

## Colloidal zirconia on corrosion resistance of low cemented alumina mixes against steel slag

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### 1-Introduction

The developments of major refractory consumers such as the steel industry exert pressure on the refractory industry to increase their quality. Corrosion of refractories in the steel industry halts production, reduces productivity, and increases costs. Therefore, corrosion improvement in refractory materials is of great importance. In the corrosion process, the matrix is the first area which was attacked; as a result, the composition of the matrix has an important effect on the resistance to corrosion. The most commonly used bonding system in refractory mass is calcium aluminate cement, but due to the presence of calcium oxide, this combination allows for low temperature phases and a loss of properties. For this reason, various bonding systems have been developed for the connection over time. Colloidal bonds such as colloid silica and colloid alumina can be named in this regard. The purpose of this project is to investigate the effects of colloidal zirconia on the development of corrosion of refractories.

### 2-Experimental

Raw materials were tabular alumina (0-4 mm) as aggregates, 5% Calcium aluminate cement as a bonding system, 3% microsilica as filler, 3% dead burned magnesia and Colloidal Zirconia with 20 wt% Solid loading. Dolapix CE64 and sodium tripolyphosphate (TPP) were used as dispersant and citric acid as a stabilizing agent. 1, 2 and 4 wt.% of zirconia replaced to the cement amount in the mix. The distribution of particle size of aggregate mass was determined using the modified Andreasen model. The coefficient of Andreasen ( $q$ ) was 0.23. The raw materials were dry mixed for 1 minute and wet mixed for about 4 minutes in a Hobart mixture. The samples were dried at ambient temperature for 12 h and dried at 110 °C for 12 h. To perform a corrosion test, a cavity was created at a depth of 2 cm in the samples and 3g of arc furnace slag of Mobarakeh Steel Company was poured into it. Samples were placed at 1620 °C for 2 hours.

### Results and Discussion

The porosity of samples C1, C2 and C4 after drying indicated that the porosity was reduced by replacing 1% of the cement with colloidal zirconia in the C1 sample, which may have been more densification occurred due to the fineness of zirconia particles. However, porosity

increased slightly in two other examples which involved the creation of bubbles in mass after the addition of colloid. The porosity of samples with colloidal zirconia after sintering at 1620 °C was higher than the reference sample. With less cement, low temperature phases which helped the sintering of the body are less formed. The cross-sectional images of samples were examined after corrosion testing. Corrosion and penetration rate was measured by the SPIP software (Figure 1). The percentage of corrosion in the C2 sample was better than the C1 and C4 samples. It can be claimed that a great improvement in the corrosion resistance of this sample was obtained. This is due to the higher porosity in the C2 sample than the C4 and  $q = 0.24$  samples. But the resistance to penetration of these specimens has decreased compared to reference, which could be due to an increase in porosity in these specimens.

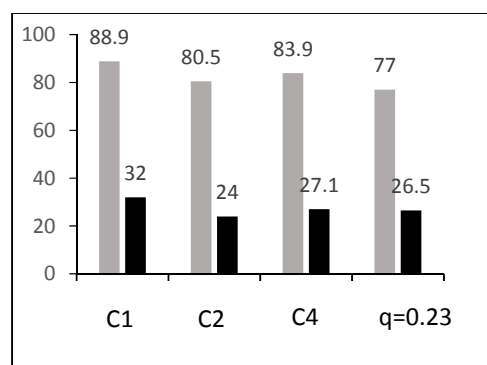


Figure 1. Corrosion and penetration in the sample

The microstructure of the samples after sintering at 1620 °C for 2 h is shown in Figure 2. The porous matrix and the gap between the matrix and the aggregate are seen. The matrix shrinks during sintering due to low temperature phases but aggregate does not participate in the sintering. Another factor is the formation of the spinel phase with increasing volume. Increasing volume can also fill porosity and it can also lead to microcracks formation. This contraction and expansion were relatively balanced in the sample  $q=0.23$ . Although the densification in the C2 sample is not higher than the other specimens, but its corrosion resistance was better. Probably, in this sample, the effect of composition is greater than the effect of densification.

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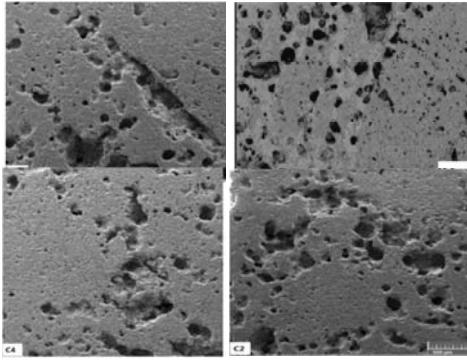


Figure 2. Microstructure of the samples after sintering at 1620 °C for 2 h

In the sample  $q=0.23$ , there was a large porosity at the contact surface of the slag and refractory because of the dissolution of matrix in the slag. In samples C1 and C4, the boundary between the penetration zone and the refractory was not detectable but the porous layer was seen at the interface of refractory/slag contact. In the sample C2, density was higher at the interface of refractory/slag contact and there was less porosity around the aggregates. Main phases of the samples were alumina and spinel (Figure 3) that the percentage of spinel does not change much. The gellenite phase is reduced by slag attack. The iron silicate phase was formed in the penetration region of  $q=0.23$  sample. Hibonite has the highest intensity in C2 sample and is low in  $q=0.23$  and C1 samples. Despite the lower Hibonite phase and the higher porosity in the C4 sample than the C1 sample, corrosion is lower at C4. This can be attributed to the presence of Zirconia in the matrix of this composition. A small zircon peak was observed in the composition of this sample. Zirconia reacts with the  $SiO_2$  from the slag and preventing its attacking the field and forming low temperature phases.

The incident that occurs in tabular alumina aggregates can be shown in Figure 4. It seems that during the reaction between aggregates and slag, the slag penetrates into some of the aggregates porosity and accelerates the corrosion.

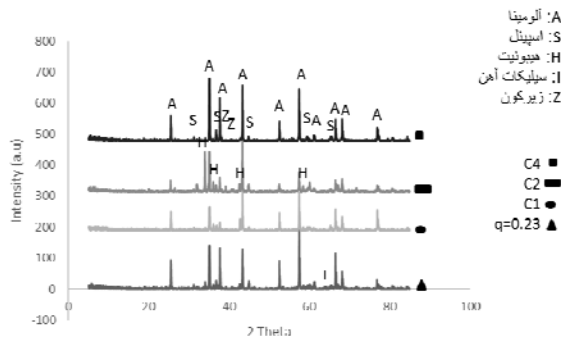


Figure 3. Comparison of x-ray diffraction of the penetration region of  $q=0.23$ , C1, C2 and C4.

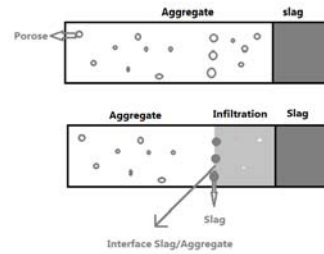


Figure 4. A large image of the slag penetration into the aggregate

## 5- Conclusion

Low cemented alumina mixes were prepared and the effects of 1, 2, and 4 wt.% added colloidal zirconia on its the porosity, microstructure and corrosion resistance was investigated. Colloidal zirconia was also prepared in this study and the cement content of alumina refractory has been replaced by colloidal zirconia. 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 1wt.% of colloidal zirconia had not a remarkable effect. Zircon formation by adding 4wt.% of colloidal zirconia 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 of thermal expansion coefficient and sinterability between the matrix and colloidal zirconia may be considered as a negative effect on the densification