

Effect of Combining Hydraulic and Phosphate Bonds on Alumina-Spinel Low Cement Castables

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Abstract

A basic alumina-spinel low cement castable (LCC) composed of sintered bauxite, reactive alumina, calcined alumina, calcined magnesia, microsilica, and high alumina refractory cement was prepared (castable A) to which 5% sodium hexa-meta phosphate was later added (castable B) to prepare samples for heat treatment at 110°C, 900°C, and 1400°C. Bulk Density (BD), Apparent Porosity (AP), and Cold Crushing Strength (CCS) were measured and XRD and SEM studies were performed. It was shown that after heat treating at 110°C, CCS of castable B increased by more than 3 times while its AP value was less than half that of castable A. The main difference between the two samples was found to lie in the presence of $Mg_2P_2O_7$ and $AlPO_4 \cdot 2H_2O$ which are responsible for increases in CCS. At the temperature range of 800-1000°C where the hydraulic bond reverses to the dehydrated condition and castable A becomes weak with high porosity, castable B showed a CCS value of more than 4 times. Needles of magnesium phosphate were found to be responsible for reinforcing the microstructure of castable B at 900°C. After firing at 1400°C, castable B showed extraordinary CCS values of up to 100 MPa (about 1000 Kg/Cm²), 5 times stronger, and AP% of below 1/5 times that of castable A. The phases present after firing were alumina, Al_2O_3 , spinel, $MgAl_2O_4$, calcium phosphate, $Ca_3(PO_4)_2$ and Enstatite, and $MgSiO_3$. Magnesium phosphate melted at 1300-1400°C and aided the formation of ceramic bonds. The Ca coming from calcium aluminate cement reacted with phosphate and developed refractory calcium phosphate.

Keywords: Powders-solid state reaction, Microstructure, Strength, Spinel, Refractories.

1- Introduction

Monolithic and castable refractories have great potentials for future use, particularly in the iron and steel industries. In the field of monolithic refractories, strong and stable bonds based on a lower cost/performance ratio are needed¹⁾. The bonds currently used in refractory castables are: hydraulic bonds, chemical bonds, and ceramic bonds.

Hydraulic bonds are based on high alumina cements (HAC) which play an important role as the binder in castables due to their good performance and properties. Calcium aluminate cement reacts with water (H) and forms a series of calcium aluminate hydrate phases. Depending on temperature and time, different forms of hydrates such as CAH_{10} , C_2AH_8 , C_3AH_6 , and AH_3 may be produced in which C, A, and H stand for CaO , Al_2O_3 , and H_2O , respectively²⁾. However, the major problem with the use of these bonds is the reduced strength due to the breakup of

the hydraulic bond at temperatures as low as 200-800°C³⁾. This was one of the reasons for developing low cement castables (LCC).

The forms of chemical bonds used in refractory castables are silicate, phosphate, chromate, and sulphate binders. It has been shown that phosphate binders provide improved high-temperature mechanical properties than silicate or sulphate binders do⁴⁻⁷⁾. It has also been observed that sodium hexa meta phosphate has greater effects in improving these same properties⁸⁾. In this case, the nature of the phosphate bond changes during the setting process. When mixed with water, phosphate binder initially forms a gel. During use, and as the temperature of the material increases from room temperature to about 1300°C, the bond changes from a gel bond to a chemical one⁹⁾. At higher temperatures, ceramic bond formation takes place by the inter-diffusion of atoms and ions among the components to develop an energetically stable structure because of the temperature increase during steel processing¹⁰⁾.

Considering the fact that each of these bonds is effective over a special range of temperature, using a combination of them could be promising as it may lead to improved physical properties of LCC over a wider range of temperatures, given the efficiency of each type of bond over a specific temperature range. In this work, alumina magnesia LCC containing both the phosphate bond and the hydraulic bond is

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produced and the physical properties of the obtained castables are measured at temperatures of 110°C, 900°C, and 1400°C. A precise XRD phase analysis and SEM observation of the microstructure are performed.

2- Experimental

The raw materials used in this study consist of sintered bauxite from China, reactive and calcined alumina from Alcoa Co., calcined magnesia from Birjand mines in Iran with a purity of about 92%, microsilica as a by-product of Azna Ferro Silica Products in Iran, and refractory cement of secar 71 from Lafarge Co. A fixed proportion of these raw materials were selected as a base of LCC and 5 wt% Sodium Hexa Meta Phosphate (P) from China was added on top of the base. The raw materials were thoroughly mixed in a laboratory mixer to which water was then added. The resulting pastes were then cast in 50×50×50mm moulds and vibrated for 60s. The samples were cured at room temperature for 24 hr. After forming, the samples were removed from the moulds and dried at 110°C for 2 hr. Some of the samples were subsequently fired at 900°C and 1400°C with a soaking time of 2 hr in an electrical furnace. Table (1) illustrates the samples and their corresponding heating temperatures and 5 wt% P. The castable samples were subsequently tested for cold crushing strength (CCS), bulk density, and apparent porosity according to ASTM standard C20. Cold crushing strength was measured by increasing force (F) on the cross sectional area of the sample (A) until fracture. The CCS value was equal to F/A. Bulk density was measured by dividing the weight W1 by volume $V=W2-W3$ in which W2 and W3 are saturated and suspended weights of the sample, respectively.

Table 1. Samples and their corresponding heating temperature and 5% P addition.

T(°C)	%P	Sample
110	0	A1
	5	B1
900	0	A2
	5	B2
1400	0	A3
	5	B3

The dried and fired castables were also characterized with respect to their solid phase composition and microstructure. XRD analysis was used for the qualitative determination of solid phase composition using a Philips 1730 diffractometer with Ni filtered Cu-K α radiation at a scan speed of 2 degrees 2 θ /min and a step size of 0.05. Finally, a Philips scanning electron microscope (SEM) was used to examine the microstructure of the samples.

3- Results and Discussion

Figures (1) to (3), respectively, show Apparent Porosity (AP, %), Bulk Density (BD, g/cm³), and Cold Crushing Strength (CCS, MPa) as a function of heating temperature (110°C, 900°C, and 1400°C) for samples without P (A₁, A₂, A₃) and with 5% P (B₁, B₂, B₃).

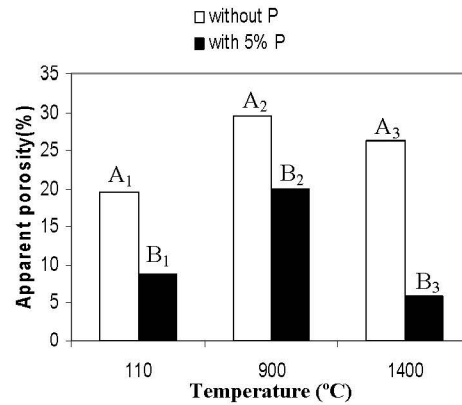


Fig. 1. Apparent porosity (%) versus heating temperature.

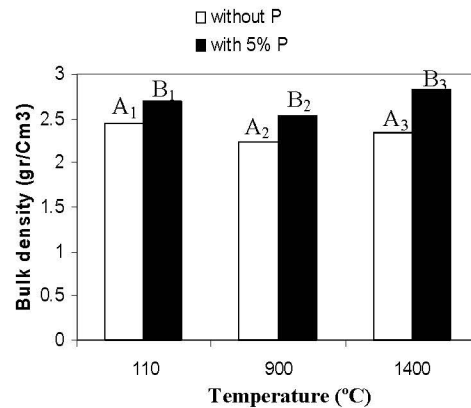


Fig. 2. Bulk density versus heating temperature.

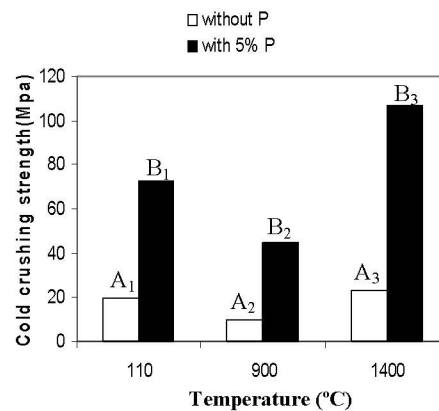


Fig. 3. Cold crushing strength versus heating temperature.

It is seen that at 110°C, both hydraulic and phosphate bonds are effective, but the comparison of samples

A_1 and B_1 in Figure (3) shows that the samples containing the phosphate bond are stronger by more than 3 times. The phosphate bond also decreases apparent porosity (Figure 1) and improves bulk density (Figure 2).

When the castable is heated to 900°C, the hydraulic bond becomes weak and the strength of sample A_2 declines to below half the strength observed at 110°C. This is a dangerous region in industrial applications as it causes serious failures in castables which must be naturally heated during use. If the castable comes into contact with molten metal and slag, the possibility of penetration into the castable will increase because then the hydraulic bond fails to hold the castable in place as it is expected to. This will lead to the evaporation of the hydraulic water and to the reversal of the cementation process. The main objective of the present study in combining the phosphate and the hydraulic bonds was to support the castable at this critical temperature, i.e., from 800°C to above 1000°C, which indicated promising results. The presence of the phosphate bond in sample B_2 compared to A_1 containing only the hydraulic bond increased strength by more than 4 times (Figure 3). The phosphate bond also had a positive effect on BD (Figure 2) and AP (Figure 1) as indicated by the comparison of sample B_2 with samples A_1 and A_2 .

By raising the temperature to 1400°C, the castables obtained the ceramic bond due to sintering. Sintering increases BD and strength but decreases AP. It is surprising that when 5% P was added to the LCC, CCS increased to the extremely high value of about 100 MPa, equivalent to around 1000 Kg/Cm², after reaching a high firing temperature of 1400°C. This is about 5 times the strength gained in the case of the hydraulic bond only (Compare samples B_3 and A_3 in Figure 3). This is accompanied by an extraordinary reduction in AP by about 5 times (Compare samples B_3 and A_3 in Figure 1). Generally speaking, the use of 5% P coupled with the hydraulic bond of the refractory cement in LCC improves almost all of the physical properties of the castable for the whole temperature range.

4- XRD Phase Analysis and Microstructure

4-1- Beyond a heating temperature of 110°C

Figure (4) shows the XRD phase analysis of sample A_1 heated to 110°C for 2 hr without P. The phases present consist of Al_2O_3 and MgO (remaining from the raw materials in the castable); Mullite (from the fired bauxite used); small amounts of $CaO \cdot 2Al_2O_3$ (CA_2) and $3CaO \cdot 5Al_2O_3$ (C_3A_5), remaining unreacted and not hydrated in the refractory cement; and $MgAl_2(OH)_8$ or $MgO \cdot Al_2O_3 \cdot 4H_2O$, which are the result of the reactions between calcined magnesite, calcined or reactive alumina, and water. Due to the similarities of this phase to spinel, $MgAl_2O_4$, or $MgO \cdot Al_2O_3$, it might be concluded that the phase could serve as a

base for the formation of fine and dispersed spinel in the castable at high temperatures.

Figure (5) shows the XRD phase analysis of sample B_1 heated to 110°C for 2 hr with 5% P. In addition to the phases alumina, magnesia, and mullite, phosphate phases such as $AlPO_4 \cdot 2H_2O$ or $Al_2O_3 \cdot P_2O_5 \cdot 4H_2O$ and $Mg_2P_2O_7$ or $2MgO \cdot P_2O_5$ could be detected, which are the results of chemical reactions of calcined magnesia and calcined or reactive alumina with P_2O_5 and water. Therefore, $MgO \cdot Al_2O_3 \cdot 4H_2O$ did not form. Traces of C_3AS ($3CaO \cdot Al_2O_3 \cdot SiO_2$) were also observed. The reason for the higher strength, higher density, and lower porosity of sample B_1 compared to sample A_1 can be attributed to the formation of the phosphate bonds.

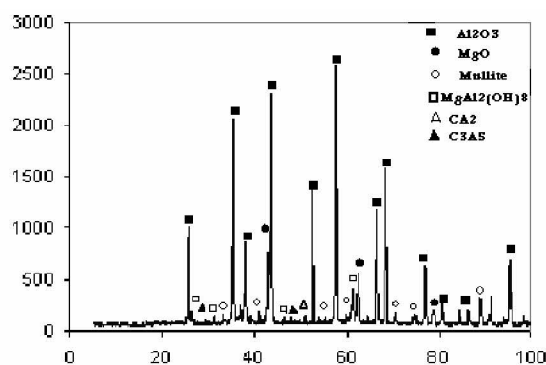


Fig. 4. XRD Analysis of A_1 (110°C, No P).

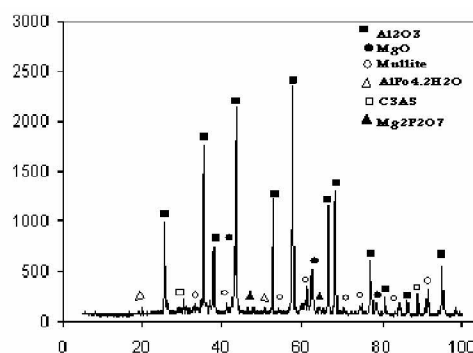


Fig. 5. XRD Analysis of B_1 (110°C, 5% P).

4-2- Beyond the heating temperature of 900°C

Figure (6) shows the XRD phase analysis of sample B_2 , heated to 900°C for 2 hr, without any phosphate bond. Al_2O_3 , MgO, and Mullite should come from the raw materials; CA_2 and C_3A_5 were detected from the remaining or probably hydrated and then dehydrated hydraulic bonds at 900°C. No hydrated product was detected.

Figure (7) illustrates SEM photomicrograph at 100X magnification. This sample had the lowest CCS among all the 6 samples (Figure 3), proving the weakness of ordinary low cement castables (LCC) used in the industry at this critical temperature while being heated up during application.

Figure (8) gives XRD information on phases developed in sample B_2 when heated to 900°C for 2

hr with 5% P. Phases like alumina, magnesia, and Mullite are due to the raw materials. The phases developed include $Mg_2P_2O_7$ ($2MgO.P_2O_5$), $Mg_3(PO_4)_2$ or $3MgO.P_2O_5$, $Ca_3(PO_4)_2$ or $3CaO.P_2O_5$, and $MgAl_2O_4$ (spinel $MgO.Al_2O_3$). The structure is more compact than the one in Figure (7) (See Figure 9) with a lower porosity. The CCS value of sample B_2 is greater than 4 times that of A_2 . The explanation for this might be derived from Figure (10) showing needles of magnesium phosphate at 3200X that reinforce the microstructure. This Figure clearly illustrates how the needles join individual particles in sample B_2 . The fact that spinel is formed in B_2 , and not yet in A_2 , indicates that phosphate bonds facilitate the formation of such high-temperature phases, which might be related to the high compaction of the matrix of B_2 castable.

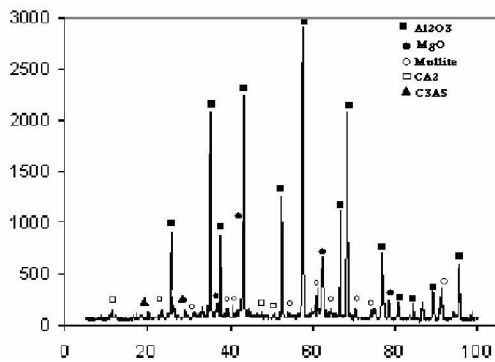


Fig. 6. XRD Analysis of A_2 (900°C, No P).

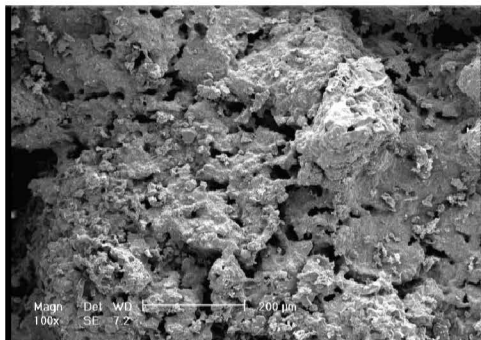


Fig. 7. SEM image of sample A_2 at 100X (900°C, No P).

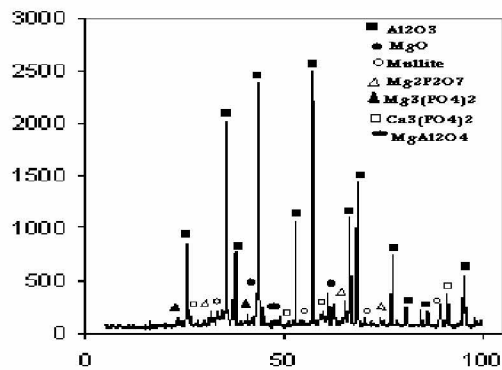


Fig. 8 XRD analysis of B_2 (900°C, 5% P).

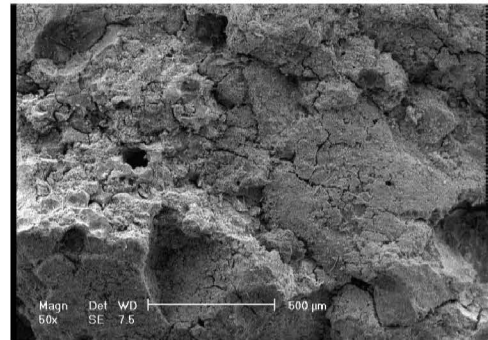


Fig. 9. SEM image of sample B_2 at 50X (900°C, 5% P).

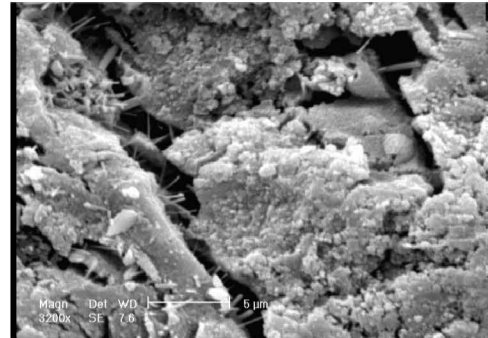


Fig. 10. Needles of magnesium phosphate in B_2 .

4-3- Beyond the firing temperature of 1400°C

Figure (13) shows XRD phases present in A_3 after 2 hr of heat treatment at 1400°C. Phases such as alumina and mullite do exist, but MgO reacted with Al_2O_3 to form spinel $MgAl_2O_4$ ($MgO.Al_2O_3$) and with SiO_2 to form Enstatite, $MgSiO_3$ ($MgO.SiO_2$).

No evidence could be found to indicate any remaining MgO. Hibonite, CA_6 ($CaO.6Al_2O_3$), also formed due to the reaction of calcium aluminates from the refractory cement with available alumina. Ceramic bonds also developed as a result of sintering. Sintering of fine alumina particles is obvious at higher magnifications (Figure 12, SEM, 1600 X).

Figure (13) reveals phases present in B_3 , fired to 1400°C with 5% P. As in all the other samples, alumina was the main matrix of LCC. Magnesia had reacted with alumina to form spinel, $MgAl_2O_4$, and with silica to form Enstatite, $MgSiO_3$. Calcium phosphate, $Ca_3(PO_4)_2$ or $3CaO.P_2O_5$, was the predominant high-temperature phosphate phase. Magnesium phosphates melted due to their low melting point below 1400°C (for example, $Mg_3(PO_4)_2$ melts at 1357°C). The melting of these phases aided ceramic bonds to form and were partly responsible for the rather high values of CCS of up 100 MPa. It is likely that the melting has also dissolved mullite and prevented the formation of Hibonite (CA_6). It must be noted that the amount of phosphate addition in the LCC should be less than 5% to avoid extensive melting. If melting exceeds a

certain limit, serious damage might be inflicted to the refractoriness under load (RUL) of the LCC. The Ca coming from calcium aluminate refractory cement in LCC is helpful in the development of calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, which is a refractory phosphate, with a melting point of 1730°C . Even the eutectic point of $\text{Ca}_3(\text{PO}_4)_2$ and Al_2O_3 is high enough (1678°C)¹¹ to support refractoriness.

Figure (14) illustrates how alumina particles are sintered to make a strong body (SEM, 1600X). It should be noticed that needles of magnesium phosphate observed in sample B₂ (Figure 10) melted and disappeared in sample B₃ (Figure 14).

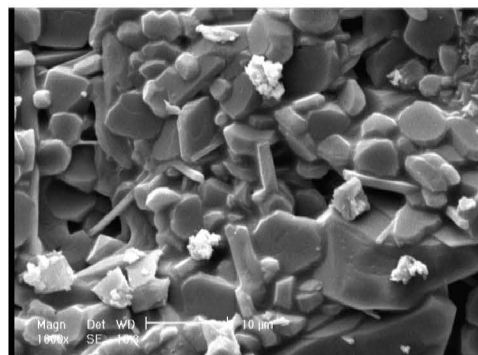


Fig. 14. Alumina particles are sintered in B₃.

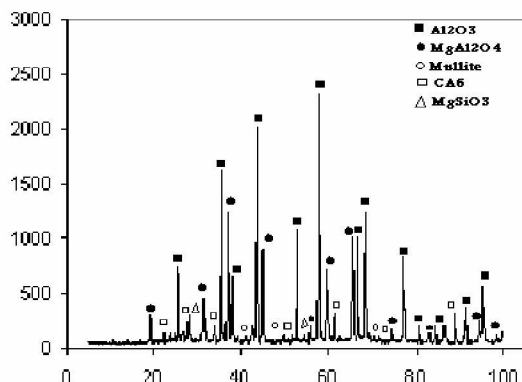


Fig. 11. XRD analysis of A₃ (1400°C, No P).

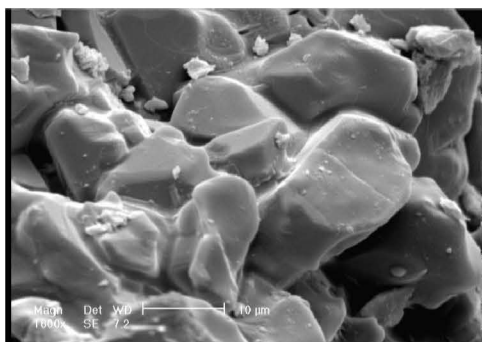


Fig. 12. Sintering of fine alumina particles of A₃ (SEM, 1600X).

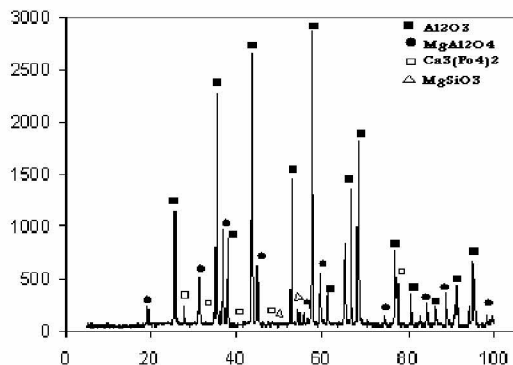


Fig. 13. XRD analysis of B₃ (1400°C, 5% P).

Conclusion

Combination of phosphate and hydraulic bonds at low temperatures gives rise to a mixture of calcium phosphate bond and strong ceramic bond at high temperatures that provides superior properties over an extensive temperature range in low cement castable. This process is especially useful at a temperature range of $800\text{-}1000^\circ\text{C}$ where the hydraulic bond is destroyed.

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