THE EFFECT OF DOLOMITE TYPE AND Al_2O_3 CONTENT ON THE PHASE COMPOSITION IN ALUMINOUS CEMENTS CONTAINING SPINEL

M. R. POUYAMEHR, Z. A. NEMATI*, M. A. FAGHIHI SANI*, R. NAGHIZADEH**

Materials Engineering Department, Science & Research Branch, Islamic Azad University, Tehran, Iran
**Faculty of Materials Science and Engineering, Sharif University of Technology, Tehran, Iran*
***Faculty of Materials Engineering, Iran University of Science & Technology, Tehran, Iran*

E-mail: m_pouyamehr@yahoo.com

Submitted January 15, 2011; accepted May 2, 2011

Keywords: Aluminous cement; Spinel; Dolomite; CA; $C_{12}A_7$

In this paper, the effect of dolomite type and Al_2O_3 content on the phase composition in aluminous cements containing MA spinel is investigated. For this reason, the raw and calcined dolomites are used as raw materials along with calcined alumina in the preparation of the cement. Then, different compositions are prepared at 1350 °C using the sintering method and their mineralogical compositions are investigated using the diffractometric technique. Also, their microstructures arre evaluated. The results indicate that raw materials used have great effect on the type and amount of formed phases in cement composition. Independently of the dolomite type used, a mixed phase product consisting of spinel accompanied by CA and CA_2 is obtained. The content of CA phase in the cement composition is decreased with increasing of Al_2O_3 in the raw materials composition. On the other hand, the content of CA_2 phase is increased with the addition of Al_2O_3. In addition, the results show that the formation of $C_{12}A_7$ is favored by use of calcined dolomite.

INTRODUCTION

The increasing application and demand for monolithic refractory materials as a substitute for conventional bricks encourage manufacturers and researchers to explore their physical, chemical and mechanical properties at elevated temperature as well as their processing techniques [1-3]. Calcium aluminate cement (CAC) is the most used hydraulic binder in refractory castables. The amount of CAC in the mix can vary from relatively low quantities to 10% or more, depending on the manufacturer and the mix. However, the presence of CaO in the composition can be deleterious to the refractoriness of some ceramic systems, such as those containing microsilica [4-6]. Nowadays, a new CAC appeared in the industry, which opened a new horizon for refractory technologists. It has been reported that the refractoriness of the high alumina cements can be increased substantially, without adversely affecting their compressive strength, when CaO in the cement clinker is partially substituted by MgO. This is due to the formation of $MgAl_2O_4$-spinel in the end product. This type of aluminous cement which contains from 6 to 13 % MgO is known as spinel-type cement [7 and 8]. MA spinel is very attractive as refractory material in thermal industries because of its high melting point (2135°C), low thermal expansion, and considerable hardness, high resistance to chemical attack, favorable chemical stability, and good thermal spalling [9, 10]. Therefore, aluminous cements containing MA spinel show increased thermo mechanical strength and minimal slag attack due to the MA spinel content. Such types of cement could be fabricated either by grinding a mixture of pre-prepared high alumina cement (>70% alumina) and prefabricated MA spinel, or the use of appropriate mixtures of raw dolomite (source of CaO and MgO) and active alumina as primary materials. Therefore, MA spinel (20-50%) in addition to the calcium aluminate hydraulic phases (CA and CA_2) is formed during the sintering process. The spinel mineral, whether artificially added or formed in situ during sintering, is hydraulically inert and does not behave as a binder, but it permits the utilization of refractory castables with a suitable aggregate (tabular alumina, spinel or dead burnt magnesite) up to 1800°C. Based on their properties these materials are being used for lining by glass, cement and steel-making applications, such as lining of steel ladles, continuous casting tundishes and degasser snorkels and lancers. Their utilization in casting ladles represents an outstanding improvement, not only in ladle service life but also in steel production quality. Due to the practical considerations mentioned above, the synthesis of aluminous cements containing spinel has attracted considerable attention. The use of aluminous refractory materials containing MA spinel has led to a major breakthrough in the service life of refractory coatings applied in the industries and in the quality of the products [8-12]. Many researches have been conducted to improve the synthetic procedures in order to reduce the production cost of these materials. The preparation of calcium aluminate cements containing MA spinel using appropriate mixtures of active alumina and dolomite from Spain and Egypt has already been reported [8]. Additionally, the effect of using different polymorphs of alumina as raw materials has been considered in many studies [10]. But, the effect of dolomite type and Al_2O_3 content on the phase composition has not been investigated. Therefore, the object of the present work is the investigation of dolomite type effect on the phase composition in aluminous cements containing MA spinel. For this reason, the effect of raw and calcined dolomites is investigated. Besides, the effect of calcined alumina content on the phase composition is studied.

EXPERIMENTAL

Raw materials and compositions

Highly pure local raw dolomite, calcined dolomite (as source of CaO and MgO) and calcined alumina (source of Al_2O_3) were employed for the preparation of aluminous cement containing spinel ($MgAl_2O_4$). The chemical compositions of these starting materials are given in Table 1.

The raw dolomite used in this investigation [derived from Shahreza regions (Iran)] was finely milled mineral dolomite [$CaMg(CO_3)_2$] supplied by Sepahan Kani Co. (Iran). Also, the calcined dolomite (doloma) was obtained from raw dolomite by calcination at 1350 °C for 3 h. The calcined alumina used was a product of Fiberona Co. (HTM 10, India). The specifications of raw materials used are shown in Table 2. Also, the XRD patterns of raw and calcined dolomite used are shown in Figure 1. This spectrum shows that only CaO and MgO are present in calcined dolomite and hence, doloma powder has well crystallized. The compositions used for synthesis of aluminous cement are shown in Table 3.

Table 1. Chemical composition of the raw materials.

	Raw material		
Oxides	Raw dolomite	Calcined dolomite	Calcined alumina
SiO_2	0.51	0.66	0.02
Fe_2O_3	0.27	0.84	0.02
Al_2O_3	0.54	0.26	99.60
CaO	31.32	60.02	–
MgO	20.16	37.86	–
Na_2O	0.01	0.01	0.15
L.O.I.	46.82	–	0.11

Table 2. The specifications of raw materials used.

	Raw material		
Specification	Raw dolomite	Calcined dolomite	Calcined alumina
Density (g cm^{-3})	2.84	3.34	3.92
d_{50} (μm)	3.20	3.70	4.00
Surface area (m^2 g^{-1})	3.10	2.80	1.00

Preparation of cement compositions

The required proportions of the starting materials of each mix were dry blended together, and then dry finely ground in a fused alumina ball mill. After being milled, the prepared mixes were formed into briquettes under pressure of 800 kg/cm^2, dried at 110°C and then fired at 1350 °C, with a soaking time of 5 h, until complete sintering was achieved. Firing was carried out in a muffle furnace under atmospheric condition. The XRD measurements were carried out with a D8ADVANCE, Bruker diffractometer with Cu Kα, Ni-filtered radiation. The fracture surface of fired samples after gold coating was evaluated by scanning electron microscope (SEM). Microstructural evaluations were performed using Jeol JSM (SEM) of model 5410 LV equipped with an energy dispersive X-ray microanalysis (EDX) unit of system 5480 IXRF.

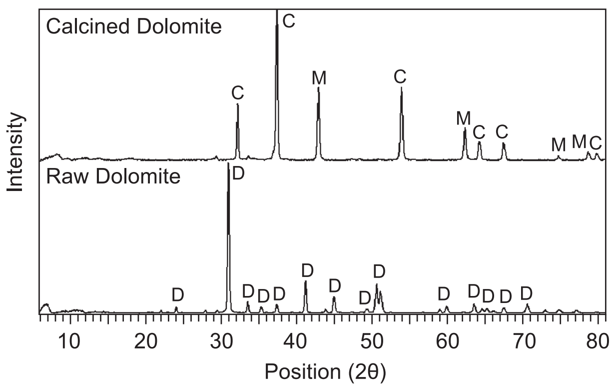


Figure 1. The XRD pattern of raw and calcined dolomite (C - CaO, M - MgO, D - Dolomite.

Table 3. The compositions used for synthesis of aluminous cement containing spinel.

	Raw material (wt.%)		
Sample code	Raw dolomite	Calcined dolomite	Calcined alumina
C1	55	–	45
C2	50	–	50
C3	45	–	55
C4	40	–	60
C5	–	50	50
C6	–	45	55
C7	–	40	60
C8	–	35	65
C9	–	30	70

RESULTS AND DISCUSSION

Phase composition of the prepared cements

The XRD results of prepared cements by use of raw dolomite after firing are shown in Figure 2.

With respect to these results, the $CaO.Al_2O_3$ (CA) phase was found in addition to spinel ($MgAl_2O_4$) phase at all compositions with different proportions. Also, a trace of remaining raw materials such as periclas (MgO) and lime (CaO) resulting of thermal decomposition of raw dolomite together with corundum (Al_2O_3) are presented. Generally, raw dolomite is decomposed into CaO and MgO with increasing of temperature. Then, these oxides are reacted with Al_2O_3 which, can lead to formation of CA and spinel. As it can be seen, $CaO.2Al_2O_3$ (CA_2) phase is formed in C_2-C_4 samples which; the highest amount of this phase is seen in C_4 sample. On the other hand, the C_4 sample has the highest amount of Al_2O_3 in its composition. Therefore, one can see that CA_2 formation depends on the Al_2O_3 content in the raw materials composition. The proportion of the different phases in the cement compositions (C1-C4) was determined by quantitative XRD analysis. The results are shown in Figure 3 as a function of Al_2O_3 content used in the cement composition.

The results show that the content of CA phase in the cement composition is decreased with increasing of Al_2O_3 and other, with decreasing of CaO in the raw materials composition. On the other hand, the CA_2 content is increased also with the addition of Al_2O_3. Therefore, it can be concluding that the content of formed phases in the cement composition (especially: CA and CA_2) depends on Al_2O_3 content and C/A ratio used in the raw materials composition. Monocalcium aluminate (CA) is the most important component of calcium aluminate cement and has a relatively high melting point (1600 °C). Also it develops the highest strength among the other phases and then, it has an important role on the improvement of the mechanical strength of refractory cements. Usually, the CA formation takes place at 950°C. Also, between 1000 and 1100 °C the expansile and exothermic reaction of spinel formation occurs. Then, in the 1000-1200 °C temperature range, CA reacts with alumina to form CA_2 [13-14]. Therefore, CA phase after reaction with alumina converts to CA_2 and its content is decreased.

On the other hand, CA_2 is a secondary phase in calcium aluminate cement and is more refractory than CA but takes a long time to set due to its low hydraulic activity. The strength of CA_2 after three days hydration is comparable to that of the pure CA. it has been found that hydraulic activity depends mainly on the ration of CA/CA_2 and also $CA/C_{12}A_7$. Hydraulic activity is affected also by fineness of the cement and additives influencing the hydration process. Therefore, it can be concluding that the properties of prepared cement such as setting time and strength depend on Al_2O_3 content in the raw materials composition. At temperatures higher than 1250 °C the sintering process occurs, first in the solid state and later in the presence of a liquid phase [13-14]. These results show that, in the reaction-sintering of the dolomite-alumina mixtures, the reaction occurs prior to densification. The XRD results of prepared cements by use of calcined dolomite after firing are shown in Figure 4.

In all the cement compositions after firing, CA, CA_2, $12CaO\cdot7Al_2O_3$ ($C_{12}A_7$) and spinel phases are formed as observed in the XRD pattern shown in Figure 4. Also, considerable amounts of remaining raw materials such as MgO, Al_2O_3 and a trace of CaO are presented. With increasing of temperature, CaO and MgO present in calcined dolomite are reacted with Al_2O_3 which, can lead to formation of CA, CA_2, $C_{12}A_7$ and spinel. Comparison between XRD results of Figures 2 and 4 reveals that $C_{12}A_7$ phase (mayenite) is formed in cement compositions containing calcined dolomite. Therefore, the obtained results indicated that calcination of dolomite used have great effect on the type and amount of formed phases in cement composition. The amount of the formed phases after firing in the cement compositions (C_5-C_9)

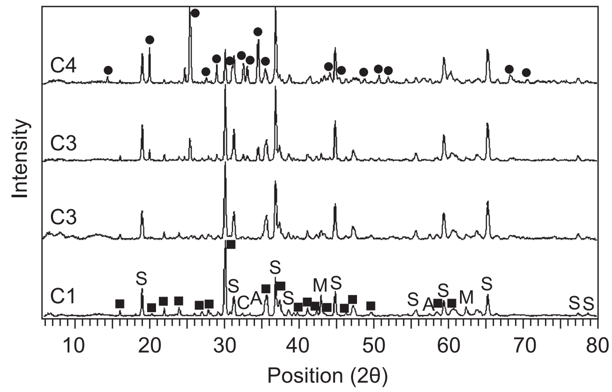


Figure 2. The XRD results of prepared cements by use of raw dolomite after firing (■ - CA, ● - CA_2, S - Spinel, M - MgO, A - Al_2O_3, C - CaO).

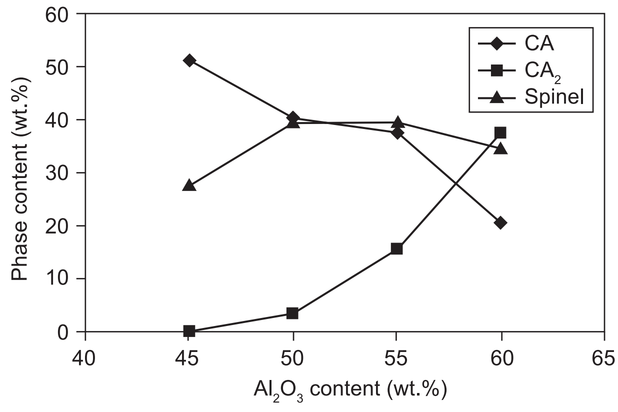


Figure 3. The effect of Al_2O_3 content on the formed phases in the cement composition containing raw dolomite after firing.

also was determined by quantitative XRD analysis. The results are plotted in Figure 5 as a function of Al_2O_3 content in the cement composition.

As it can be seen from the results of Figure 5, changes in the composition of phases with increasing of Al_2O_3 content are similar to the results of Figure 3. Thus, the content of formed phases in the cement composition depends on Al_2O_3 content in the raw materials composition containing calcined dolomite too. According to these results, the content of CA and $C_{12}A_7$ phases in the cement composition are decreased by increasing of Al_2O_3 content while, the CA_2 content is increased. By use of calcined dolomite for producing of cement, $C_{12}A_7$ can be formed at low temperatures because of high reactivity of CaO particles in the calcined dolomite. Generally, $C_{12}A_7$ hydrates rapidly and has a relatively low melting point (1415-1495 °C). By increasing of temperature $C_{12}A_7$ can be converted to CA phase according to reaction: $C_{12}A_7 + 5A \rightarrow 12CA$. On the other hand, CA phase gradually reacts with the alumina to form CA_2. The CA phase formed from the Al_2O_3 and $C_{12}A_7$ reaction can be observed from 800 °C onwards and can reach its maximum degree of recrystallisation at 1000 °C [13-14]. The mayenite phase has the lower melting point among the other formed phases in cement composition. Therefore, the service temperature of these refractory cements shifts to lower temperatures by use of calcined dolomite in the raw materials composition.

Microstructural evaluation of the prepared cements

Figures 6 and 7 demonstrate the microstructure of cement composition C1 containing raw dolomite after firing.

As it can be seen, the microstructure of C1 sample is porous and contains the crystalline phases with different grains size. The pores in the microstructure are produced via thermal decomposition of raw dolomite used in the cement composition. According to XRD results of Figure 2, the present phases in the cement composition C1 contain CA and MA spinel that linked together via sintering process. CA presents a globular morphology while spinel phase is seen as aggregates with some cluster of cubic shape crystals. The SEM photomicrograph of

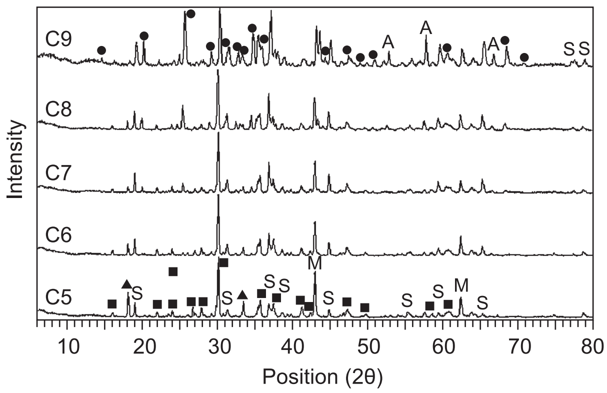


Figure 4. The XRD results of prepared cements by use of calcined dolomite after firing (■ - CA, ● - CA_2, ▲ - $C_{12}A_7$, S - Spinel, M - MgO, A - Al_2O_3, C - CaO)..

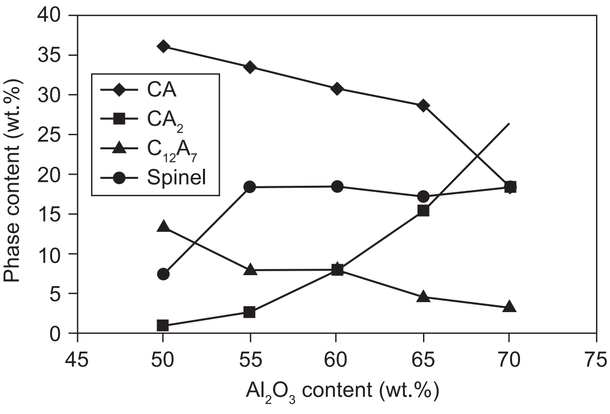


Figure 5. The effect of Al_2O_3 content on the formed phases in the cement composition containing calcined dolomite after firing.

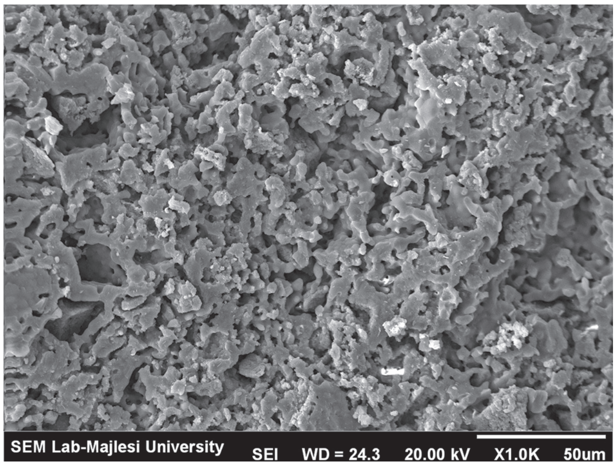


Figure 6. SEM micrograph of the C1 sample after firing.

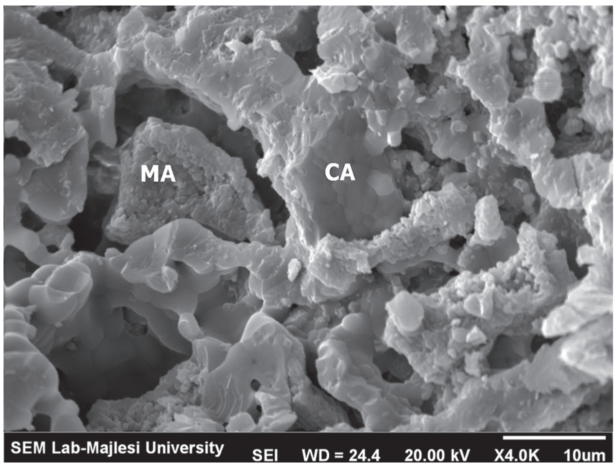


Figure 7. SEM micrograph of the C1 sample after firing.

these clusters is shown in Figure 8 and the SEM/EDX analysis of these cubic crystals is depicted in Figure 9. This analysis indicates that these cubic crystals are MA spinel phase.

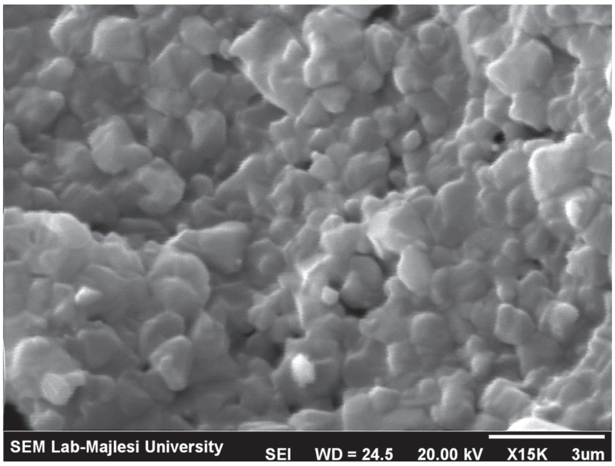


Figure 8. SEM micrograph of the some cluster of cubic shape crystals in the C1 sample.

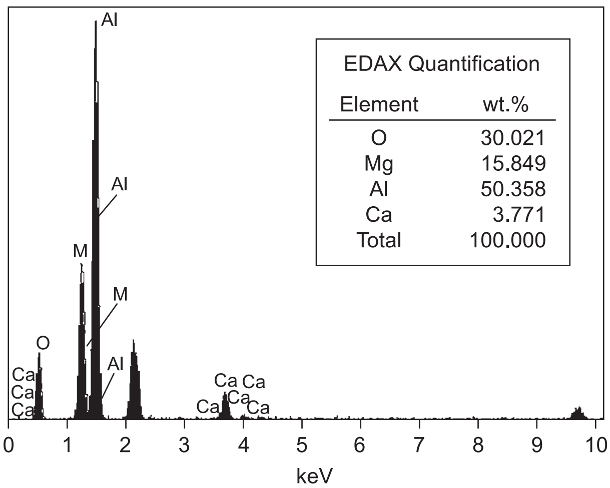


Figure 9. SEM/EDX analysis of cubic crystals in Figure 8.

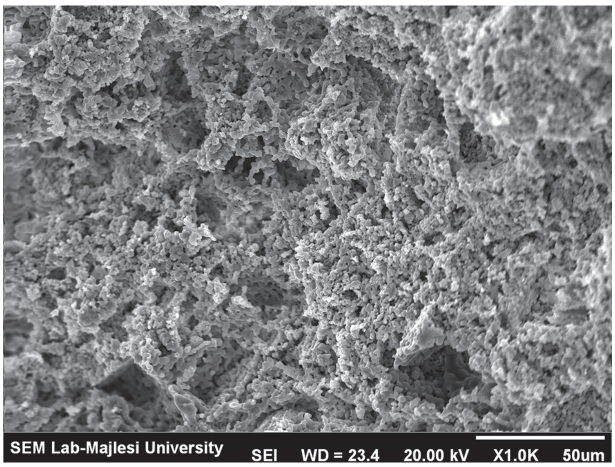


Figure 10. SEM micrograph of the C3 sample after firing.

Typical SEM images of the C_3 sample after firing are shown in Figures 10 and 11.

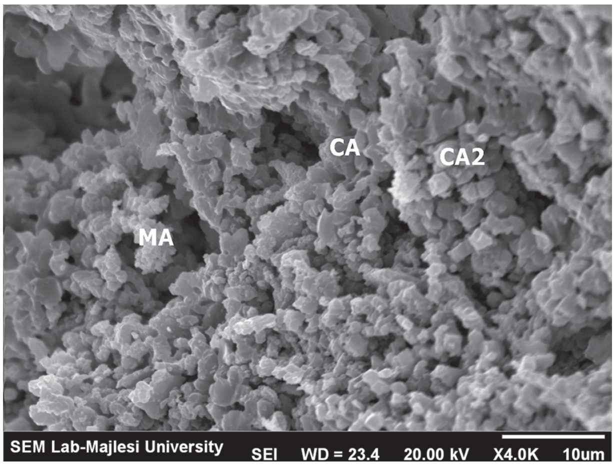
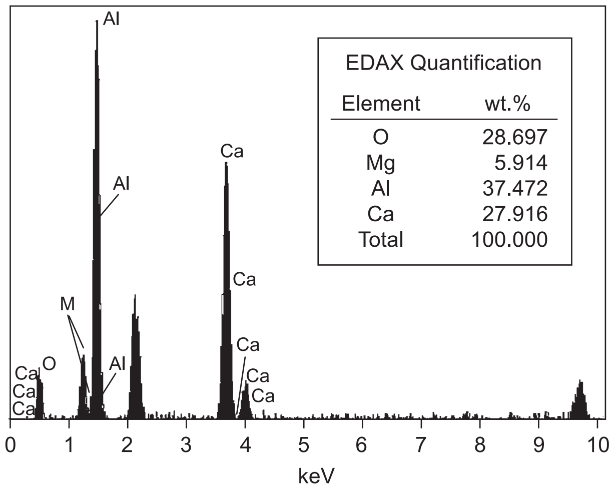
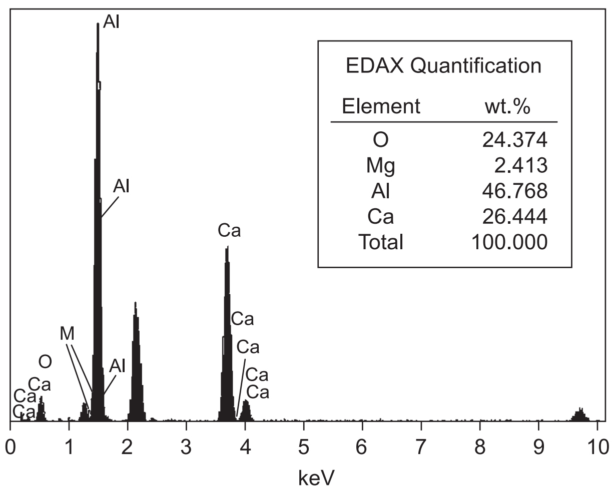


Figure 11. SEM micrograph of the C3 sample after firing.



a)



b)

Figure 12. The SEM/EDX analysis of: a) CA and b) CA_2 phases.

The C3 sample has lower raw dolomite in its composition than C1 sample. Therefore, it can be seen from SEM photomicrograph of Figures 10 and 11 that lower porosity in the microstructure of C3 sample is produced. According to XRD results of Figure 2, the present phases in the cement composition C3 contain CA, CA_2 and spinel. Micrograph of a fracture of the cement after firing (see Figure 11) shows globular crystals of CA_2 that give a cohesive microstructure. To distinguish between CA and CA_2 EDS analyses were necessary because both phases present similar contrast. The SEM/EDX analysis of CA and CA_2 phases are presented in Figure 12.

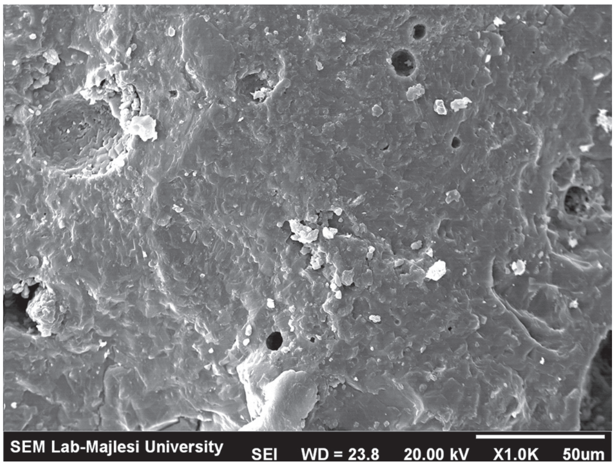


Figure 13. SEM micrograph of the C5 sample after firing.

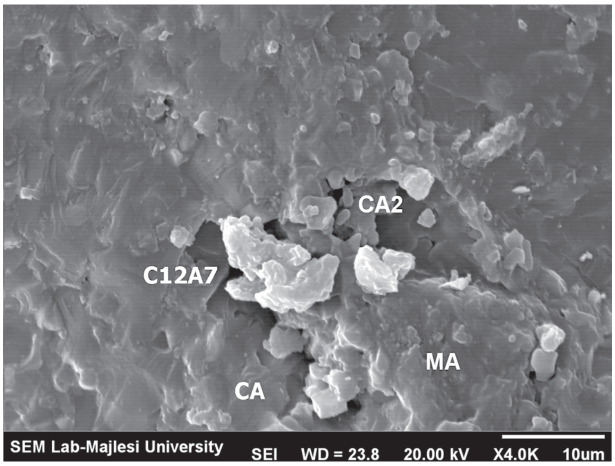


Figure 7. SEM micrograph of the C5 sample after firing.

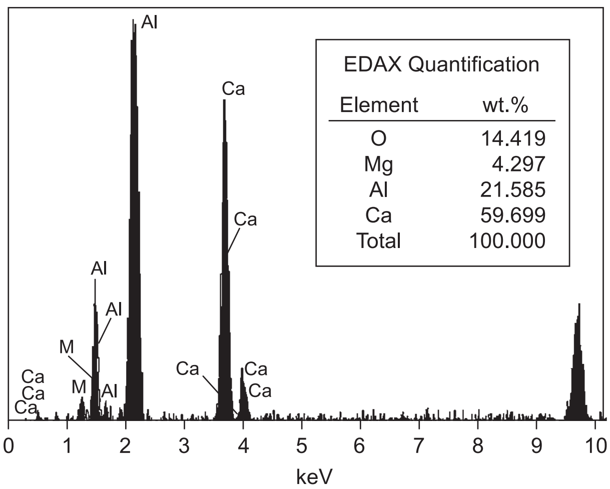


Figure 15. The SEM/EDX analysis of $C_{12}A_7$ phase.

The microstructures of cement composition C5 containing calcined dolomite after firing are presented in Figures 13 and 14.

With microstructural evaluation of cement composition containing calcined dolomite, one can see that very low porosity is produced in the microstructure and then, dense crystalline structure is formed. As shown in XRD results of Figure 4, the microstructure of C5 sample after firing comprises of CA, CA_2, spinel and $C_{12}A_7$. Examination of the fracture surface of the C5 sample by SEM showed that the $C_{12}A_7$ possesses the pseudomorphic appearance which, the SEM/EDX analysis of this phase is depicted in Figure 15.

CONCLUSION

This study confirmed the strong influence that dolomite type and Al_2O_3 content exert on the phase composition of aluminous cements containing spinel. The results indicated that the mineralogical compositions of these cements were spinel, in addition to CA and/or CA_2 phases depending on the composition of the starting materials. According to the results the content of formed phases in the cement composition depends on Al_2O_3 content and C/A ratio used in the raw materials composition. So that, the content of CA phase in the cement composition is decreased with increasing of Al_2O_3 content in the raw materials composition. On the other hand, the CA_2 content is increased with addition of Al_2O_3. Also, the results revealed that $C_{12}A_7$ phase (mayenite) is formed in cement compositions containing calcined dolomite. Therefore, the calcination of dolomite used has great effect on the type and amount of formed phases in cement composition. With respect to great effect of formed phases on the properties, addition of alumina and also the calcination of dolomite can alter the properties of aluminous cements containing spinel.

References

1. Ismael M.R., dos Anjos R.D., Salomao R., Pandolfelli V.C.: Ref. Appl. News. *11*, 16 (2006).
2. Gerotto M. V., Studart A.R., Pileggi R.G., Pandolfelli V.C.: Am. Ceram. Soc. Bull. *79*, 75 (2000).
3. Mukhopadhyay S., Pai P., Nag B.: Ceramics International *33*, 175 (2007).
4. Badiee S.H., Otroj S.: Ceramics – Silikáty *53*, 1 (2009).

5. Oliveira I.R., Studart A.R., Pandolfelli V.C.: Am. Ceram. Soc. Bull. *81*, 27 (2002).
6. Anjos R.D., Ismael M.R., Oliveira I.R., Pandolfelli V.C.: Ceramics International *34*, 165 (2008).
7. De Aza A.H., Pena P., Rodriguez M.A., Torrecillas R., De Aza S.: Journal of the European Ceramic Society. *23*, 737 (2003).
8. Khalil N.M.A., El-Hemaly S.A.S., Girgis L.G.: Ceramics International. *27*, 865 (2001).
9. Domanski D., Urretavizcaya G., Castro F.J., Gennari F.J.: J. Am. Ceram. Soc. *87*, 2020 (2004).
10. Lavat A.E., Grasselli M.C., Lovecchio E.G.: Ceramics International *36*, 15 (2010).
11. Díaz L.A., Torrecillas R.: Journal of the European Ceramic Society 29, 53 (2009).
12. Díaz L.A., Torrecillas R., de Aza A.H., Pena P.: Journal of the European Ceramic Society *27*, 4623 (2007).
13. Díaz L.A., Torrecillas R., de Aza A.H., Pena P, De Aza S.: Journal of the European Ceramic Society *25*, 1499 (2005).
14. Díaz L.A., Torrecillas R.: Journal of the European Ceramic Society *27*, 67 (2007).