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Short Communication

Development and Evaluation of the Magnesium Potassium Phosphate Cement Based Refractory

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ABSTRACT

In this work, the phosphate bonded refractory was developed using magnesium potassium phosphate cement. The Cement was prepared from the caustic calcined magnesium oxide with the addition of mono potassium phosphate. The characterization of the cement was done by XRD and SEM to examine the change in phase and morphology which occurs after the hydration of magnesium potassium phosphate cement which is in the struvite phase. To evaluate the physical, mechanical and thermal properties, refractory samples were casted and subsequently dried and fired at temperatures ranged from 1300 °C to 1500 °C. The effect of temperature on the bulk density, apparent porosity and crushing strength were analyzed. It was found that the properties of the chemically bonded refractory were better than the conventionally bonded calcium alumina cement refractory.

1. Introduction

Phosphate bonded materials exhibit an increase in the strength on heating [1]. They remain highly refractory and possess good wear resistance after heating [2]. The properties of the phosphate bonded castable depend on the type and amount of the bonding agent used and the type and grading of the aggregate used. The acids of phosphate are claimed to result in much higher strengths than the metal phosphates [3]. Phosphoric acid is the preferred binder for attaining the maximum bond strength and the hygroscopic tendencies of these compositions can be eliminated by curing at 350 °C [4, 5]. The high bond strength, dimensional stability and resistance to wear are retained at temperatures of above 1200 °C in these compounds and resistance to wear improved by the use of acids of phosphates [6]. Stiffening and the subsequent loss of the work ability observed in phosphate-bonded high-Al_2O_3 refractories are believed to be caused by the precipitation of insoluble orthophosphates formed as a result of the reaction between acid salts and Al_2O_3 bearing materials in the mix [7].

The main objectives of the project work were:

- To develop magnesium phosphate cement.
- To develop chemically bonded phosphate

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refractory by magnesium phosphate cement.

- To investigate the physical, thermal and mechanical properties of the refractory.
- To compare the results of properties with convention calcium alumina refractory.

2. Materials and methods

2.1. Preparation of the caustic calcined magnesia (CCM)

A known amount of pure magnesium oxide in the powder form was mixed with a known caustic soda. The sufficient amount of water was added to the mixture and the slurry was stirred by using a clean glass rod. The mixture formed semi-solid mass which was dried in oven at 110 °C for 5 h to remove moisture. The dried material was then transferred to the clean refractory crucible and calcined in the furnace at 1000 °C for 2 h. After cooling, the agglomerates were grinded and sieved through 120 mesh.

2.2. Preparation of the magnesium potassium phosphate cement slurry

The prepared caustic calcined magnesia (CCM) powder was mixed with distilled water to form a slurry to which mono basic Potassium Phosphate (MKP) was added with continuous while stirring by using a clean glass rod. Due to the fast reaction between CCM and MKP, the cement material hardens quickly. To retard this rapid setting, a small quantity of boric acid was added to the mixture. Boric acid reduces the rate of reaction between CCM and MKP and gives sufficient time to work withit.

2.3. Preparation of magnesium potassium phosphate refractory

The raw material was weighed depending on the respective percentages and then it was mixed with the magnesium phosphate cement slurry (the percentage of added binder is varied to better analyze properties). Water is added (up to 4 to 6 wt %) to the mixture wich was poured inside the moulds of different shapes and allowed for vibration for few min. Due to the vibration the aggregates and matrix occupy the shape of the moulds and they are then allowed to cure. After curing, in order to remove the moisture, they are dried for 5 hours at 110 °C. After drying they are sintered at the temperature of 1300 °C to 1500 °C to be provided with strength. They are being tested for analysis of physical, mechanical and thermal properties.

2.4. Characterization of magnesium potassium phosphate refractory

2.4.1. Phase analysis by XRD

The samples for X-ray diffraction were prepared by crushing the fired samples into the fine powder. The XRD patterns were recorded over the Bragg's angle (2Θ) range 10^{o}-40^{o} using Philips X-ray diffractometer and diffraction patterns were recorded.

2.4.2. Apparent porosity and the bulk density

Samples were placed in a water bath and saturated for 1 hour. After removing the specimens Afre removing the specimens from the water bath, the amount of the saturated water was calculated by the difference between the initial and final weights. From recorded weights, apparent porosity and bulk density were calculated with the equations (1) and (2) respectively.

$$\text{Apparent porosity} = \frac{\text{Saturated weight} - \text{Dry weight}}{\text{Saturated weight} - \text{Suspended weight}} \times 100 \qquad (1)$$

$$\text{Bulk density } \left(\frac{g}{cc}\right) = \frac{\text{Dry weight of sample}}{\text{Saturated weight} - \text{Suspended weight}} \times 100 \quad (2)$$

2.4.3. Crushing strength

The compressive strength of a material is an indication of the strength of the refractory used in the lining of furnaces and other high temperature application units. It is a measure of both strength and also bonding system for the refractory.

The crushing strength of the sample was measured by placing the sample on a flat surface followed by the application of a uniform load to it. The load is applied through a standard mechanical or hydraulic compression. The load at which the specimen shows cracking represents the crushing strength of the specimen. The load applied on the refractory specimen is uniform on a flat position. The crushing strength was expressed in MPa.

2.4.4. Refractoriness under load (RUL)

It is measuring the refractory of specimen with a combined effect of heat and load. A cylindrical sample with the dimensions of 5 cm in diameter by 5 cm in height was used. It was placed between two graphite cylinders. A load of 2 kg/cm^2 was applied on the sample. The changes in the dimensions of the specimen caused by heating were measured by the dial gauge apparatus. The change in temperature was measured by an optical pyrometer. The load at which the height of the specimen decreases by 20 mm from its original height at a corresponding temperature denotes the RUL value.

2.4.5. High temperature abrasion resistance

The specimen was placed inside the furnace and heated up to 1000 °C. After reaching the target temperature, the material was soaked for half an hour. Then 1 kg of silicon carbide sand is passed inside the furnace with a high pressured compressed air at the pressure of 4.5 kg/cm^2 through the nozzle. The time of passing it was noted down. Then the furnace was allowed to cool till reaching room temperature. Then the change in the weight was calculated. Experiment is repeated for different angles.

3. Results and discussion

3.1. Characterization of the cement

The prepared magnesium potassium phosphate cement was tested for the phase analysis and microstructure analyses. Refractory samples were tested for the physical, mechanical and thermal properties and results were compared with those of ceramic calcium alumina cement bonded refractories.

3.1.1. Phase analysis of the cement

The XRD patterns of magnesium phosphate cement paste prepared with magnesium oxide and calcined magnesium oxide are shown in Figures 1 and 2. There are two phase crystal products in the XRD patterns, one phase is the unreacted periclase of magnesium oxide (P), and the other phase is the struvite of magnesium potassium phosphate (M), $MgKPO_4.6H_2O$ (MKP). The caustic calcined magnesia has a high intensity, and does not react completely during the hydration due to the presence of crystalline phases.

There are many diffused diffraction peaks observed around the main highly diffracted peaks. The peaks show that the struvite exists in the crystal form and the amorphous form. The cement prepared with uncalcined magnesium oxide is amorphous but has smaller particles, whereas calcined magnesium oxide is less amorphous and has bigger particles. This is due to the fact that the amorphous struvite has a continuous structure and can fill the voids of the grains. The formation of the amorphous struvite has a significant effect on the paste's character. Periclase is of the crystalline material and at the higher temperature softens and becomes reaction resistant. Other materials like calcium expand due to the low softening point. Magnesium potassium phosphate shows both crystalline and amorphous characters.

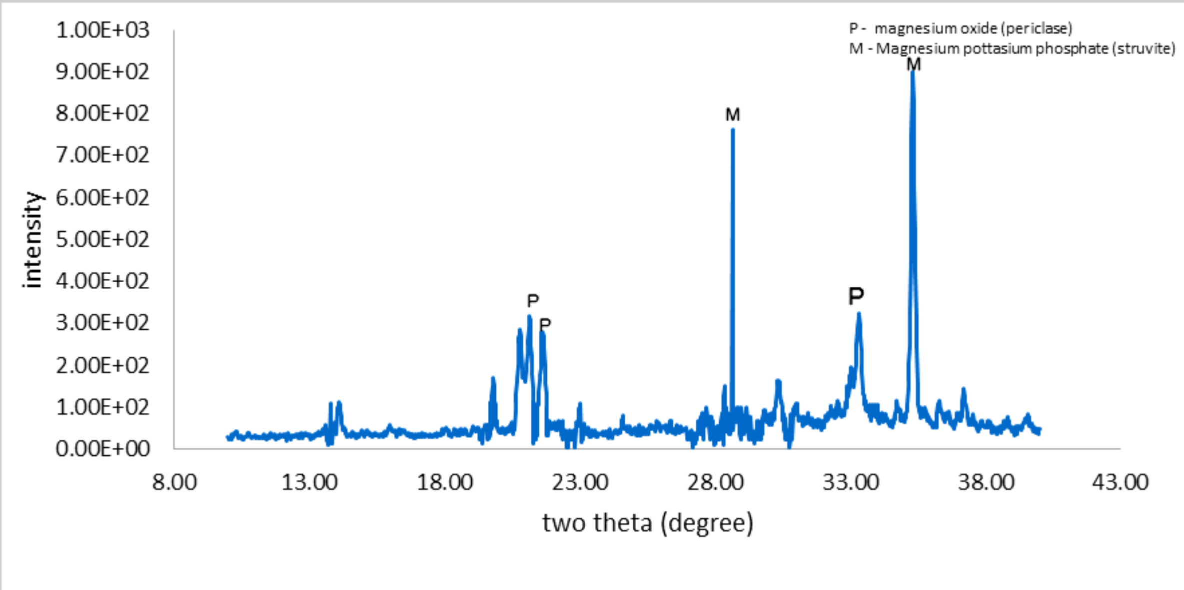

Figure 1. XRD pattern of the cement prepared with uncalcined magnesium oxide.

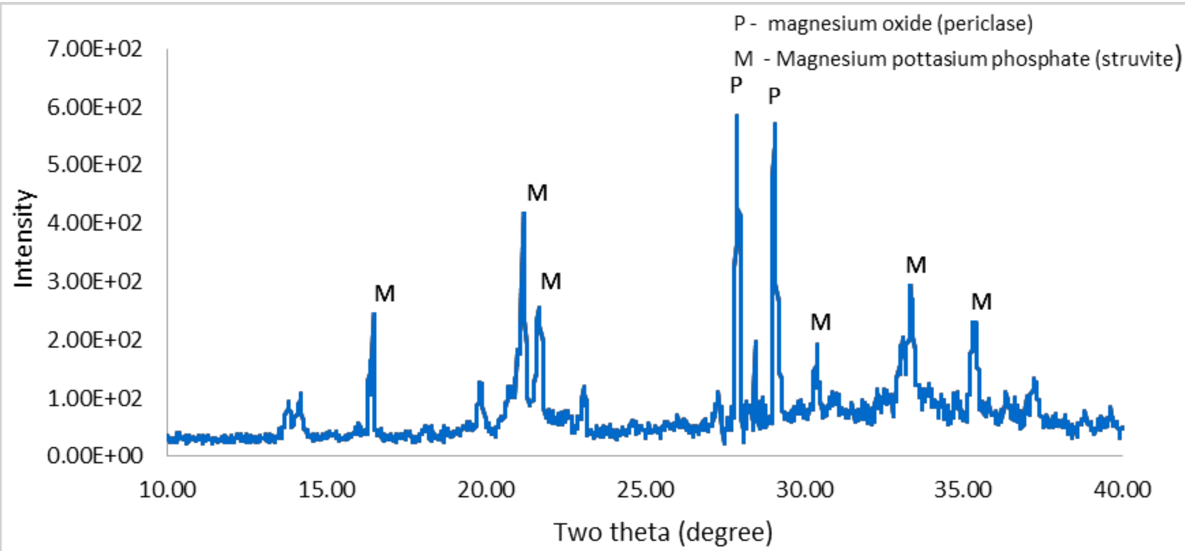

Figure 2. XRD pattern of the cement prepared with calcined magnesium oxide.

3.1.2. Microstructural analysis of the cement by SEM

The calcination of magnesium oxide at 1000 °C reduces the porosity of particular grains by increasing the particle size. The cement prepared with magnesium oxide when observed under an electron microscope, shows porous structure whereas the cement prepared with calcined magnesium oxide is a hard mass and has bigger particles.

The SEM images of the cement prepared with uncalcined and calcined MgO are depicted in Figures 3 and 4 respectively. The grain surface of the uncalcined powder appears to be covered with a powdery or microcrystalline substance, while the particle surface of the calcined powder appears smooth, indicating the reduction of the amorphous coating on individual grains that are resulted from the crystallization with an average particle size of 10 μm.

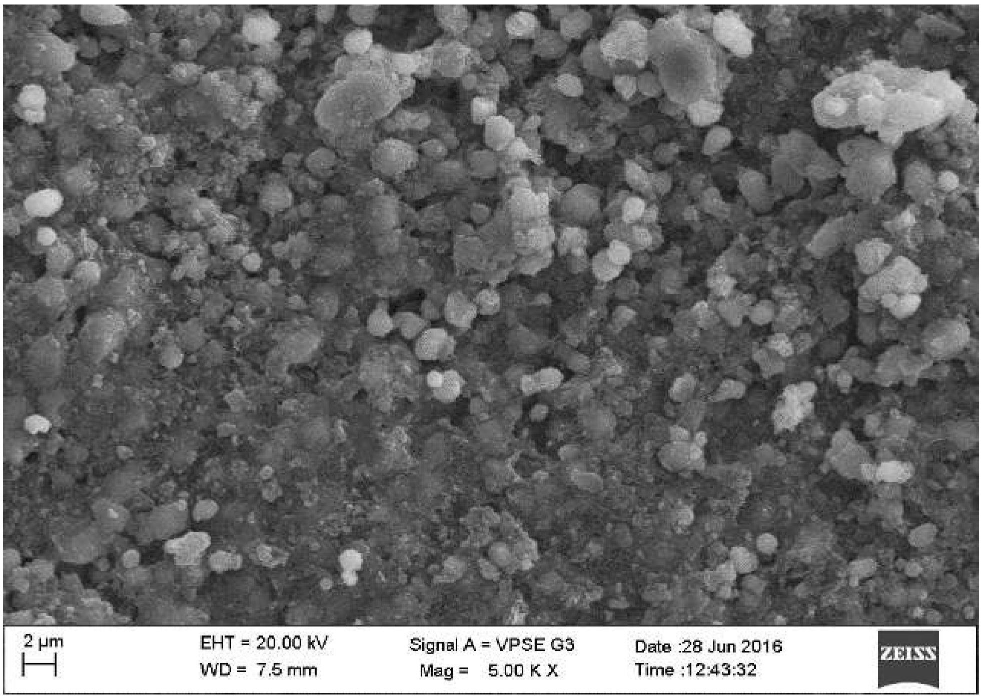

Figure 3. Cement prepared with uncalcined magnesium oxide.

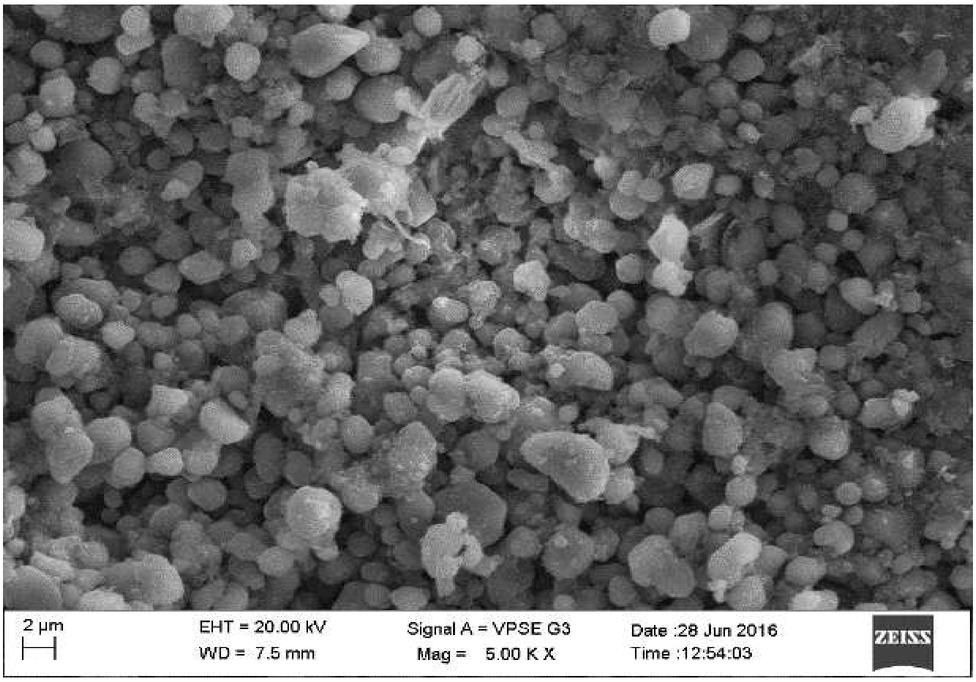

Figure 4. Cement prepared with calcined magnesium oxide.

3.2. Analysis of the physical properties of the casted refractory

3.2.1. Effect of the type of binder on the setting time of the casted refractory

In all specimens, the setting time of refractory is affected by the type and quantity of the binders used. Magnesium potassium phosphate bonded refractories showed a higher reduction in the setting time than the conventionally bonded ceramic calcium alumina cement refractories. The samples prepared with ceramic calcium alumina cement bond showed the longest setting time of 210 min (Figure 5). The setting time of magnesium potassium phosphate cement refractory was affected by the concentration of the bonding agent. In the casting of refractory castable, the magnesium phosphate bond (MKP-5 %), the setting starts from 21 min and continues to the final setting time of 170 min. However, an increase in the amount of the bonding agent decreases the setting time and affects the other properties of refractory castable.

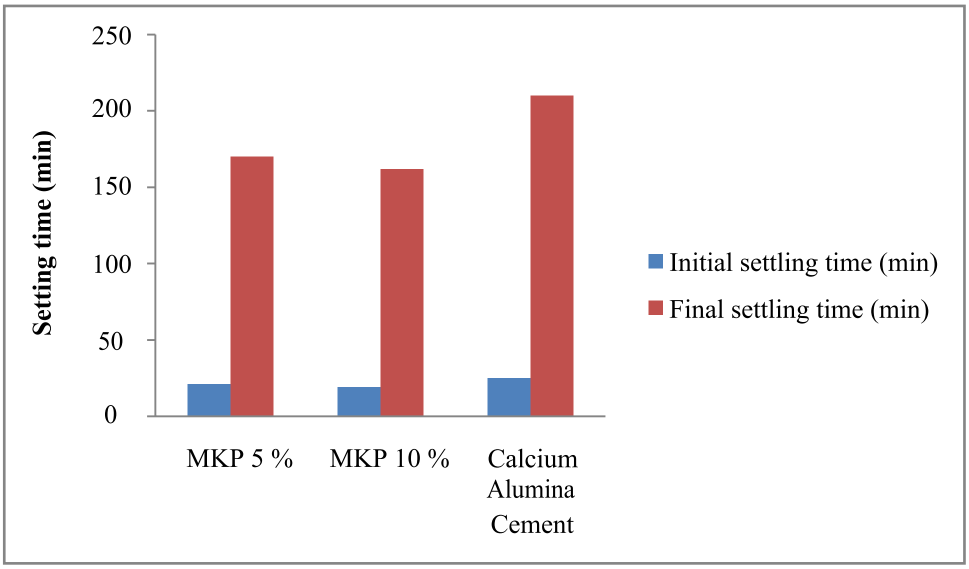

Figure 5. Comparison of the settling time of magnesium potassium phosphate cement with calcium alumina cement.

3.2.2. Effect of temperature on the bulk density of the casted refractory

The densification of the ceramic material improves with the increase in the sintering temperature [9]. Figure 6 shows the effect of temperature on the bulk density of magnesium phosphate cement and calcium alumina cement bonded refractory castable. For magnesium phosphate cement bonded refractory, the bulk density increases with increasing temperature (similar to ceramic calcium alumina bonded refractories). At temperatures<1400 °C, calcium alumina cement bonded refractories show low densities due to the higher sintering temperature of bonding. In contrast, the chemically bonded refractory castable developsthe bond strength at room temperature and magnesium phosphate starts developing the bond strength at 1200 °C.

3.2.3. Effect of temperature on the apparent porosity

The porosity of the specimen decreases with increasing the sintering temperature of material or by the softening of the specimen at higher temperatures. The formation of the amorphous phase in the composition helps with decreasing the porosity by filling the voids in the grain. Figure 7 shows the effect of temperature on the apparent porosity for chemical magnesium potassium phosphate and calcium alumina cement bonded materials. Similar to ceramic bonded refractory, magnesium phosphate cement bonded refractory exhibited a decrease in porosity with the increase in temperature. Ceramic calcium alumina cement bonded refractory showed the maximum porosity due to the weak bonding below 1400 ºC.

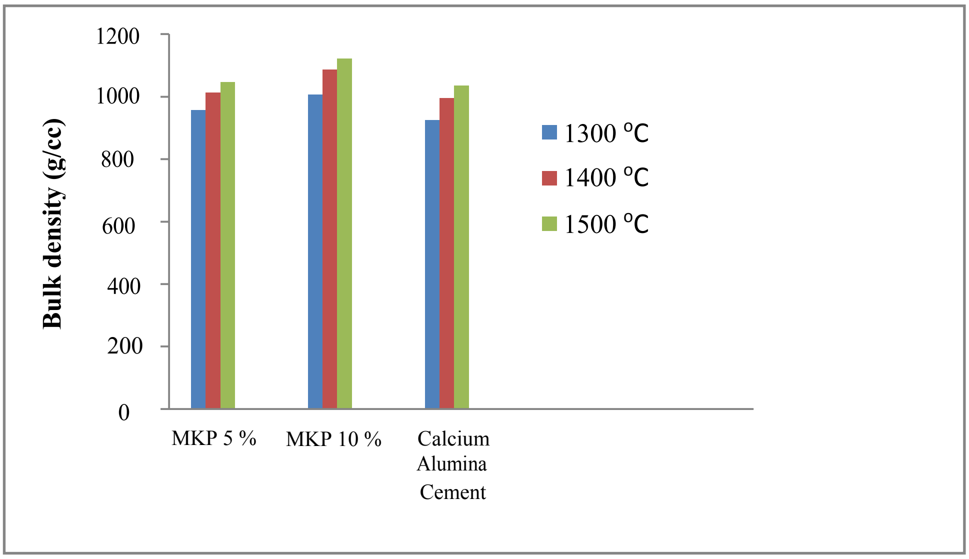

Figure 6. Effect of temperature on the bulk density.

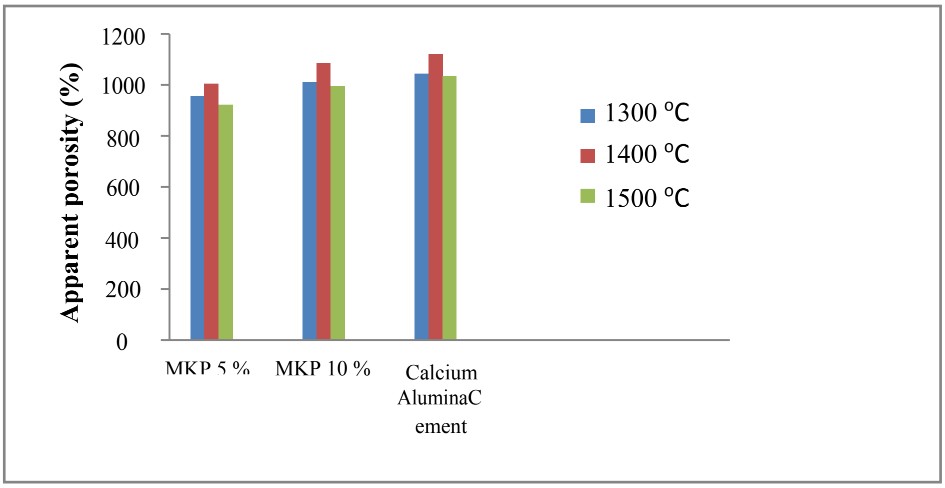

Figure 7. Effect of temperature on the apparent porosity.

3.2.4. Effect of temperature on the apparent porosity

The Cold Crushing Strength (CCS) depends on the bond strength and densification of the material after sintering. CCS values are normally higher when being sintered at higher temperatures due to the bonding between the grains and the fine powder. At temperatures above 1300 ºC, the refractory material shows better results. It is evident from Figure 8 that, refractories developed with magnesium phosphate bond result in better densification than refractories developed from calcium alumina cement. CCS increased with the increase in the sintering temperature and the highest value was observed for MKP-10 % (1121 kg/m^3). Thus, the 10 % addition of magnesium phosphate to the refractory exhibited the highest bond strength as compared to other types of the binding materials used.

3.2.5. High temperature abrasion

The high temperature abrasion is the key property for the refractory. Refractories which are used for high temperature applications must show resistance to the high temperature abrasion. When the specimen is heated at high temperatures, it loses mechanical properties due to the softening of materials, resulting in the weight loss of the specimen. Table 1 shows the results of the high temperature abrasion. It can be observed that, MKP-5 % and MKP-10 % refractories show lower erosion rates as compared to the calcium alumina refractory.

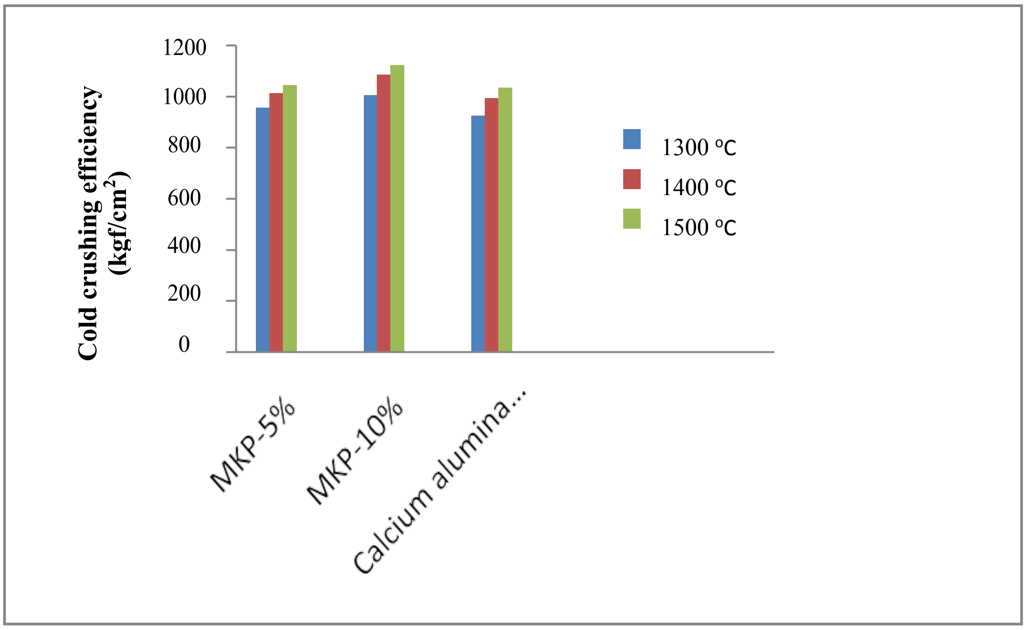

Figure 8. Effect of temperature on the cold crushing strength of the refractory.

Table 1
Results of the high temperature corrosion.

Angle (°)	Type of bond	Weight loss (g)	Bulk density (g/cc)	Volume loss (cc)	Average erosion rate (g/min)	Average erosion value (mm^3/g)
90	MS metal	3.5	7.85	445.8	0.4	0.76
	MKP-5 %	0.0041	3	1.4	0.138	0.6
	MKP-10 %	0.0037	3.29	1.11	0.123	0.5
	CA Cement	0.0052	3.03	1.7	0.18	0.8
30	MS metal	2.7	7.8	346.15	0.31	0.6
	MKP-5 %	0.0027	3	0.9	0.115	0.5
	MKP-10 %	0.0023	3.3	0.7	0.1	0.4
	CA Cement	0.0037	3.03	1.2	0.138	0.63

3.2.6. Refractory under load RUL

Refractoriness under load is the melting or softening temperature for a material under similar conditions corresponding to the disrupt or breakage of the test specimen. The test specimen comprises a cylinder of 50 mm of diameter and 50 mm of height. The refractory under load depends on the bond strength of refractories.

Table 2
Results of the RUL of the refractory.

	Temperature of deformation specimen fire at different temperatures in °C	
Type of bond	1300	1400
MKP-5 %	1430	1510
MKP-10 %	1500	1510
CA Cement	1530	1480

At high temperatures, magnesium phosphate bonded refractories shrink due to the crystallization of magnesium oxide in it. Calcium (ceramic bonded) based bonds expand due to the low melting point as they lose the bond strength at high temperatures. From Table 2, the refractories of magnesium phosphate bond sintered at high temperatures showed a high strength at high temperatures of up to 1510 °C.

4. Conclusions

Magnesium potassium phosphate cement was prepared using the caustic MgO and potassium phosphate and used in the developing refractory castable. The cement formed having used the caustic MgO (calcined with NaOH) showed a faster setting (8 min) than the cement formed having used uncalcined MgO (25 min). After setting, the phases formed were struvite ($MgKO_4.6H_2O$) and periclase (MgO). SEM images showed a larger grain size after setting (10 microns) in case of the caustic MgO (calcined with NaOH) cement and uncalcined MgO cement showed 3 microns.

The apparent porosity and bulk density of the magnesium phosphate bonded refractories showed a slight increase with the increase in the sintering temperature from 1300 °C to 1500 °C, whereas calcium alumina cement shows poor results below 1400 °C. At higher temperatures, the magnesium phosphate bonded refractories showed the high crushing strength of above 1000 kg/cm^2. The weight loss due to the wear of magnesium phosphate bonded refractories was less than the same in the calcium alumina bonded refractories at room and high temperatures (1000 °C) i.e. below 0.7 mm^3/g.

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