Effect of the colloidal zirconia on corrosion resistance of low-cemented alumina mixes against steel slag

M. Ebadi, H. Majidian, E. Salahi and A. Faeghinia

Abstract
The corrosion resistance of the low-cement alumina base refractory against the slag of the electric arc furnace using zirconia was studied. Colloidal zirconia was replaced at the expense of the calcium aluminate cement by 1, 2, and 4 wt.% (C1, C2, and C4). The Andreasen coefficient of q = 0.23 was used to provide a reference sample with the 5 wt.% of the cement. The corrosion tests at 1620°C for 2 h were done and penetration zones were analyzed. In the case of samples prepared by colloidal zirconia, the penetration zone was enlarged due to the created porosity. The corrosion resistance of the C2 sample was improved. The new-formed calcium aluminate phase acts as a protective layer in the C2 sample. In the case of the C4 sample, the weight percentage of the calcium aluminate phase was significantly reduced. This can be related to the concentration gradient of calcium oxide in the slag and the matrix composition. However, the existence of the zircon phase in the C4 sample showed that the zirconia can react with the SiO2, leads to a lower temperature phase, and improve the corrosion resistance.

1. Introduction
Refractory materials are defined by the definition of heat-resistant materials and are subjected to the mechanical stress, strain, tensile, and thermal strain. Also they were corroded and abraded by solids, liquids, and gases. The gas penetration and mechanical abrasion at various temperatures could be occurred in these materials [1]. Mainstream consumer development, such as the steel industry as well as other industries such as aluminum, copper, lead, zinc, glass, and cement has pushed the refractory industry to increase the quality of the refractories [2-3]. The driving force behind the change, is to improve the production technology or the longer product life. During the corrosion, the matrix is the first phase that has been attacked. Therefore, the composition of the matrix has an important effect on corrosion resistance. Calcium oxide can react with alumina and form the phytomineral phase (Ca6). Several studies have pointed to the protection of alumina by this compound [4–6]. Various types of bonding systems have been developed, and in a mixes, multiple bonding systems can be used simultaneously. The most commonly used bonding system is calcium aluminate cement (CAC) refractory mixes. However, due to the presence of calcium oxide, this combination causes the low-temperature phase’s formation which degraded the properties. For this reason, many other bonding systems were created. Among these bonding agents, colloidal bonds have been studied [7]. The colloidal silica and colloidal alumina have been used for suppressing the low-temperature phase formation [8]. Mukhopadhayay et al. investigated the effect of mullite and spinel sols as the bonding systems in ultralow alumina-based cements [9]. To generate the molten sols, microsilica was added to the alumina based, and magnesium chloride, was added to the alumina based, which produces the spinel sol. The mixes by the mullite sol bonding system, showed better corrosion resistance. The dense samples which contain more mullite, have more corrosion resistance. Corrosion of refractories in the steel industry stops production, reduces efficiency, and increases costs. Therefore, the improvement of corrosion in refractory materials has great importance in this industry.

It is expected that by adding the zirconia to the mixes, new phases will be formed that will improve the corrosion resistance. The purpose of this work is to investigate the effect of colloidal zirconia on the improvement of corrosion in low-cemented alumina mixes against steel slag.

2. Experimental procedure
Tabular alumina (99.5%, 0–4 mm, Alcan France) was selected as the aggregate phase. The matrix was prepared by tabular alumina, calcium aluminate cement (Secar 71, Kerneos, France) as a binding system, microsilica (U971, Elkem) as a filler/modifier, and dead-burned magnesia (calcined MgO at about 1750°C, 98%, Iran). Monoclinic zirconia was used to prepare the colloidal zirconia (Guangzhou, China). Dolapix CE64 (an electrostatic dispersant, ammonium salt of a polycarboxylic acid) (Zschimmer and Schwarz),
Dolapix CE64 (Zschimmer & Schwarz GmbH Co., Germany), were used in this study as a dispersing agent. It is an ammonium salt of a polycarboxylic acid, that acts through electrosteric stabilization [10]. Sodium tripolyphosphate (TPP) and citric acid were used as additives as well. The particle size distribution of mixes aggregates was chosen according to the modified Andreasen model [11].

Andreasen model based on a de-similarity condition between large particles and smaller particles in the following equation: \[ \text{CPFT}_{100} = \left( \frac{D}{D_\text{c}} \right) \] was created in order to maximize the compacting density of compacts.

Where CPFT = Accumulated percentage of particles smaller than the D size; D = particle diameter; Dc = Size of the largest particle in the system; q = distribution module which is named here as Andreasen index [11]. The Andreasen index in our work was chosen q = 0.23. The particle size distribution and the reference composition were presented in Figure 1 and Table 1, respectively.

Raw materials were mixed in a Hobart mixer. Water added to the mixture in 1 min and stirred continuously (about 4 min) which a self-flowing mixture was reached. Flow behavior was measured using ASTM C230 C standard. The mixture was poured into a 5 × 5 × 5 cm³ mold. The surfaces of the specimens were covered with plastics. In order to complete the cement setting, the samples were placed at ambient temperature for 12 h, and dried at 110°C for 12 h.

Colloidal zirconia (20 wt. % solid loading) was prepared by wet milling of zirconia (Figure 2(a) shows the XRD pattern and Figure 2(b) shows the size distribution of zirconia), Dolapix CE64, and sodium dodecyl sulfate (SDS) in a planetary mill (280 rpm, 24 h) using zirconia cup and zirconia balls. This suspension was stirred for 20 min by magnetic stirrer and subsequent ultrasonicated (10 min) to break the agglomerates and reach more stabilization. 1, 2, and 4 wt% of colloidal zirconia was added to the mixture in replaces of cement (C1, C2, and C4 samples).

The bulk density (BD) and apparent porosity (AP) were measured using the ASTM C20 standard. In order to carry out the corrosion test, cylindrical holes were created in the specimens (1.4 cm diameter, depth of 2 cm). 3 g of slag (by the chemical composition which presented in Table 2) was poured into the holes and the specimens were placed at 1620°C for 2 h.

Subsequently, the samples were cut for further investigation. In order to identify and observe the structure and morphology of the prepared refractories, scanning electron microscopy (SEM, Cambridge Stereo Scan 360UK), field emission SEM (FESEM, MIRA3 TESCAN, Czech Republic), and X-ray diffraction (XRD, Siemens D500) were used. The Zetasizer Nano ZS (Malvern Instruments, UK) with a 633 nm red laser was used which was capable of both particle size analysis (using dynamic light scattering as the basic principle of operation) and zeta-potential measurement (using Doppler electrophoresis as the basic principle of operation).

Scanning Probe Image Processor Software (SPIP) is an advanced software package for processing and analyzing microscopic images at the nano- and micro-scale. It has been developed as a proprietary software by Image Metrology and is unique in the microscopy and microscale research market.

![Figure 1. Particle size distribution of the used mixes aggregates.](image)

| Table 1. The composition of reference sample (q = 0.23). |
|-----------------|---------|
| Composition     | wt.%    |
| Tabular alumina | 62.14   |
| Tabular alumina | 25.86   |
| magnesia        | 3       |
| microsilica     | 4       |
| Calcium aluminate cement | 5     |
| additive        | 0.2     |
To determine the grain distribution within each specimen, image analysis of the microscopic images was conducted using SPIPversion 6.7.7 software (Image Metrology 2018). For each specimen, three images at different magnifications (i.e., 20×, 50×, 100×, and 200×) were selected. Using images at different magnifications minimized the measurement error [12].

3. Results and discussion

3.1. Porosity

The porosity of the C1, C2, and C4 samples after drying at 110°C and after sintering at 1620°C are given in Figure 3. The apparent porosity decreased slightly by the replacement of cement with 1 wt.% of colloidal zirconia (C1 sample) after drying. Further increase of zirconia leads to the higher porosity in samples (C2 and C4). It was expected that using fine colloidal zirconia results in lower porosities and higher densities. However, the main reason for the increment of porosities relates to the mass’s bubbles after the mixing, which was more severe in the C2 sample.

The C1, C2, and C4 samples show 2%, 1.5%, and 1.6% reduction in porosity after sintering, respectively. While the q = 0.23 sample (C) showed a porosity reduction of about 5%. When Colloidal zirconia was replaced by cement. The decrease of the cement content occurred. Therefore, the low-temperature phase formation as the sintering aids was suppressed.

It has been shown that by changing the Andersen coefficient, the size distribution of the porosities also changes [10]. On the other hand, in this work, if the porosities were perfectly aligned, the amount of penetration would probably be much greater. The composition of the slag at the end of the penetration path is different from the composition of the slag at the beginning. This indicates that the slag is moving forward by resolving the matrix within itself. It can be said that the existence of more porosity and cracks in the matrix brings the porosities closer together and allows more slag to penetrate.

Table 2. The chemical composition of the used slag.

| Composition | SiO₂ | CaO | Al₂O₃ | P₂O₅ | Fe₂O₃ | MgO | K₂O | Na₂O | MnO | TiO₂ | S |
|-------------|------|-----|-------|------|-------|-----|-----|------|-----|------|---|
| Wt.%        | 43.90%| 37.16%| 7.18% | 3.10%| 1.02% | 1.17%| 0.53%| 0.42%| 0.39%| 0.11%| 0.72%|
3.2. Corrosion

The arc furnace slag of Mobarakeh Steel Co. was used for the corrosion test. Zirconia was supposed to increase the corrosion resistance of refractories due to its inherent high-temperature refractoriness and good resistance in corrosive environments [4]. Cross-sectional images of the samples after the corrosion test have been shown in Figure 4(a, b) shows that the corrosion index of the C2 sample is better than C1 and C4 samples. The corrosion index of C2 is minimum (24 pixels) among the other samples, although it has higher porosity compared to q = 0.23 sample. Also, the C2 sample has the lowest penetration index compared to C1 and C4 samples. Higher slag penetration to these refractories by the addition of colloidal zirconia can be attributed to the increased porosity in these specimens.

Figure 5(a) shows the penetration zones in the C2 sample after corrosion testing at 1620°C. As in the C1 sample, zone D appears to be part of an aggregate that has not been attacked by slag. Points B and C are part of the matrix or part of the aggregate in which the slag has reacted with them. The diffraction pattern and the element amounts of B, C, D points are given in Figure 5(b, 4c, 4d) and Table 3, respectively. Zone D (Figure 5(d)) has a composition close to alumina aggregate and is clearly unaffected by slag. The percentage of Si, Ca, and Fe elements in region C (Figure 5(c)) has increased sharply, the percentages of these elements are 8.21, 7.67, and 3.28, respectively. The percentage of these three elements is higher in zone B, which is closer to the corroded region. The percentage of these elements is less than the corroded area in sample C1. These three elements are the main causes of corrosion and penetration in refractories. The percentage of zirconia in B and C areas, which are slag penetration areas, is higher than in area D. It can be explained by this fact that the region D relates to the aggregate composition, not to the background composition.

The results of the SPIP (Scanning Probe Image Processor) software that measure the corrosion and penetration indexes of the samples have been also shown in Figure 6. Corrosion here is defined as regions of refractory completely replaced by slag. The number of pixels in the corroded area of sample q = 0.23 was assumed to be 100, and the other values were calculated in comparison with this number. These numbers indicate the extent of corroded and penetrated areas and are termed corrosion and penetration indexes [12].

3.3. Microstructure

Microstructures of the prepared samples after sintering at 1620°C for 2 h are shown in Figure 7. All specimens have a porous matrix. Pores and cracks were formed at the interfacial of the matrix and the aggregates. The matrix shrinks by sintering, due to the low-temperature phase formation. Obviously, the aggregate does not participate in the sintering process. Thus, the difference in the degree of shrinkages between the matrix and the aggregate may be led to cracking [13].

Another effective factor is the new-created phases. Spinel forms in this compound due to the reaction between magnesia and alumina. The formation of the spinel phase is supplemented by the volume increasing. The increment of the volume is a beneficial factor in filling the pores and the distances between the matrix and the aggregate. On the other hand, it can also lead to microcrack formation. It seems that in the q = 0.23 sample there is a relative balance of the mentioned contraction and expansion. Therefore, closed pores are seen which have smaller sizes than the others. This is a proof of the lower porosity of q = 0.23 sample in Figure 3.

The matrix densification prepared by colloidal zirconia was low and composed of large interconnected channel pores. Therefore, higher penetration rates of slags into these samples are expected; while, corrosion resistances of these compounds have not degraded or somehow they have been improved (C4). In this way, it is supposed that the effect of the composition is more
pronounced than the effect of densification. It seems that 2 wt.% (C2) reduced cement and replacing it with colloidal zirconia could increase the indirect corrosion.

The more influencing factor is the new phases formations (zircon) during the corrosion of slag by slags which are responsible for the observed improvement in the corrosion resistance. The microstructures of the corroded regions of the samples are shown in Figure 8. It can be seen that the depth of the corrosion varies in the samples. In the q = 0.23 sample, a large amount of porosity has been created at the contact surface of the slag and the refractory, which is attributed to the dissolution of the matrix in the slag phase. The interface of the refractory and penetration zone is not detectable in the case of C1 and C4 samples.

During the corrosion test, the aggregate, which inhibits the slag penetration, moves into the slag then the surface of the matrix become more corroded. In the slag diffused region, a relative dense structure is created caused by the filling of the pores by slag. In the case
of C1 and C4 samples, the interfacial layer of the refractory/slag is porous. However, a relatively dense microstructure is formed at the interface of refractory and slag in the C2 sample, and less pores were observed around the aggregates. In the cross-sectional image of the C2 sample (Figure 4), it is clear that the slag/refractory layer is relatively flat and less corroded.

### 3.4. Phase analysis

X-ray diffraction and X'Pert software (X'Pert High Score Plus, X-ray Powder Pattern Analysis, Philips X'Pert System) were used to detect the phases of the sintered refractories. XRD patterns of q = 0.23 and C4 samples are shown in Figure 9. The main phases of q = 0.23 sample are alumina, spinel (MgAl2O4), and gehlenite (Ca2Al2SiO7). Mullite is not formed in this sample (Figure 8(a)). Spinel helps to increase the corrosion resistance of refractories, but gehlenite may not be helpful [14]. The zirconia phase suppressed the gehlenite formation; the thermodynamical characters of gehelenite are Ca2Al2SiO7 by the molar mass of 274.20 g/mol: \( \Delta H^0_{\text{el}}(298.15 \text{ K}) = -3982.4 \pm 3.9, S_0 \text{ [J/ (K mol)]} = 210.1 \pm 0.6 \text{ g}, \Delta G^0_{\text{el}}(298.15 \text{ K}) \text{[kJ/mol]} = -3782.9 \pm 3.9 \text{ [15]}. \) Gehelenite phase is a low-temperature phase that has been suppressed by the zirconia addition.

Figure 9(b) shows the XRD pattern of the C4 sample. Alumina and spinel are the two main phases in C4. Adding 4 wt.% of colloidal zirconia and reducing the cement amount (from 5 wt.% in q = 0.23 sample) to 0.1 wt.% in C4 sample results to the inherent alumina’s peak intensity. It is clear that the undesirable gehelenite phase has decreased in the C4 sample.

The penetration zone of the prepared samples was analyzed by XRD (Figure 10). In the penetration zone of q = 0.23 sample (Figure 10(a)), alumina and spinel are still present after the corrosion test. However, gehlenite has decreased and iron-rich phases (Fe2SiO4) have been created as the reaction of slags and the refractory occurred. In fact, iron oxide attacked phases with low chemical resistance or low melting temperatures. On the other hand, the new hibonite ((Ca,Fe)(Al,Ti,Mg)12O19) phase was created which acts as a protective layer [15].

It was observed that the main phase in the penetration zone of C1, C2, C4 samples is still alumina. The spinel phase is also present. The intensity of spinel diffraction peak in C1, C2, C4 samples does not change. This can be due to the fixed ratio between alumina and magnesia in the raw material. However, the gehelenite's
The relative intensity has been reduced by slag attacking. The iron silicate phase (Fe$_2$SiO$_4$) which had been formed in the penetration region of q = 0.23 sample was decreased in C samples. The Hibonite phase was also present in various compositions. It has the highest relative intensity in C2, while almost disappeared in C4. The relative intensity of the hibonite peak was low in q = 0.23 and C1 samples.

The relative intensity of alumina diffraction peaks in the C2 sample was reduced, which may be due to the use of alumina to form hibonite. C4 sample has a lower hibonite phase and higher porosity, and also it has higher corrosion resistance compared to the C1. This could be due to the higher amount of zirconia phase in the matrix of C4. A small peak of zircon (ZrSiO$_4$) was observed in the C4 sample. The reaction of zirconia with the slag’s SiO$_2$ prevents the C4’s matrix from the more slag attack and forbids the low-temperature phase formation.

**Figure 6.** Corrosion and penetration indexes of the prepared samples.

**Figure 7.** Microstructure of the prepared samples (a) q = 0.23, (b) C1, (c) C2, (d) C4 after sintering at 1620°C for 2 h.
Figure 11(a) shows the boundary between the penetration zone and C4 sample (white line). The left side is the penetration zone (with slag composition and refractory including SiO$_2$, Na$_2$O, K$_2$O, CaO) and the right side is refractory (aggregate with Alumina). Energy dispersive spectrometry (EDS) analysis of the white line is shown in Figure 11(b). The amount of CaO in the boundary was more than 10 wt.%, while it is known that this should be less than 0.3 wt.%. The presence of calcium oxide may lead to the low-temperature phase formation. The presence of a high percentage of CaO in the boundary layer is due to the high amount of CaO in the slag. CaO was not present in the refractory and this makes a gradient of CaO at this boundary. In fact, this gradient could be one of the main reasons for the higher corrosion of the C4 sample compared to the C2 sample. The hibonite phase may be formed, but due to the gradient and the high ratio of CaO it may convert to a low-temperature
phase such as CA2. The event that occurs in tabular alumina aggregate can be summarized in Figure 12. By the reaction among the aggregate and slag, the slag penetrates into the some of the coarse porosity of the aggregate and enhances the corrosion [16].

During the reaction between the aggregate and the slag, the slag penetrates into the some of the larger aggregate pores, intensifying the corrosion. However, small pores help nucleated phases such as hibonite, which acts as a protective layer. Figure 12 is given to a better understanding of what is happening in aggregate. During the reaction between refractory and slag, slag can penetrate the refractory pores and intensifies the corrosion. Aggregates are generally much less porous than the other areas of refractory that they could be corrosion resistant. However, the corrosion occurred in the aggregate. By slag penetration into the pores, the composition of pores changes which the corrosion developed.

Figure 10. XRD of the penetration area (a) q = 0.23, (b) C1, (c) C2, (d) C4 samples after the corrosion test.

Figure 11. (a) The boundary between penetration zone and refractory of C4 sample, (b) EDS analysis of point F.

Figure 12. Schematic of the slag and aggregate before (up) and after penetration (down) of the slag to the aggregate.
4. Conclusions

Low-cemented alumina mixes were prepared and the effects of 1, 2, and 4 wt.% added colloidal zirconia on its porosity, microstructure, and corrosion resistance were investigated. Colloidal zirconia was also prepared in this study and the cement content of alumina refractory has been replaced by colloidal zirconia. The corrosion resistance of alumina refractory was improved by adding 2 wt. % of colloidal zirconia, while the porosity was increased. In the samples using 2 wt.% of colloidal zirconia (C2 sample), the new-formed phase acted as a protective layer against the attack of the slag and pronounced as the main factor in the improvement of the corrosion resistance. Corrosion resistance was also improved by adding 4 wt.% of colloidal zirconia while, adding 1 wt.% of colloidal zirconia (C1) had not a remarkable effect. Zircon formation by adding 4 wt.% of colloidal zirconia (C4) was responsible for the improvement of corrosion resistance. Adding colloidal zirconia with different particle size distribution and sinterability properties of the alumina refractory by optimized size distribution needs more compatibility of particle size distribution and homogenous mixing. The difference in thermal expansion coefficient and sinterability between the matrix and colloidal zirconia may be considered as a negative effect on the densification.

Note

1. A magnesia refractory is defined by the American Society for Testing and Materials (ASTM) as a dead-burned refractory material consisting predominantly of crystalline magnesium oxide (MgO). Magnesite is delivered in three forms as the following: (1) Brute; (2) Calcined at 850°C; (3) Dead burned and agglomerated bricks at 1500–1800°C. In fact, dead-burned magnesia has been calcined at temperatures ranging from 1500°C to 2000°C in a high-temperature shaft kiln yielding a material with very little reactivity. Dead-burnt magnesia does not exhibit high reaction rates in comparison to caustic magnesia at high temperatures, however, and its low reactivity can be used to control the formation of brucite in a microstructure. Dead-burnt magnesia's behavior, therefore, results in fewer drawbacks during the initial processing steps of magnesia-containing castables.

Disclosure statement

No potential conflict of interest was reported by the authors.