit.

TABLE 1. 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 ₂ O ₃	0.6	0.6
Al ₂ O ₃	1.6	2.8
SiO ₂	0.8	0.7
L.O.I	0.3	0.44

TABLE 2. characterize of nano- additives

	Impurity (%)	Density (g/cm ³)	specific surface area (m ² /g)	Average particle size (nm)
Nano-Fe ₂ O ₃	40±45	159±18	0.15	>99.9
Nano-ZrO ₂	10±15	105±70	0.568	>97

TABLE 3. code of samples

CaO (Wt. %)	Nano-ZrO ₂ (Wt. %)	Nano-Fe ₂ O ₃ (Wt. %)	Code
35	0	0	MC ₃₅
35	0	2	MC ₃₅ F ₂
35	0	4	MC ₃₅ F ₄
35	0	6	MC ₃₅ F ₆
35	0	8	MC ₃₅ F ₈
35	2	0	MC ₃₅ Z ₂
35	4	0	MC ₃₅ Z ₄
35	6	0	MC ₃₅ Z ₆
35	8	0	MC ₃₅ Z ₈

The Phase identification sintered product was done by X-ray diffraction (XRD) study (Jeol-8030, Cu-K α , and 25Kv).

3. PHASE ANALYSIS

Figures 1-5 shows the XRD patterns of samples without, with 2% and 8 wt% nano Fe₂O₃ and nano ZrO₂. For the sample without additives; MgO and CaO were the main crystalline phases and for the sample with 2% and 8 wt. % nano Fe₂O₃; MgO, CaO, C₂F (2CaO.Fe₂O₃) were the main crystalline phases and the exist of Al₂O₃, as an impurity in starting materials, caused the C₃Al₂O₆ (3CaO.2Al₂O₃) phase creat. CaO react with nano Fe₂O₃ and formed C₂F (2CaO.Fe₂O₃) and CAF with low melting point (lower than 1450°C) [4, 6, 13]. The aforementioned phases (C₂F, CAF, and Ca₃Al₂O₆) at the sintering temperature (1650°C) are in the melting state that is the source of glassy phase in the microstructure. The presence of nano Fe₂O₃ in MgO–CaO system forms liquid phase above 1500°C at grain boundary and promotes sintering [2, 7]. Increasing additive content helps to generate more liquid phases among the grains. Therefore, the wet ability of grain increases and led to grain growth through solution and precipitation. The amount of glassy phases increases with increasing the additive concentration.

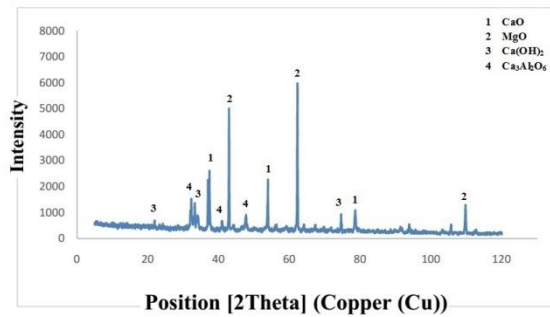


Figure 1. XRD patterns of MgO–CaO refractories without additives

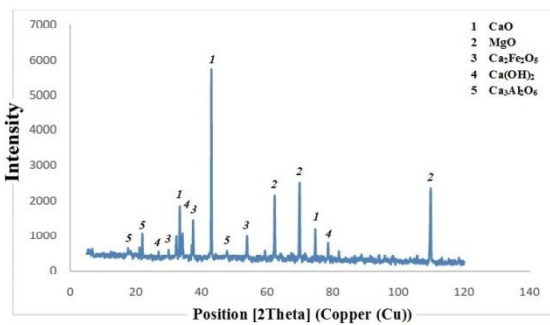


Figure 2. XRD patterns of MgO–CaO refractories with 2 wt.% nano Fe_2O_3

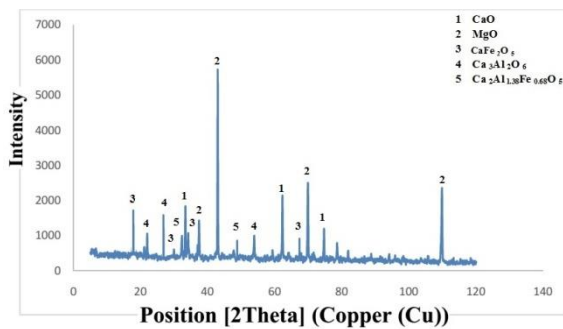


Figure 3. XRD patterns of MgO–CaO refractories with 8 wt.% nano Fe_2O_3 .

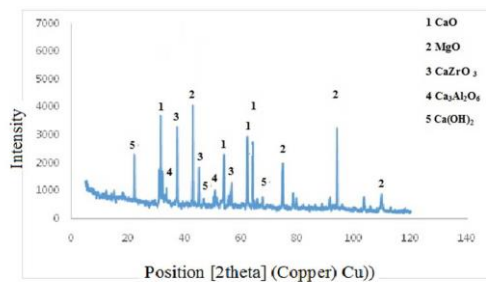


Figure 4. XRD patterns of MgO–CaO refractories with 2 wt.% nano ZrO_2

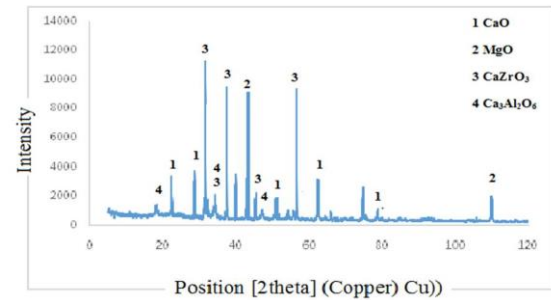


Figure 5. XRD patterns of MgO–CaO refractories with 8 wt.% nano ZrO_2

Also, for the sample with 2 and 8wt% nano ZrO_2 , MgO, CaO and CaZrO_3 were the main crystalline phases, and ZrO_2 phase not exists. It indicates that all added nano ZrO_2 had reacted with CaO to form CaZrO_3 phase (Equation (2)). No change in lattice parameter of MgO phase was measured when nano ZrO_2 was added. It indicates that nano ZrO_2 did not formed solid solution with MgO phase.

The position of the diffraction peaks attributable to the CaO was shifted as a result of adding nano ZrO_2 , suggesting that Zr^{4+} entered in to the CaO lattice, changing the lattice parameter of CaO. However, no apparent change in the positions of MgO diffraction peaks was detected. The CaO lattice constant of the samples was determined (Table 4) by comparing the peak positions (2θ) of the XRD patterns using the least square method. The lattice constant of CaO in the samples without nano ZrO_2 addition was found to be 4.7978 \AA [9, 14], which was in accordance with the lattice constants of pure CaO. Adding nano ZrO_2 increased the lattice constant of CaO. When the amount of nano ZrO_2 added was 8 wt. %, the lattice constant of CaO reached the highest point with $a_{\text{CaO}} = 4.8972 \text{ \AA}$. Generally, the solid solution of metal oxides forms mainly by the replacement of positive ions in the solvent. Radius of positive ions directly affects the binding energy of positive and negative ions in ionic crystals and hence influences the solid solubility. When the difference in the radius of positive ions is less than 15%, it is easy to form a solid solution; when the difference is larger than 30% [3, 7]; it is not possible to form a solid solution. In this study, the difference in radius between Ca^{2+} (0.099 nm) [14, 15] and Zr^{4+} (0.098 nm) [12] was about 1%, but the difference in radius between Mg^{2+} (0.072 nm) [12-14] and Zr^{4+} was nearly 36%. Therefore, nano ZrO_2 is expected to dissolve easily in CaO but not in MgO, which is confirmed by the results of XRD analysis.

TABLE 4. Calculated lattice constant for sintered samples

Sample	Parameters	(111)	(200)	(220)	(311)	(222)	$a(\text{Å})$
MC ₃₅	$2\theta(^{\circ})$	31.31	37.51	53.4	63.54	67.08	4.7978
	$d(\text{Å})$	1.654	2.382	1.678	1.457	1.387	
MC ₃₅ Z ₂	$2\theta(^{\circ})$	31.45	37.45	53.39	64.37	67.45	4.8023
	$d(\text{Å})$	2.674	2.3842	1.674	1.457	1.347	
MC ₃₅ Z ₄	$2\theta(^{\circ})$	31.47	37.39	54.06	64.62	67.47	4.8544
	$d(\text{Å})$	2.745	2.377	1.701	1.444	1.358	
MC ₃₅ Z ₆	$2\theta(^{\circ})$	32.37	37.89	54.09	64.66	67.54	4.8871
	$d(\text{Å})$	2.761	2.387	1.712	1.478	1.384	
MC ₃₅ Z ₈	$2\theta(^{\circ})$	32.88	37.92	54.12	64.87	67.66	4.8972
	$d(\text{Å})$	2.774	2.701	1.725	1.502	1.398	

4. MICROSTRUCTURE ANALYSIS

Figures 6 and 7 shows the typical microstructure of the fractured surfaces of the samples with various amounts of nano Fe₂O₃ and nano ZrO₂. In the sample without additives, there is a lot of pores and porosity (point D in Figure 6) and due to the existence of impurities in the starting materials, some low melting point phases (point C in Figure 6) were observed at the grain boundaries and triple point besides MgO (dark gray) and CaO (light gray) grain (point A and B in Figure 6). EDX analyses (Table 5) do not show the phases but the elements, so XRD and EDX results confirm that the presence of some low melting point phases which were formed by the reaction of CaO (in doloma) with impurities such as Al₂O₃, Fe₂O₃, SiO₂ to generate calcium aluminate, calcium ferrite, calcium ferrite aluminate, etc. MgO (dark gray area), CaO (light gray area), and low melting phases (white area) were observed in the microstructure (Figure 6). The grain size for the sample without additive is 4.5 μm and pores are present in intergranular position. By increasing the additive to 8wt. % the grain size has increased to 15 μm and the amount and the size of the pores is decreased. The microstructure of sintered MgO-CaO with 8wt. % shows that the grain growth take place substantially in the presence of additive. Also, glassy phases uniformly distributed among the CaO and MgO grains. Figure 7 shows the typical microstructure of samples containing various amounts of nano ZrO₂.

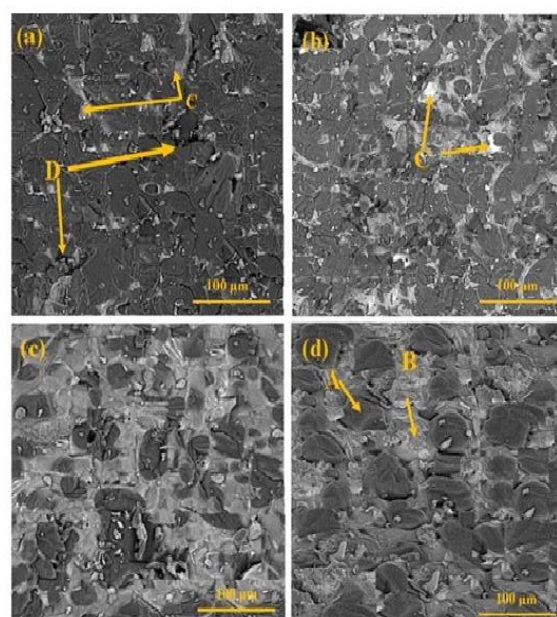


Figure 6. SEM images of fractured surfaces of the samples with various nano Fe₂O₃ addition: (a) without Fe₂O₃, (b) 2% Fe₂O₃, (c) 4% Fe₂O₃ and (d) 8 wt.% Fe₂O₃

The Formation of CaZrO₃ phase inhibit of the grain growth of CaO and MgO. MgO (dark gray) was the continuous phase (Table 6) and surrounding the lime phase (light gray) and caused grains growth of the CaO was hindered by the difficulty for Ca²⁺ to diffuse across the matrix during the sintering process.

It can be seen that the number of pores decreased progressively as the nano ZrO₂ content was increased to 8 wt%. It can be also noted that the pores were present at the boundaries between MgO and CaO grains. The number of pores at grain boundaries will decrease during the sintering process as a result of grain boundary migration, lead to the formation of bigger pores on crystal surface, which may be eliminated as the sintering process progressed.

TABLE 5. EDX analyses of 1) A, 2) B, and 3) C point

Element	Point A (Wt.%)	Point B (Wt.%)	Point C (Wt.%)
O	38.20	22.42	69.35
Mg	61.56	-	1.56
Si	-	-	2.96
Ca	-	57.19	15.15
Fe	-	19.8	1.7
Al	-	-	9.1
Au	0.24	0.59	0.18

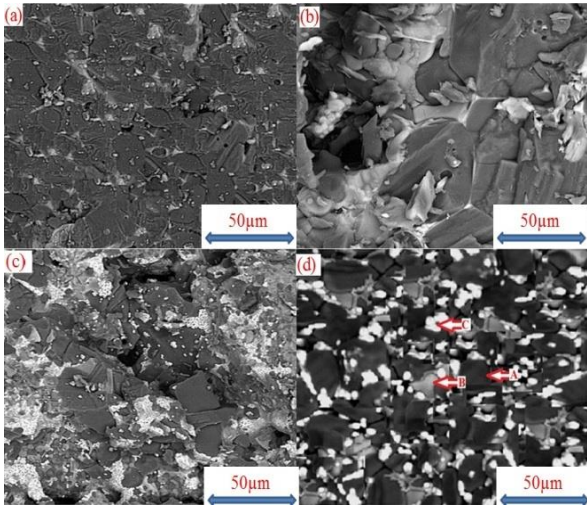


Figure 7. SEM images of fractured surfaces of the samples with a) without, b) 2%, c) 6% and d) 8wt. % nano ZrO_2

TABLE 6. EDX analysis of A) MgO B) CaO and C) $CaZrO_3$

Element	Point C (wt%)	Point B (wt%)	Point A (wt%)
Mg	-	-	57.19
Ca	11.2	55.56	-
O	20.22	44.20	42.2
Zr	58.5	-	-
Au	0.15	0.24	0.59

5. HYDRATION RESISTANCE

Figures 8 and 9 shows the effect of nano Fe_2O_3 and nano ZrO_2 addition on hydration resistance of MgO-CaO samples. Refractories based on magnesium oxide and bearing calcium oxide can undergo hydration in humid atmosphere. In this case the powder grains break, the material is pulverized [3-9]. 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 decrease [4,5,12]. From Figures 8 and 9 it is observed that the mass gain of MgO-CaO refractories decreased appreciably with addition of both Nano- additives. For sample without addition, the mass gain after 72 hours was 1.72%, which was sharply decrease with increasing the amount of Nano-additives. Increasing the amount of additives reduces the weight gain due to more grain growth and lower grain boundary and porosity for the samples contain nano Fe_2O_3 and convert of free CaO phase to $CaZrO_3$ phase and formation solid solution for samples that contain nano ZrO_2 .

The degree of hydration is related to the absorption 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 [1-6, 14, 15]. When nano Fe_2O_3 was added, the promotion of the hydration resistance of the refractories is considered due to the following reason **First**, the promotion of densification by the addition of nano Fe_2O_3 decreased the porosity of the refractories and thus its reaction specific area was decreased while the refractories were exposed to a humid environment. **Second**, by increasing the addition of nano Fe_2O_3 , the content of free CaO in refractories decreased and thus the hydration resistance of refractories was Improved. **Third**, it is well known that the hydration reaction always begins from the sites with crystal defect. Thus, the grain boundaries especially the triple points, are the poor hydration resistance sites.

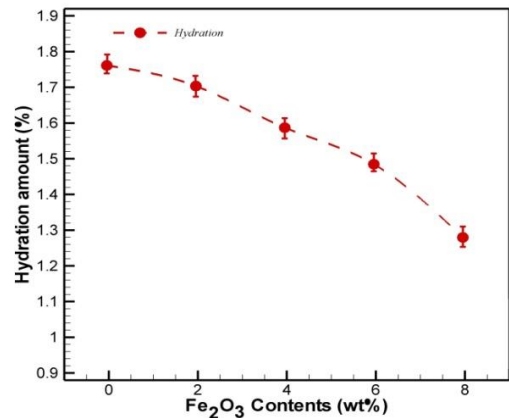


Figure 8. Effect of nano Fe_2O_3 addition on improvement of hydration resistance of samples.

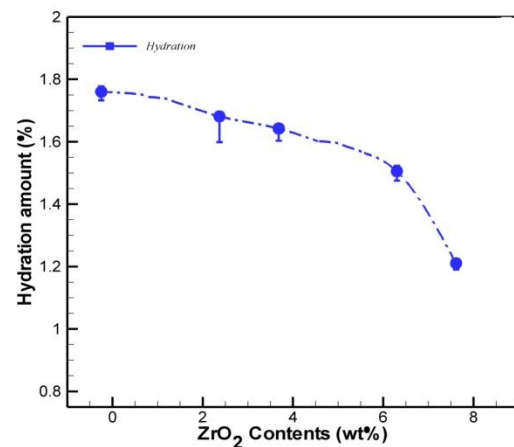
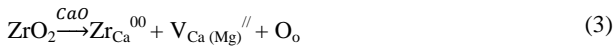


Figure 9. Effect of nano ZrO_2 addition on improvement of hydration resistance of samples.

When nano Fe₂O₃ was added, they formed some low melting point phases such as C₂F, CAF, and Ca₃Al₂O₆ located at grain boundaries and the triple point of CaO and MgO grains, thus preventing the hydration resistance of the refractories. Also, a possible explanation for the effect of nano ZrO₂ on the improvement of the densification and hydration resistance of MgO-CaO refractories involves a solution process in which Zr⁴⁺ cations are added to CaO (MgO) to form a solid solution:



The same amount of two nano- additives; nano ZrO₂ adding has higher than effect on decrease the hydration resistance than nano Fe₂O₃ adding.

4.CONCLUSION

In this work, the effect of variety of Nano-additives doping on the hydration resistance and microstructure of calcined materials in the MgO-CaO system was investigated. The results are:

1. The use of both additives (nano Fe₂O₃ and nano ZrO₂) improved the hydration resistance.
2. The important role of the higher-valence cation (nano ZrO₂) in improvement of the hydration resistance of MgO-CaO materials was due to the formation of vacancies in solid solution of CaO or MgO with higher-valence cations was revealed.
3. The used of nano- Fe₂O₃ led to the formation of some low melting phases such as C₂F (2CaO.Fe₂O₃), CF (CaO.Fe₂O₃), C₃A (3CaO.Al₂O₃). The formation of these low melting point phases surrounded the CaO and MgO grain, grain-boundaries and thus promoted the hydration resistance of MgO-CaO refractories .
4. The hydration resistance of MgO-CaO refractorie was improved due to modification of the microstructure by nano Fe₂O₃ and nano ZrO₂ addition.

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**RESEARCH
NOTE**

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در این پژوهش تاثیر افزودنی های نانو بر مقاومت به هیدراتاسیون سیستم MgO-CaO مورد بررسی قرار گرفته است. نمونه ها با استفاده از دولومیت و منیزیت کلسینه شده، تهیه شد. از مواد نانو با ظرفیت مختلف (سه و چهار ظرفیتی) به عنوان افزودنی استفاده شد. دانسیته بالک، تخلخل و مقاومت به هیدراتاسیون نمونه ها اندازه گیری شده است. همچنین بررسی های فاز توسط دستگاه پراش اشعه ایکس و بررسی های ریزساختاری با استفاده از SEM بررسی شده است. استفاده از هر دو نوع افزودنی موجب افزایش مقاومت به هیدراتاسیون نمونه ها شد اما نمونه های دارای افزودنی با ظرفیت بالاتر مقاومت به هیدراتاسیون بالاتری داشتند. دلیل آن تشکیل جاهای خالی در فرآیند انحلال جامد کلسیا و منیزیا با استفاده از جایگزینی یون Zr^{4+} در کاتیون CaO بوده است. همچنین کاتیون های سه ظرفیتی منجر به ایجاد فازهای زودگداز از قبیل $C_3A.CF$ ، C_2F شد که تشکیل این فازهای زودگداز با پوشش دانه های کلسیا و منیزیا و کاهش تخلخل در سیستم منجر به افزایش مقاومت به هیدراتاسیون نمونه ها شده است.

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