

Improving Deskulling Properties of Tundish Linings by some Sulphate Binders

Some phosphates normally used as binders for the expendable lining of tundishes develop as sintering aids and chemical bonding agents as well as lowering the melting point of the host oxide MgO, thus making deskulling difficult and sometimes impossible. In the present paper, three sulphate binders of $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$, $\text{CaSO}_4 \cdot 0,5 \text{H}_2\text{O}$ and $\text{Al}_2(\text{SO}_4)_3 \cdot 16 \text{H}_2\text{O}$ were studied at 110, 1100 and 1400 °C and the mechanical and physical properties of the samples were measured. The results together with SEM and XRD analyses show that magnesium sulphate is a suitable bond which provides high strength at 110 °C and dissociates to MgO (s) and SO_3 (g) at slightly more than 1100 °C with no side effects on deskulling. Aluminium sulphate was the next and calcium sulphate the least effective in providing the desired properties.

Seyed Moosa Siadati
Ahmad Monshi

Department of Materials Engineering
Isfahan University of Technology
Isfahan, 84156, Iran

Corresponding author:
s_m_siadati@ma.iut.ac.ir.

Table 1 Size density

Grain Size / mm	Bulk Density / g/cm ³	Na ₂ O + K ₂ O	Fe ₂ O ₃	CaO	SiO ₂	MgO
0 – 1	3,33	0,2	1	3,3	4,5	0,91

Introduction

A tundish is an intermediate vessel used in the continuous casting of metals; it is provided with a permanent lining of high temperature resistant refractory material, usually high alumina bricks or castables. But the contact with molten metal and slag is through a disposable lining which acts as a thermal and chemical barrier. This lining is based on magnesia (MgO) [1–2], a suitable binder and a density reducing fibre such as pulp, fibre glass, slag wool, etc.

The binder is selected from the group of phosphates including sodium hexametaphosphate, tripolyphosphate, potassium phosphate, ammonium phosphate, magnesium phosphate, calcium phosphate and/or from the group of silicates such as water glass (sodium silicate). The disposable lining might be trowellable, gunnable or sprayable. As the disposable lining material has a coefficient of thermal expansion that differs from that of the permanent lining, one would expect that its deskulling or removal can be easily accomplished due to shrinkage differences. However, alkali oxides, such as Na₂O and K₂O can react with the permanent lining material at elevated temperatures of steel-making and force the two refractories to fuse in some areas [3], causing difficulties for deskulling and letting the disposable lining penetrate into the depth of the permanent lining. Inorganic phosphates, often favoured in refractory formulations, undergo chemical bonding reactions with the host oxides at temperatures as low as 1000 °C, and the polyvalent nature of the P atom leads to cross-link bonding in the host structure of MgO [4]. As a result of both the sintering aid alkaline oxides fusing with refractory materials and chemical bonding reactions of phosphates with MgO, deskulling of

the disposable lining becomes difficult and the permanent lining can be damaged during the deskulling process. In addition, contamination of the permanent lining caused by fusion of the expendable lining increases the coefficient of thermal expansion on the surface of the permanent lining, and the difference in the expansion rate of the surface and the remainder of the lining can result in spalling and premature failure. In this regard, three sulphates of $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$, $\text{CaSO}_4 \cdot 0,5 \text{H}_2\text{O}$ and $\text{Al}_2(\text{SO}_4)_3 \cdot 16 \text{H}_2\text{O}$ are compared in this study as binders to improve deskulling properties, increase the life of the lining and reduce losses. A combination of phosphate binders such as sodium tripolyphosphate and sodium hexametaphosphate were added to improve both the green and firing strengths of tundish lining mixtures [5]. This might increase the side effect of the phosphate bonds.

Experimental Procedure

Sintered magnesia from Birjand mines in Iran, with the analysis given in Table 1, was employed as the aggregate. For the binder studies, 95 % of aggregate was mixed with 5 % of three kinds of sulphates, $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$ (sample A), $\text{CaSO}_4 \cdot 0,5 \text{H}_2\text{O}$ (sample B) and $\text{Al}_2(\text{SO}_4)_3 \cdot 16 \text{H}_2\text{O}$ (sample C) with 10 %, 12,5 % and 11,7 % water respectively to obtain a comparable mass. Samples were cast in 125 cm³ steel moulds and kept for one day. Then, in groups of 3 samples each, they were treated at room temperature (25 °C), dried at 110 °C for 2 h, fired at 1100 °C for 3 h, and fired at 1400 °C for 3 h. The mechanical test of cold crushing strength (CCS, MPa) according to ASTM C-133-97 and physical tests of apparent porosity (AP, %) and bulk density (g/cm³) according to ASTM C-20-92 were evaluated.

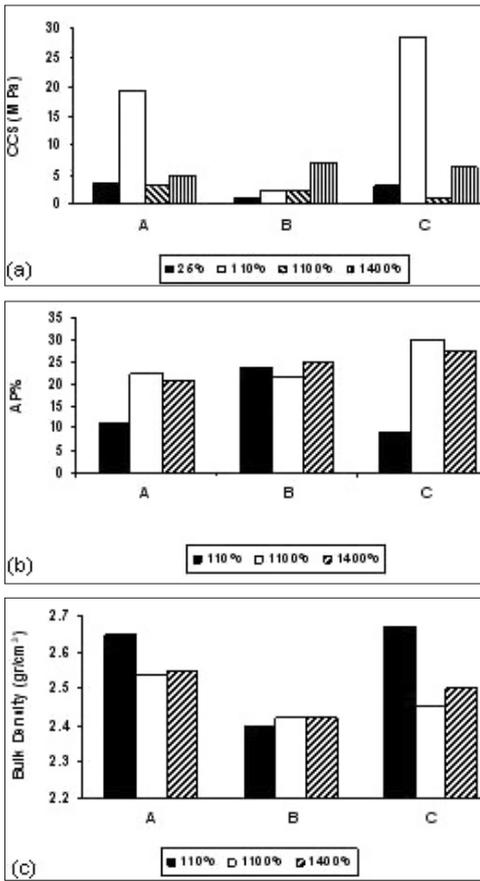


Fig.1 Mechanical properties of samples with different binders after different heat treatments, a) Cold crushing strength, b) Apparent porosity, c) Bulk density

XRD and SEM studies were performed to make the comparison between the samples possible.

Results and Discussion

Fig.1 shows the CCS of sample A ($MgSO_4 \cdot 7 H_2O$ binder), sample B ($CaSO_4 \cdot 0,5 H_2O$ binder) and sample C ($Al_2(SO_4)_3 \cdot 16 H_2O$ binder) after different heat treatments. Suitable binders are considered as having higher strengths at low temperatures to support the application of lining and avoid spalling and rupture while the heavy tundish is being mo-

Table 2 Some comparative data of three binders

SO ₃	pH	CCS / MPa	CCS / MPa	CCS / MPa	CCS / MPa	Binder
%		1400 °C	1100 °C	110 °C	25 °C	
70	3,6	6,2	0,9	28,5	3	$Al_2(SO_4)_3 \cdot H_2O$
66	4,4	5	3	19,3	3,5	$MgSO_4 \cdot 7 H_2O$
58	11,2	7	2	2,3	1	$CaSO_4 \cdot 0,5 H_2O$

ved, but not those which provide sintering aids, and not those which develop high CCS when fired at high temperatures. In this regard, samples A and C are favourable. Fig. 1 also illustrates bulk density and AP of samples. Bulk density of sample B is generally lower showing a lower bonding effect of $CaSO_4 \cdot 0,5 H_2O$.

Fig. 2 compares SEM photomicrographs of three samples after drying at 110 °C. Flaky phase is developed in samples A and C, but not in B. This is most probably related to strength development which, in turn, is very likely caused by magnesium sulphate cement. The cementing effect is due to the reaction of basic MgO and acidic SO₃. The cement is dispersed throughout the refractory mass. The amount of this MgO-SO₃ cement is observed in C more than in A, which is in agreement with the increased CCS in Fig. 1. Fig. 3 shows XRD results of sample A. The phases at 110 °C are MgO, Mg(OH)₂ and magnesium sulphate. At 1100 °C Mg(OH)₂ has disappeared and magnesium sulphate is reduced. At 1400 °C MgSO₄ is eliminated and enstatite, MgSiO₃ and forsterite Mg₂SiO₄ develop in small amounts as reaction products of MgO with SiO₂ impurities. Fig. 4 shows XRD results of sample B. Mg(OH)₂ is observed at 110 °C and eliminated at 1400 °C, as expected, but CaSO₄ remains. Peaks of MgO are shifted to lower 2θ values. This is explained by the fact that some CaO is replaced with some MgO of periclase as solid solution at 1400 °C. Ca²⁺ (r = 0,99 Å) is a larger ion than Mg²⁺

(r = 0,66 Å) and such a replacement increases the interplanar distance d. When Bragg's Law is employed $n\lambda = 2d \sin\theta$ with n = 1 and λ = 1,5045 Å for Cu Kα radiation, then sinθ and therefore 2θ are reduced.

Fig. 6 shows SEM photographs of three samples fired at 1400 °C. There are no signs of melting in sample A, but evidence of melting is observed in samples B and C.

Conclusions

Magnesium sulphate is considered to be a very suitable binder for tundish lining materials. It shows high strength of nearly 200 kg/cm² when dried at 110 °C and dissociates to MgO (s) and SO₃ (g) at 1100 °C. This means that sintering aids, chemical bonds and melting effects coming from sodium tripolyphosphate and sodium hexametaphosphate, which are commonly used, cannot be observed. The final product at the high temperatures of steel making is the same as the host oxide, MgO. The reason why calcium sulphate is not as effective was studied. A prepared solution of $MgSO_4 \cdot 7 H_2O$ in water showed a pH of 4,5 (acidic), while the pH of $Al_2(SO_4)_3 \cdot 16 H_2O$ was 3,6 (acidic) and that of $CaSO_4 \cdot 0,5 H_2O$ was 11,2 (basic). The low temperature reaction with MgO (basic) is more favourable in magnesium sulphate and aluminium sulphate and is higher for the latter due to having a higher content of SO₃ = 70 %. With pre-heating of the tundish to 1200–1250 °C, SO₃ evaporated and the strength was reduced.

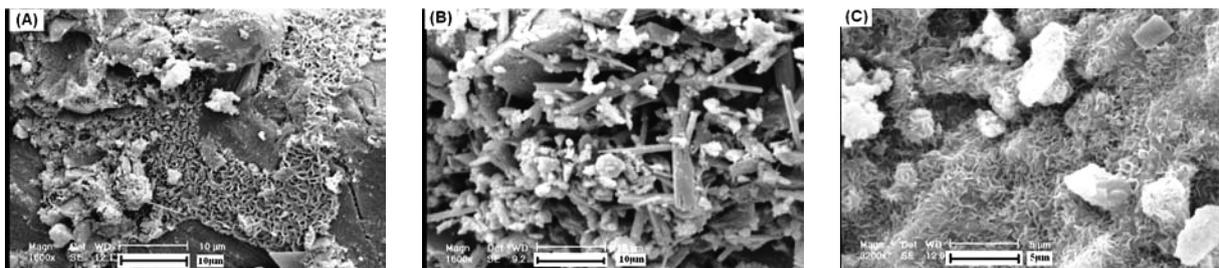


Fig. 2 SEM micrographs of samples A (1600x), B (1600x), C (3200x) at 110 °C

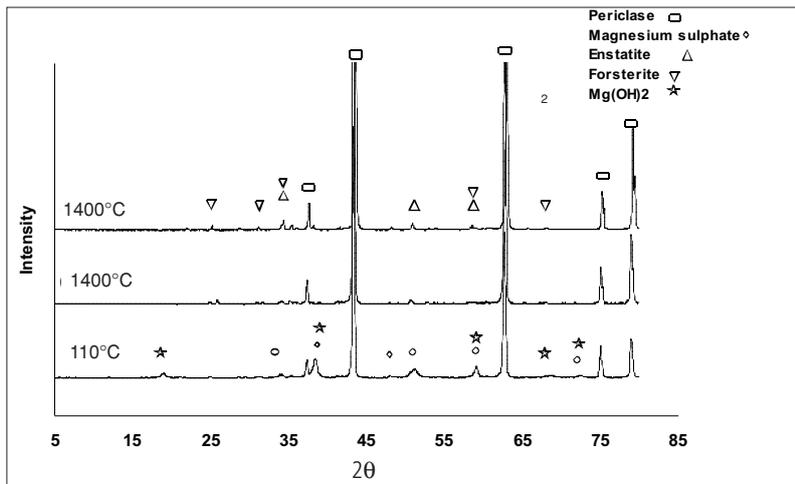


Fig. 3 XRD results of sample A with $MgSO_4 \cdot 7 H_2O$

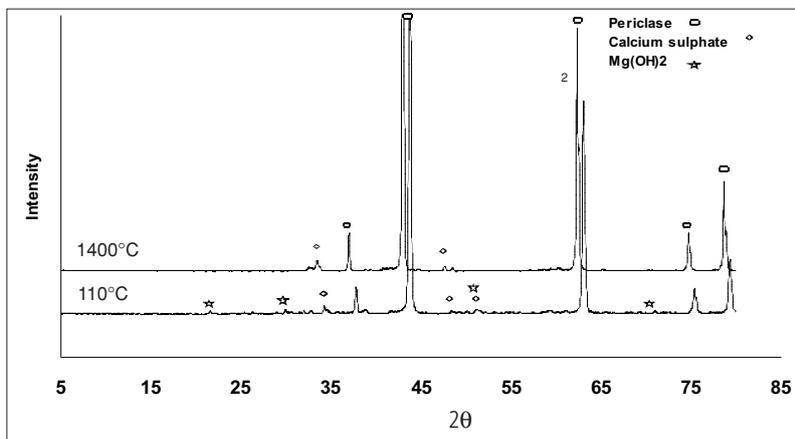


Fig. 4 XRD results of sample B with $CaSO_4 \cdot 0,5 H_2O$

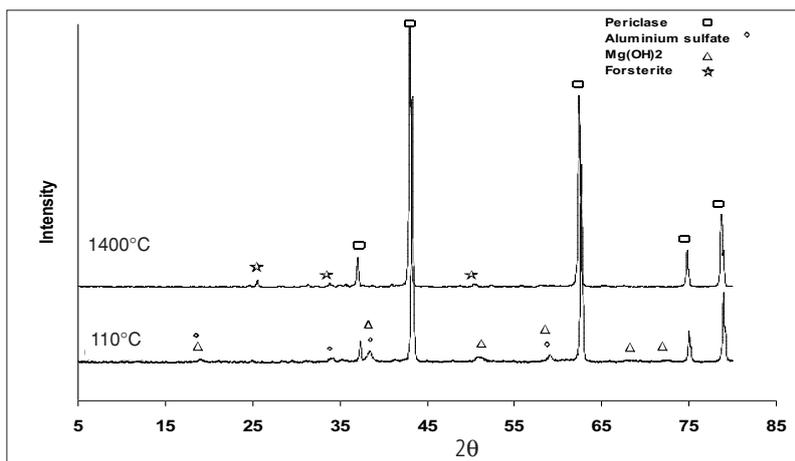


Fig. 5 XRD results of sample C with $Al_2(SO_4)_3 \cdot 16 H_2O$

This weakening is greater in aluminium sulphate. Al_2O_3 reacts with MgO at and above 1400 °C and provides higher strength (6,2 MPa). $MgSO_4 \cdot 7 H_2O$ is found to be the best. It provides adequate strength at 110 °C (drying) and 1100 °C (preheating of tundish),

but yields MgO at and above 1400 °C with no sintering and no side effect on deskulling. On the other hand, $CaSO_4$ was found to melt at about 1450 °C and play the role of a sintering aid, which is not favourable.

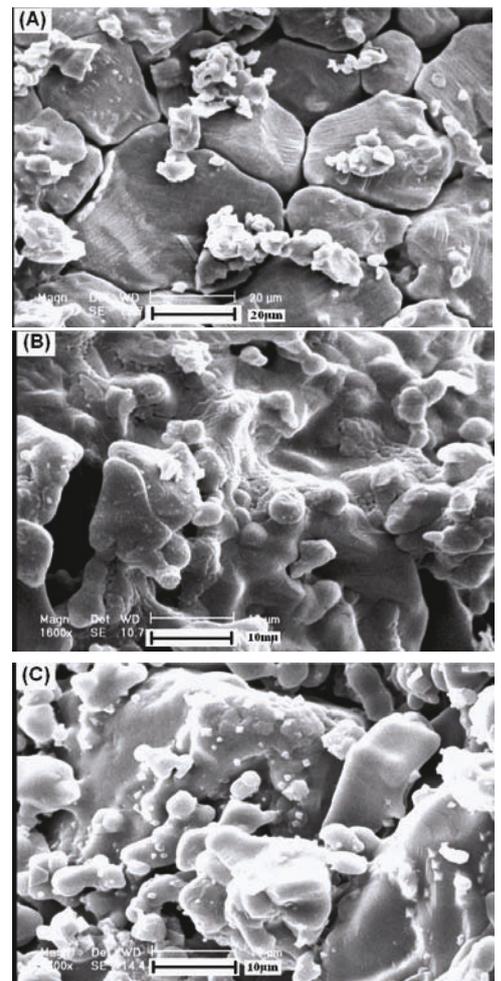


Fig. 6 SEM photographs of three samples fired at 1400 °C

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