

MICROSTRUCTURE AND PROPERTIES OF COLLOIDAL SILICA BONDED MAGNESITE CASTABLE REFRACTORIES

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Abstract: Efforts have been carried out in order to use microsilica to develop a forsterite bond rather than other types of binders in the basic refractory castables. According to the higher drying rate and sinterability of colloidal silica, it has been proposed in the recent years. In the present work, effects of replacement of microsilica by colloidal silica evolution of forsterite bond have been studied in magnesia based refractory castables. In this way, Physical properties of prepared samples with different amount of colloidal silica versus temperature were investigated. In addition, phase variation and microstructural evolution of sintered specimens at 1000, 1200 and 1400 °C were studied by X-ray diffraction (XRD) and scanning electron microscope (SEM) respectively. Results showed that, due to Reaction of magnesia with microsilica and colloidal silica, magnesium hydrate and magnesium silicate hydrate formed in the dried samples strengthening the texture of the samples while forsterite formed from about 1000 °C and gradually increased with temperature rise. Also, better forsterite formation would be appeared by increasing the colloidal silica content. Further investigation carried out on the type of silica addition on properties of the castable refractory samples. It was found that the presence of micro silica and colloidal silica simultaneously (MS_3C_3 sample) at 1400 °C, caused modifying mechanical strength in compare with sample with only micro silica (MS sample).

Keywords: Magnesite refractory castables, Microsilica, Colloidal silica

1. INTRODUCTION

Refractory castables are combinations of refractory aggregates, matrix component, bonding agent, and admixtures [1]. Easy production of refractory castables along with cheap installation and similar performance to shaped products are the reasons for the growing market of monolithic refractories, at the expense of traditional bricks. Calcium aluminate cement is the most used hydraulic binder in refractory castables compositions. Nevertheless, CAC amounts higher than 2-3 wt% in Al_2O_3 -CaO- SiO_2 systems may induce liquid formation at lower temperatures [2]. In addition to the above disadvantageous property of high cement bonded conventional castable, it requires a high water demand on mixing, resulting low density and high porosity products. These drawbacks led to the development of low cement castable (LCC) and no cement castables (NCC) [3].

Micro silica, which is a by-product of ferro-silicon manufacture, when present in the bond system of refractory castable batches reduces the amount of mixing water required and facilitates flow and ease of placement. Magnesia-silica

bond systems have been developed in magnesia-based, cement-free castables [4] forming forsterite in the bond on firing. The HMOR reached a maximum at 1200°C but deteriorated at higher temperatures due to the effect of raw material impurities [5].

Recently different kinds of sols which form coagulation bonding have been tried as binder in low, ultralow and no cement bonded refractory castable compositions. Colloidal silica sols are stable water-based suspensions, containing up to 50 wt% of nanometric spherical amorphous silica particles (8-15 nm diameter). When combined with other solid particles, colloidal silica can be linked together in branched chains, in a process known as gelation [3], which can be induced by water removal. During the drying step, the hydroxyl groups (Si-OH) on the surface of the particles generate siloxane bonds (Si-O-Si), which results in a three-dimensional network (figure 1) [5]. Gelation can also be induced by pH changes and a salt or water miscible organic solvent addition, named gelling agents. With the proper selection of these agents or the pH variation, the colloid is gelled around the solid particles providing mechanical strength to the

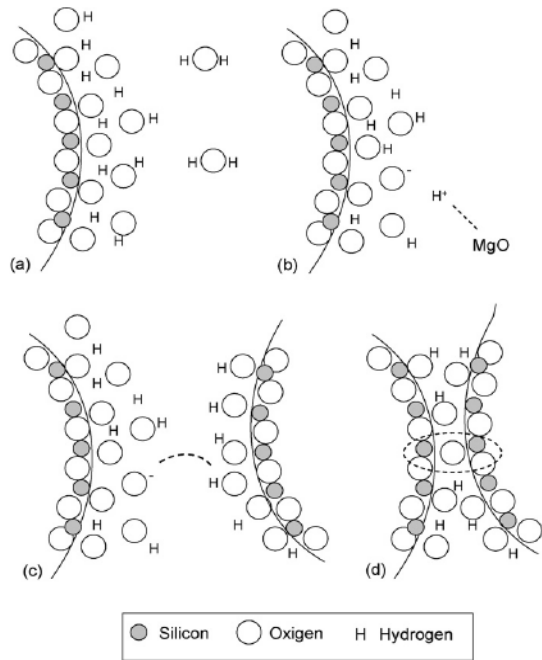


Fig. 1. Schematic representation of colloidal silica consolidation through the Gelling mechanism: (a) colloidal silica particle surface, (b) MgO addition, (c) siloxane bonds formation and (d) siloxane bonding (-Si-O-Si-)

Table 1. Chemical analysis of the raw materials
Colloidal silica

	Magnesia (wt %)	Micro silica (wt %)	Colloidal silica (wt %)
MgO	97min	0.1	0
SiO ₂	0.6max	97.5	40.2
CaO	1.5 max	0.2	0
Fe ₂ O ₃	1 max	0.4	0
Al ₂ O ₃	1 max	0.4	0
K ₂ O	0	0.2	0
Na ₂ O	0	0.1	0
L.O.I	0.2 max	0.6	59.8

Table 2. Composition of castables

Castable Composition (wt %)	Grade	MC	MS ₃ C ₃	MS
Magnesia	Iran	94	94	94
Micro silica	Ferroalloy of Iran	0	3	6
Colloidal silica	Beechems	6	3	0
Additive	Castament	0.3	0.3	0.2
Water		8.5	6.65	5.25

system after drying. The micro silica-magnesia-colloidal silica system presents a pH value around 4–6, which is closer to the pH where the colloidal silica gelling rate is maximum (around pH 5). In this context, colloidal silica has been pointed out as an alternative for a calcium-free binder agent for refractory castables [6].

In the present research the influences of colloidal silica addition on casting process as well as properties are investigated.

2. EXPERIMENTAL PROCEDURE

2. 1. Materials

Chemical analyses of the raw materials used in this study are listed in Table 1 and the recipes of the studied castables are provided in Table 2.

2. 2. Castable Preparation and Testing

For each sample, a 3kg batch mixture using the formulation in Table 2 was prepared, by dry mixing for 2 minutes at slow speed, using a Hobart mixer with 5 liter capacity mixing bowl. Then wet mixing was prepared by addition of water, colloidal silica after 30 second and further 3 minutes mixing at medium speed. Test samples were prepared by casting the mixture into the stainless steel moulds, having the dimensions of 160×40×40 mm, vibrated at 50HZ for 1 minute. The castables were cured at 24°C and a relative humidity of 95% for 24 hours. After 24 hours curing time, the samples were allowed to be dried at the temperature of 110°C, and then fired at 1000°C, 1200°C and 1400°C for 3 hours. The cold strength (CCS, CMOR) was measured according to the ASTM C109. Permanent linear changes (PLC) of the samples fired at 1000°C, 1200°C and 1400°C for 3 hours were measured. Bulk density and apparent porosity were all

determined by standard methods. Phase analyses were performed using a JEOL JDX 8030 model X-ray diffractometer. For microstructural observation, scanning electron microscopy (SEM) was used.

3. RESULTS AND DISCUSSION

3.1. Apparent Porosity and Bulk Density

Apparent porosity and bulk density of the samples as a function of temperature are shown in figures 2, 3.

According to the evaporation of bonding water with increasing temperature till 1000 °C, the apparent porosity of all samples increased; moreover; the bulk density of them decreased. After increasing temperature till 1200 °C, in all the samples except MS₃C₃, the apparent porosity and bulk density were stable. Between 1200 °C to 1400 °C, as a result of sintering, the apparent porosity of all the samples decreased; in contrast;

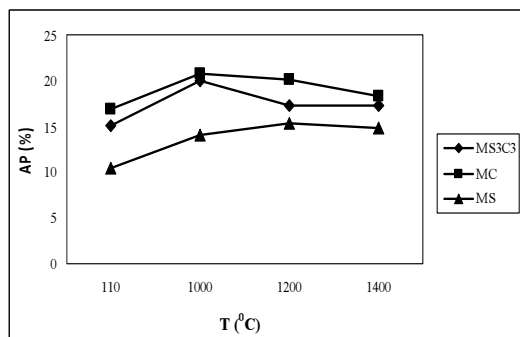


Fig. 2. Apparent porosities of samples as a function of temperature.

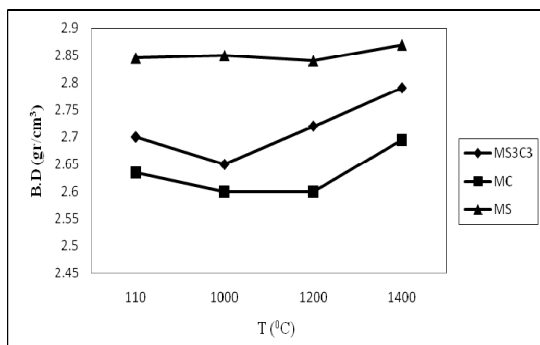


Fig. 3. Bulk densities of samples as a function of temperature.

the bulk density increased. Figures 2 and 3 show that MS sample which contained 6 wt.% micro silica, had minimum apparent porosity and maximum bulk density in all temperatures. Apparent porosity and bulk density are directly related to the water content [2]. For the sintered magnesia–colloidal silica system the reaction was so fast that it was not possible to prepare a homogenous suspension. During mixing, silica particles immediately gelled around the magnesia ones, forming an impermeable external layer, which hindered the powder dispersion. Therefore we forced to add extra water in order to achieve suitable rheological condition. In this way, the increase in apparent porosity and the decrease in bulk density observed in which samples contain colloidal silica in compare with samples contain micro silica. Furthermore powder density of micro silica is more than the colloidal silica [3] which is another reason for increasing the bulk density of MS sample in compare with MC one.

3.2. Cold Mechanical Strength

In the next step variations of bending and cold crushing strength with firing temperature for different formulations are shown in figure 4 and 5.

Water content, particle size distribution and sintering condition of the castable samples are the most important factor which influences mechanical strength [7]. As figure 4 and 5 show, mechanical strength of MS sample is higher than other samples in 110 °C. Formation of MgO.SiO₂.H₂O phase in this temperature can be the reason of this matter [5]. According to figures 4 and 5 increasing temperature till 1200 °C, the

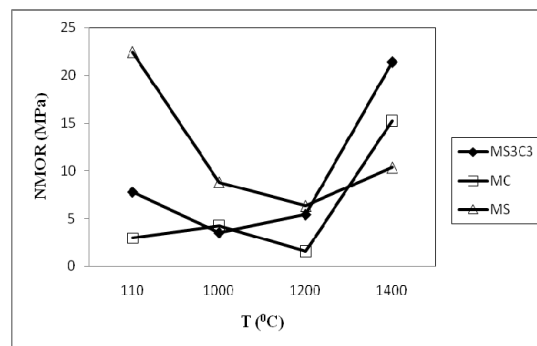


Fig. 4. Cold Bending strength as a function of firing temperature

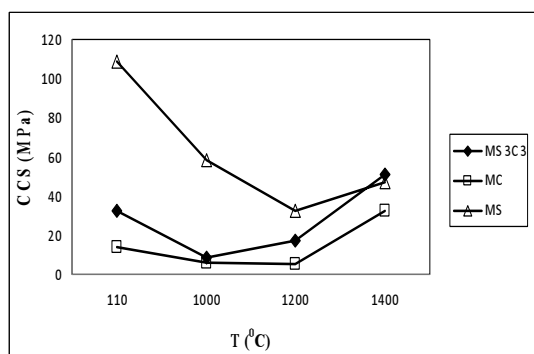


Fig. 5. Cold crushing strength as a function of firing temperature

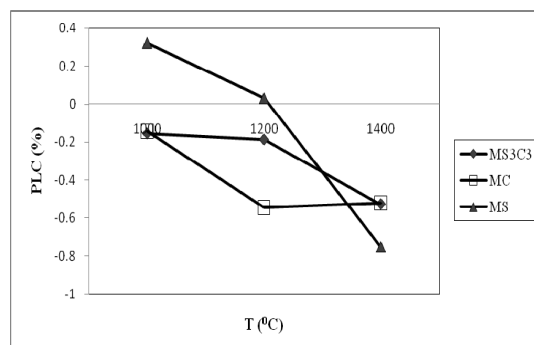


Fig. 6. Permanent linear changes of samples in 1000 °C, 1200 °C, 1400 °C

absence of bonding water, caused decreasing mechanical strength in all samples. After that, by increasing temperature till 1400 °C formation of forsterite bonds during sintering process resulted increasing mechanical strength in all samples. Higher mechanical strength for MC sample was expected than MS but because of fast gelation of colloidal silica and addition of extra water, mechanical strength in MS became higher than MC. The other point is that in 1400 °C, the mechanical strength of MS₃C₃ sample was higher than MS sample. In fact using micro and colloidal silica simultaneously caused improving mechanical strength of the fired samples because micro silica improved particle size distribution consequently, flow of the castables and higher reactivity of colloidal silica caused to form higher amount of forsterite upon sintering.

3. 3. Permanent Linear Change (PLC)

Permanent linear changes of the samples in 1000, 1200, 1400 °C are shown in figure 6.

Permanent linear change (PLC) depends on sintering temperature, reaction between aggregates and bonding agents. Principally shrinkage is caused by sintering and also glass phase formation; on the other hand; expansion is caused by phase transition in the sample's matrix.

As figure 6 shows, MS₃C₃ sample had lower Permanent linear change (PLC) than the other ones. Also by increasing formation of forsterite during sintering process, more shrinkage resulted increasing the PLC.

3. 4. Phase Analyses and Microstructural Observations

XRD patterns showed that the presence of micro silica could inhibit the hydration of magnesia; furthermore it caused formation of magnesium silicate hydrate which bonded the aggregates together [8].

Forsterite is a crystalline magnesium silicate with chemical formula Mg₂SiO₄, which shows good refractoriness due to high melting point (1890 °C), relatively low thermal expansion ($100 \times 10^{-7} \text{K}^{-1}$ between 20 and 500 °C), good chemical stability and excellent insulation properties ($K=1.4 \text{ J/m} \cdot \text{sec} \cdot \text{0K}$ at 1300 °C) even at high temperatures [8].

Increasing the silica content in magnesite refractories can change the CaO/SiO₂ molar ratio and phase formation. But in this study, in order to forsterite formation, specific content of silica was added. According to a) low content of impurity and b) short accessibility of impurities to SiO₂ in grains, formation of low melt phases would be limited. Furthermore this refractory has been considered for application in less than 1600 °C range. So the contents of low melt phases are negligible. On the other hand this small amount of low melting phases makes a little decrease in the service temperature of the refractories.

XRD pattern of MS₃C₃ sample after firing at 1000, 1200, 1400 °C are shown in figure 7. In addition to periclase as the main phase, forsterite and quartz phases formed at 1000, 1200 °C. Quartz phase eliminated at 1400 °C because of its reaction with magnesia in this temperature. Furthermore it can be seen, by increasing the temperature, forsterite phase formation was

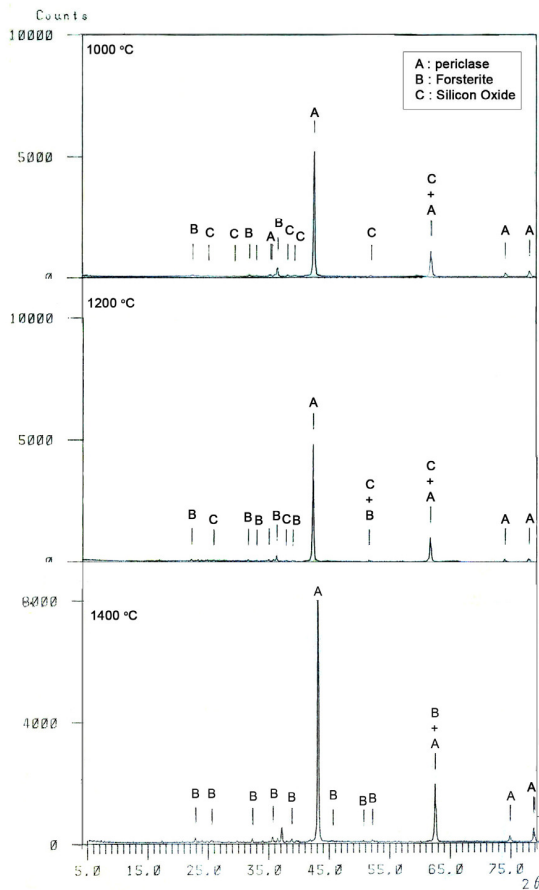


Fig. 7. XRD pattern of MS_3C_3 sample after firing at 1000, 1200, 1400°C

developed and the intensity of forsterite peak was increased.

XRD pattern of MS_3C_3 and MC samples after firing at 1400°C are shown in figure 8. Result showed the bonding formation of forsterite started to form in the sample fired at 1200 °C which increased by further firing at 1400 °C. The intensity of forsterite's peaks in MC sample is higher than MS_3C_3 in the sample. It may be needed to explain that many researchers introduce an optimum amount for colloidal silica addition as higher amount of colloidal silica deteriorate flow behavior and workability of the castable samples leading to strength decreased [5, 6, 8].

SEM micrographs of MS_3C_3 sample after firing at 1400°C with different magnifications are shown in figure 9. According to EDS analyses, high grey matrix indicated magnesia phase (point A), and light grey matrix indicated the forsterite phase (point B) which resulted by reaction between particles.

SEM micrographs of MC sample after firing at 1400°C with different magnifications are shown in figure 10. According to EDS analyses, high grey matrix indicated magnesia phase (point A), and light grey matrix indicated the forsterite phase (point B) which resulted by reaction between particles.

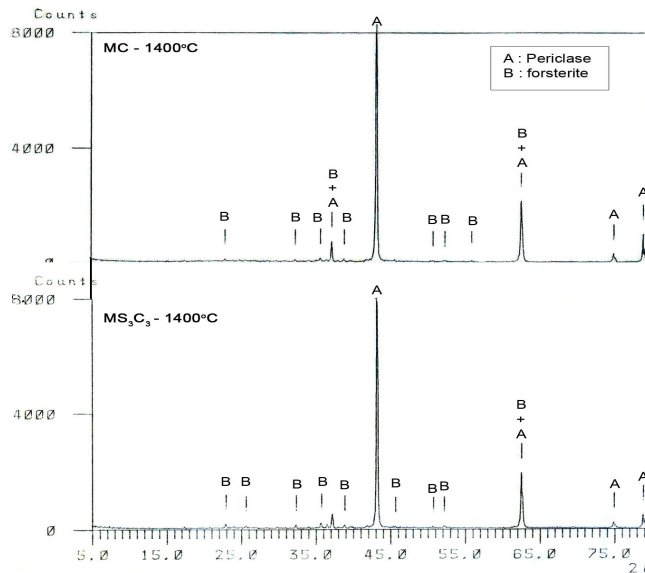


Fig. 8. XRD pattern of MS_3C_3 and MC samples after firing at 1400 °C

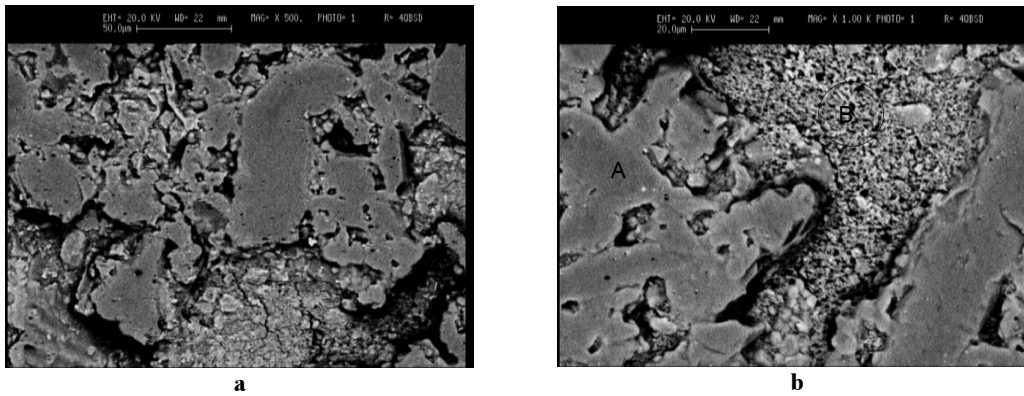


Fig. 9. SEM micrographs of MS_3C_3 sample after firing at $1400^\circ C$, in magnification of a) $\times 500$, b) $\times 1000$

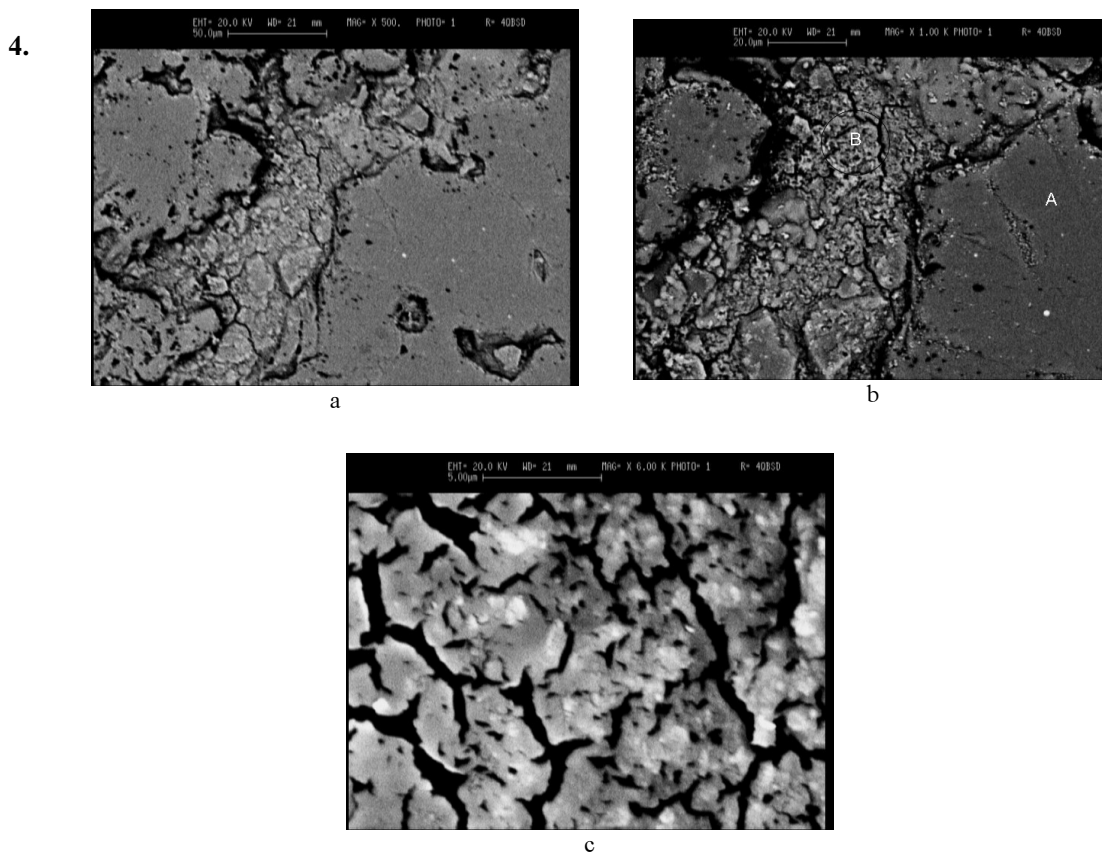


Fig. 10. SEM micrographs of MC sample after firing at $1400^\circ C$, in magnification of a) $\times 500$, b) $\times 1000$ c) $\times 6000$

CONCLUSIONS

- The addition of colloidal silica individually caused to use extra water; therefore; mechanical strength decreased in all samples at $110^\circ C$, $1000^\circ C$, and $1200^\circ C$.
- The presence of micro silica and colloidal

silica simultaneously in MS_3C_3 sample at $1400^\circ C$, caused better formation of forsterite phase and modifying mechanical strength in compare with MS sample. So there is an optimum amount of colloidal silica (3 %wt) providing better workability of the castable as well as forsterite

formation upon sintering.

- In all the samples, the formation forsterite phase started approximately at 1000°C and gradually increased by increasing the temperature.
- X-ray analyses results showed that the intensity of forsterite's peaks in MC sample are higher than those in MS_3C_3 sample at 1400°C.

REFERENCES

1. Krebs, R. "Unshaped Refractory products" Proceedings of International Seminar on Monolithic Refractory materials, Tehran, Iran, 1997.
2. Ismael, M. R, Anjos, R. D., Salomao, R. and Pandolfelli, V. C, Colloidal Silica as a Nanostructured Binder for Refractory Castables. *Refractories Applications and News*, 2006, 11, 16-20.
3. Daspothdar, D., Swapan, Kr. D. and Daspothdar, P. K., Effect of Silica of Different Routes on the Properties of Low Cement Castables, *Indian Bull. Mater. Sci.*, 2003, 26, 227-231.
4. Myher, B., Cement free castables in the system $MgO-SiO_2$; the effect of bond phase modifiers on strength. *Am.Cer.Soc.93rd.* 1991, Elkem a/s Refractories report.
5. Ghanbari Ahari, K., Sharp, J. H., Lee, W. E., Hydration of refractory oxides in castable bond systems— II: alumina–silica and magnesia–silica mixtures. *Journal of the European Ceramic Society*, 2003, 23, 3071–3077.
6. Anjos, R. D., Ismael, M. R., Oliveira, I. R., Pandolfelli, V. C., Workability and setting parameters evaluation of colloidal silica bonded refractory suspensions, *Ceramics International*, 2007, 34, 165-171.
7. Subrata, B. *Monolithic Refractories: A Comparative handbook.* Am. Ceram. Soc. Bull, 77, USA, 1998.
8. Pilevari, Sh., Sarpothlaki, H., "Influence of temperature on microstructure and properties of forsterite bonded castable refractories", 6th Iran Ceramic Conference. 2009.