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Acidic and basic binders for magnesite based aggregate in plaster of tundish

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Abstract

Binders are generally inorganic, organic or organomineral and have an important influence on the performance and corrosion resistance of slag line and deskulling. Since silicate and phosphate binders have some side effects, in this work sulphate binders such as sulphamic acid, H_2NSO_3H; aluminum sulphate, $Al_2(SO_4)_3$; ammonium sulphate, $(NH_4)_2SO_4$; magnesium sulphate, $MgSO_4$; calcium sulphate, $CaSO_4$; sodium sulphate, Na_2SO_4; and potassium sulphate, K_2SO_4, are investigated. Cold crushing strength at different heat treatments of room temperature, 110 °C, 1100 °C, 1400 °C is measured. Apparent porosity of samples without pulp and bulk density together with pH of the binder solution is evaluated and XRD and SEM studies are performed. Among these sulphate binders $MgSO_4$ was found to be the best. It is acidic in nature and develops strong bonds to the basic aggregate, MgO, at low temperatures. At high temperatures it dissociates from MgO(s) and SO_3(g) and the remained portion of MgO is the same as host oxide, with no corrosion and easy deskulling. Basic binders such as calcium sulphate, sodium sulphate and potassium sulphate could not strongly bond the MgO aggregates.

Keywords: A. Sintering; C. Strength; D. MgO; E. Refractories

1. Introduction

Binders for refractories are classified according to Table 1 [1]. The laboratory tests usually performed for a suitable binder are pH, chemical composition, binding properties or the time–temperature relation to setting and ultimate compressive strength. Refractories for the consumer are frequently discussed [2–4].

Tundish is composed of a permanent layer, which is usually a high alumina brick or monolithic, and a consumable lining to protect the permanent layer, which has usually high magnesite base. The most popular mixture is a refractory plaster containing over 85% MgO (periclase). Scandinavian countries widely use a mixture based on olivine (magnesium silicate or Forsterite based, Mg_2SiO_4) [2]. The Forsterite–periclase compounds were used as monolithic tundish linings in the case of water glass as a binder and a hardener [3]. As the first approximation the mechanism of hardeningthe mixture of water glass with the self-dispersing ferrochrome slag (hardener) may be represented in the following manner:

$$Na_2O \cdot SiO_2 \cdot nH_2O + 2CaO \cdot SiO_2 + H_2O \rightarrow Na_2O \cdot mCaO \cdot \rho SiO_2 \cdot nH_2O + Si(OH)_4 \quad (1)$$

In heat treatment above 400 °C the sodium disilicate reacts with calcium orthosilicate with the formation of alkali-lime silicate:

$$Na_2O \cdot 2SiO_2 + 2CaO \cdot SiO_2 \rightarrow Na_2O \cdot 2CaO \cdot 3SiO_2 \quad (2)$$

which is analog of the mineral combeite.

It is obvious that the binder of tundish plaster has an important role in the reaction with slag and base of the refractory, which leads to high influence on corrosion resistance and performance of the product. Tundish plaster should have a high level of porosity to be insulator. The drop in temperature from the molten steel is shown in Fig. 1 [4].

The continuation of temperature drop is shown when the tundish is normal with a previously heated brick lining (curve 1) and with a cold lining (curve 2). The porosity is performed usually by a burning filler such as pulp, or volume increasing

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Table 1
Classification of binders for refractories [1].

Number	Type	Group	Basic process of structure formation
1	Inorganic	1.1. Clays with water	Coagulation–adhesion
		1.2. Clays with salt solutions	Solvation
		1.3. Ceramic suspension	Polymerization–condensation
		1.4. Sol–gel binders	The same
		1.5. Hydraulically hardening binders	Hydration–condensation
		1.6. Solutions of salts, acids, or bases	Formation of new compound and their polycondensation
		1.7. Thermal benders	SHS
		1.8. Ceramic binders	Sintering upon heating: endogenic processes, endothermal binders
		1.9. Condensed dispersions	Formation of aqua sols
		1.10. Inorganic binders	Polymerization–condensation
2	Organic	2.1. Hydrocarbon	Polymerization and polycondensation
		2.1.1. High-carbon	
		2.1.2. Medium-carbon	
		2.1.3. Low-carbon	
		2.2. Organo silicon	
		2.2.1. Organofluorine	
		2.2.2. Organometalic	
		2.3. Organo nanobinders	
3	Organomineral	3.1. Mechanical mixtures of solid organic and mineral substances ($S_1 + S_2$)	Polymerization and polycondensation
		3.2. Mixtures of inorganic acids and sols with liquid organic substances ($L_1 + L_2$)	Synthesis of new hetero-organic compounds
		3.3. Mixtures of solid and liquid organic and mineral substances (S + L)	
		3.4. Organomineral nanobinders	

material. High fraction of porosity in the tundish plaster increases the possibility of steel melt and slag penetration into plaster and the damage by reaction and corrosion. Therefore the binder plays a very important role in corrosion resistance.

The binder is selected from the group of phosphates such as sodium hexa meta phosphate, tri-poly phosphate, potassium phosphate, ammonium phosphate, magnesium phosphate, calcium phosphate and or the group of silicates such as water glass (sodium silicate).

The disposable liner might be trowellable, gunnable or sprayable. As the disposable lining material has a coefficient of thermal expansion that differs from that of the permanent liner, it would be expected that deskulling or removal of the coating would be easily accomplished due to shrinkage differences.

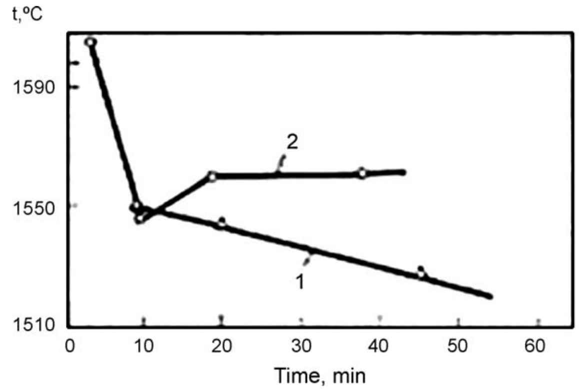

Fig. 1. The drop in temperature when the tundish has a normal previously heated brick (curve 1) and cold lining (curve 2) [4].

However, alkali oxides, such as Na_2O and K_2O can react with the permanent lining material at elevated temperatures of steel making and force the two refractories to fuse at some areas [5], causing difficulties for deskulling and penetrating into depth of permanent lining. Inorganic phosphates often favoured in refractory formulations, undergo chemical bonding reactions with the host oxides at a temperature as low as 1000 °C and the polyvalent nature of the P atom leads to cross-link bonding in the host structure of MgO [6].

As a result of both sintering aid of alkaline oxides with refractory materials and chemical bonding reactions of phosphates with MgO, deskulling of liner becomes difficult and the permanent lining can be damaged during the deskulling process.

In addition, contamination of the permanent layer caused by the fusion of expendable liner increases the coefficient of thermal expansion of the surface of the permanent layer, and the difference in the rate of expansion of the surface and the remainder of the layer can result in sheet spalling and premature failure. Combination of phosphate binders such as sodium tri-poly phosphate and sodium hexa meta phosphate have been added to improve both green and firing strength of tundish coating mixtures [7]. This might increase the side effect of phosphate bonds.

Magnesia refractories bonded with sulphamic acid together with boric acid, chrome oxide (Cr_2O_3) and calcium nitrate are studied [8] with special attention on gunning mixes. High hot crush strength is obtained at 1000 °C firing when 2.0% sulphamic acid, 0.5% chrome oxide and 0.5% calcium nitrate are added as binder to 96.5% magnesite refractory grains of 98% MgO purity.

Table 2
Analysis of sintered magnesia used in the samples.

MgO	SiO_2	CaO	Fe_2O_3	Al_2O_3	$Na_2O + K_2O$	LOI	Bulk density (g/cm^3)	Grain size (mm)
91	4.5	3.3	0.8	0.3	0.1	0.2	3.33	0–1

The patent claims that up to about 10% by weight of sulphamic acid as a binder and a maximum of 5% boric acid can be used. Sulphamic acid reacts readily with periclase grain and forms a ceramic binder system when used with boric acid and ceramic sintering aids, such as Cr_2O_3 and $Ca(NO_3)_2$. Yousheng et al. have worked on magnesia based dry vibrating mix for tundish, which is a relating new technology, and concluded that $Na_2SiO_3 \cdot 5H_2O$ was an environment friendly binder though magnesia based vibrating mix had higher cold crushing strength after heat treated at $250\,^{\circ}C \times 24\,h$, $1100\,^{\circ}C \times 3\,h$, $1500\,^{\circ}C \times 3\,h$ separately when phenolic resin and boric acid used as binder [9]. Inorganic binders are used to stabilize the lining at high temperatures. The thermal shock resistance of periclase is relatively low. Therefore, and for the purpose of drying, the tundish lining is pre-heated to temperatures of up to 1250 °C prior to the lining being exposed to liquid steel [10]. Gas burners are used for heating. The open porosity of even to 50 vol.% might be produced that guarantees a low heat conductivity and consequently good isolation properties.

Another important factor is mineralogical and microstructural properties of sintered, dead burned, and or fused magnesia grains. Chemical analysis of the magnesia refractories derived from the firing of natural cryptocrystalline magnesia at various temperatures has shown [11] that their compositions lie essentially in the CaO–MgO–SiO_2 system. Their CaO and SiO_2 contents vary considerably but their variation is confined mainly to the periclase bond phases. The silicate phases coexisting with MgO differ substantially from those predicted to accrue on the basis of bulk CaO/SiO_2 ratios. The composition of periclase changes slowly with rising temperature. A limited CaO solubility in periclase crystals varies with temperature and/or the CaO/SiO_2 ratios. A low level of impurity and high sintering temperature gives lead to large crystals of periclase with a considerable degree of direct bonding. CaO, SiO_2, FeO and Al_2O_3 components present as impurities can react with MgO to produce a variety of calcium-silicate phases with different melting points such as Monticellite, Merwinite, Diopside, Akermanite, Rankinite, Wollastonite, Enstatite, Forsterite, Dicalcium silicate, tri calcium silicate and so on. It is obvious that not only the binder composition as the main constituent, but even the impurities associate with the binder play important roles in refractoriness and slag–plaster interactions. General performance, corrosion resistance and deskulling properties of tundish plaster are directly related to the binder.

Table 3
The binders and required water.

Sample code	Binder (4%)	Water %
AS	Sulphamic acid	10
AlS	Aluminum sulphate	11.7
AmS	Ammonium sulphate	11
MgS	Magnesium sulphate	10
CaS	Calcium sulphate	12.5
SoS	Sodium sulphate	11.5
PoS	Potassium sulphate	11.5

In this work a fundamental study is performed on some sulphate binders such as sulphamic acid, H_2NSO_3H; aluminum sulphate, $Al_2\ (SO_4)_3$; ammonium sulphate, $(NH_4)_2SO_4$; magnesium sulphate, $MgSO_4$; calcium sulphate, $CaSO_4$; sodium sulphate, Na_2SO_4; and potassium sulphate, K_2SO_4.

2. Experimental procedure

Sintered magnesia from Birjand mines in Iran, with the analysis given in Table 2, was employed as the aggregate. For binder studies 96% of aggregate was mixed with 4% of binders and with 10–12.5% water to obtain a comparable mass.

Different binders studied with the required water amount and sample codes are given in Table 3.

Samples were cast in 5 cm × 5 cm × 5 cm steel mold and kept for 1 day. Then in groups of three samples each case, were treated in 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. 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/cm^3) according to ASTM C-20-92 were evaluated. X-ray diffraction (XRD) and scanning electron microscope (SEM) studies were performed to make the comparison between the samples possible.

3. Results and discussion

Fig. 2 shows CCS of samples after different heat treatments. Suitable binders are considered as having higher strengths at low temperatures to support the application of coating and avoid spalling and rupture during the movement of the heavy tundish, but, not to provide sintering aids and not to develop high CCS when fired at high temperatures.

Sample AS showed the highest CCS at 25 °C and 110 °C. Sulphamic acid causes rapid hardening with the release of a lot

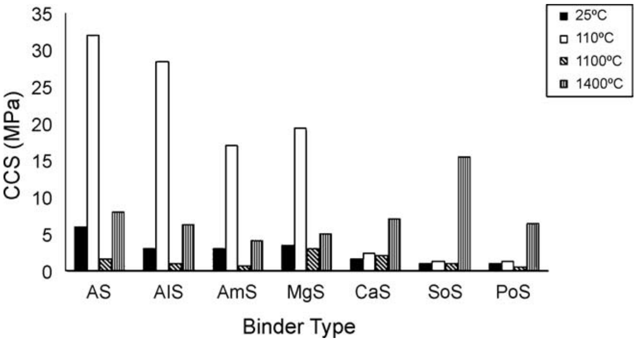

Fig. 2. Cold crushing strength of samples at different heat treatments.

Table 4
Sulphate binders with pH < 7 (acidic) and pH > 7 (basic).

Binder	Chemical formula	CCS (MPa)				σ (1400 °C)/σ (1100 °C)	pH	SO_3 %
		25 °C	110 °C	1100 °C	1400 °C			
Sulphamic acid	H_2NSO_3H	6	32	1.5	8	5.3	1.3	82.5
Aluminum sulphate	$Al_2(SO_4)_3$	3	28.5	1	6.2	6.2	3.6	70
Ammonium sulphate	$(NH_4)_2SO_4$	3	17	0.7	4	5.7	4.1	61
Magnesium sulphate	$MgSO_4$	3.5	19.3	3	5	1.7	4.4	66
Calcium sulphate	$CaSO_4$	1.5	2.3	2	7	3.5	11.2	58
Sodium sulphate	Na_2SO_4	1	1.2	1	15.5	15.5	8.9	56
Potassium sulphate	K_2SO_4	1	1.2	0.4	6.4	16	9.4	46

of heat. This exothermic heat accelerates drying and the highest CCS at room temperature. Sample AlS (aluminum sulphate), sample MgS (magnesium sulphate), and sample AmS (ammonium sulphate) are respectively the next in CCS at 110 °C, and are suitable as the binder. Samples CaS (calcium sulphate), SoS (sodium sulphate) and PoS (potassium sulphate) yield low values of CCS after temperature of 110 °C and are not suitable as a real binder in heavy industry of tundish plaster production. The reason for such a difference in the behaviour of sulphates AS, AlS, AmS, MgS in comparison with CaS, SoS and PoS was investigated. It was interesting to find that the solution of first group in water produces an acidic solution with pH values measured to be under 7. While the second group in water develops basic solutions with pH values of over 7. The pH values are given in Table 4. When acidic solutions contact basic MgO, the complex reactions develop which results in bonding and hardening at low temperatures of ambient and drying. When the basic solutions contact basic MgO, apparently no complex reaction occurs at 25 °C and 110 °C. Very low CCS at 110 °C seems to be more a physical adsorption of very fine MgO particles rather than a chemical reaction.

Fig. 3 shows SEM photomicrographs of acidic samples dried at 110 °C. Some scaly reaction products are observed on the fracture of samples AlS, MgS, AmS and in a different manner on AS. These scaly phases are most probably magnesium sulphate cement [8]. Apparently when different sulphates of ammonium, aluminium and magnesium are dispersed in water, SO_3 ion and water produce sulphuric acid. This acid reacts with magnesium hydroxide from the matrix to develop hydrated magnesium sulphate, which is responsible for the bonding. Other hydrated sulphates such as ammonium and aluminium can also play a similar role in bonding of the system. Table 4 illustrates that by having more calculated SO_3% in the binders as 82.5%, 70%, 66%, 61% in samples respectively AS, AlS, MgS, AmS, CCS values of 32 MPa, 28.5 MPa, 19.3 MPa, 17 MPa are obtained in dried samples. The more SO_3% means more acidic of the binder and stronger bond with MgO. Table 5 shows bulk density and apparent porosity of samples measured at different heat treatments.

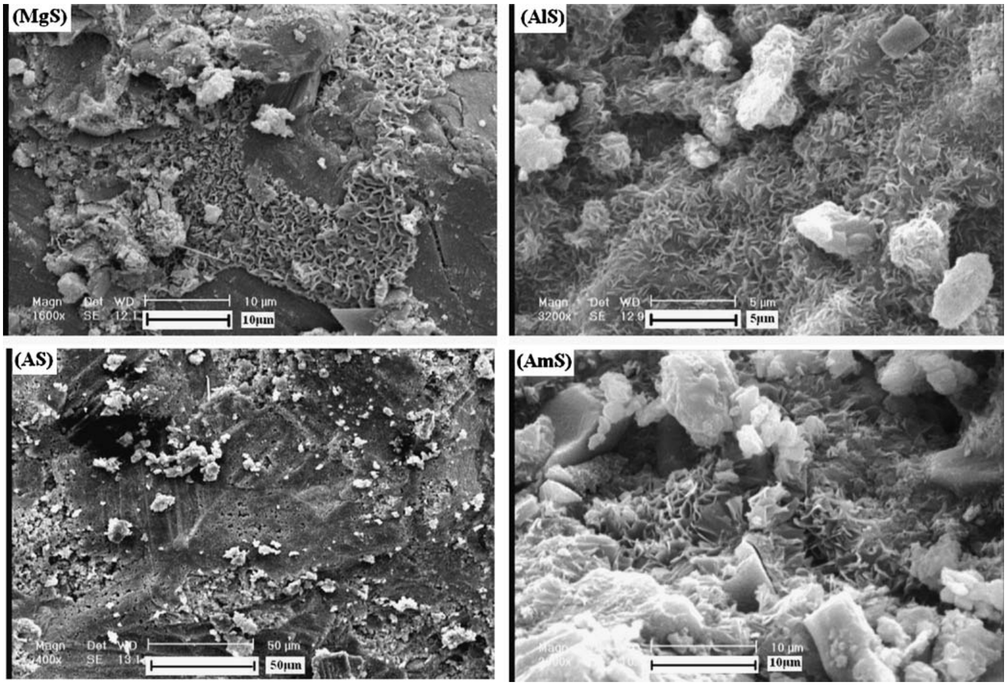

Fig. 3. SEM photomicrograph of fracture surface in acidic samples.

Table 5
Bulk density and apparent porosity of samples at different heat treatments.

Sample code	%AP			B.D. (g/cm^3)		
	110 °C	1100 °C	1400 °C	110 °C	1100 °C	1400 °C
AS	11.3	25.2	23.9	2.62	2.51	2.49
AlS	11	31	28	2.67	2.43	2.5
AmS	11	–	31	2.64	–	2.5
MgS	11.2	22.7	21	2.64	2.54	2.53
CaS	24	23	24	2.4	2.43	2.45
SoS	–	–	23	–	–	2.51
PoS	–	–	28.5	–	–	2.48

These samples are made free of void forming agents. This was because the size and distribution of a burning material such as pulp could have a side effect on the results of laboratory sample size scale.

Sulphates of calcium, sodium and potassium are basic in nature without any chemical reaction and hardening of magnesite. Probably if SO_3% content of the binder reduces to below 60%, acidity vanishes and the nature becomes basic. The values of 58, 56 and 46 are obtained for samples CaS, SoS and PoS, respectively.

By the increases of heat treatment to 1100 °C for 3 h, the strength of samples with acidic pH drops sharply and the values approach to those of basic pH. The reason was investigated and it was found that the reason is the evaporation of SO_3 from the system. The dissociation to the oxide and SO_3 is as follows:

$$MgSO_4(s) \xrightarrow{1100\,^\circ C} MgO(s) + SO_3(g) \tag{3}$$

$$Al_2(SO_4)_3(s) \xrightarrow{900\,^\circ C} Al_2O_3(s) + 3SO_3(g) \tag{4}$$

The evaporation of SO_3, destroys the chemical bond, reduces the bonding effect and hardening, also produces porosity and generally the strength is dropped. Acid sulphamic (H_2NSO_3H) and ammonium sulphate ($(NH_4)_2SO_4$) dissociate at about 200 °C and 300 °C, respectively, since H and N are gas in nature and can evaporate at a much lower temperature, while MgO and Al_2O_3 in Eqs. (3) and (4) are refractory. Comparing these four acidic binders favours magnesium sulphate $MgSO_4$, with a higher dissociation temperature. This is good for handling and movement of the tundish after drying and prior to heat treatment near final destination in continuous casting system, to be heated above 1000 °C. The second advantage of $MgSO_4$ is that it yields MgO after dissociation, which has the same nature of magnesite aggregate. No low melting point phases can be formed between MgO of the binder and MgO of the periclase. In the case of aluminum sulphate, that is a possibility of spinel formation:

$$Al_2O_3 + MgO \rightarrow Al_2MgO_4 \tag{5}$$

Some reactions in the $MgO–Al_2O_3–SiO_2$ system might also occur with low melting points. These could have a side effect in deskulling.

The third advantage of $MgSO_4$ with respect to $Al_2\,(SO_4)_3$ is that only 1 mol and 3 mol of SO_3 are evaporated per mole of each sulphate. Less SO_3 is better for the steel industry, and it

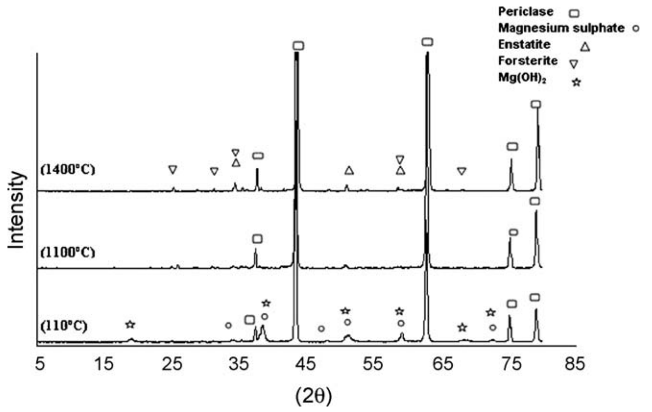

Fig. 4. XRD results of sample with $MgSO_4$.

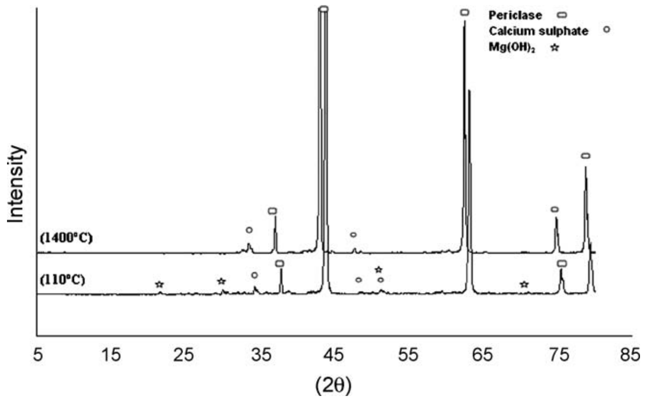

Fig. 5. XRD results of sample with $CaSO_4$.

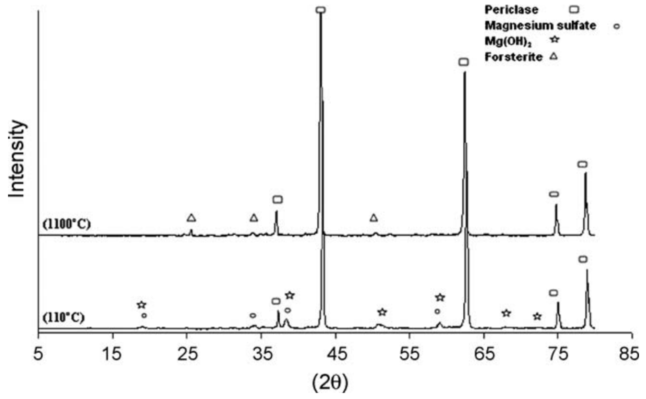

Fig. 6. XRD results of sample with $Al_2\,(SO_4)_3$.

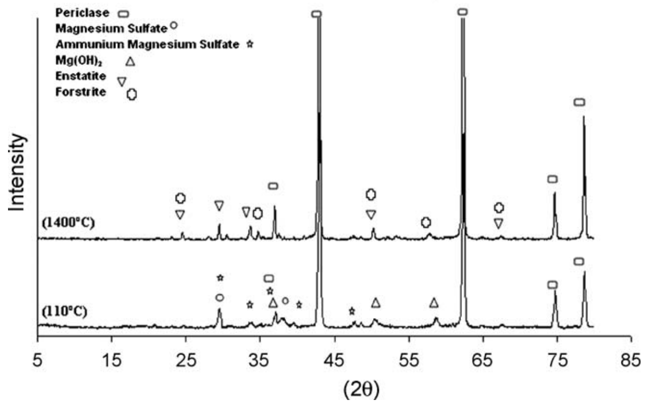

Fig. 7. XRD results of sample with $(NH_4)_2SO_4$.

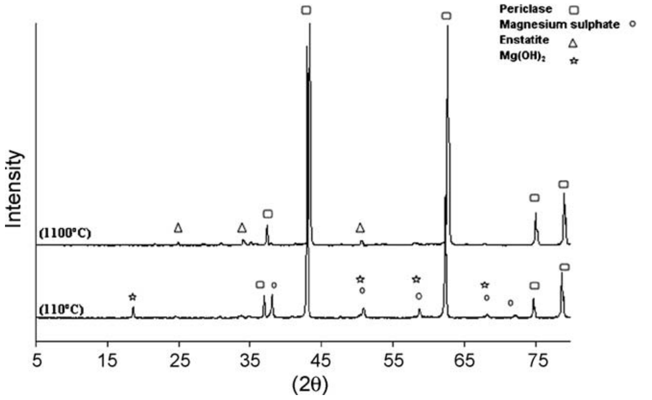

Fig. 8. XRD results of sample with H_2NSO_3H.

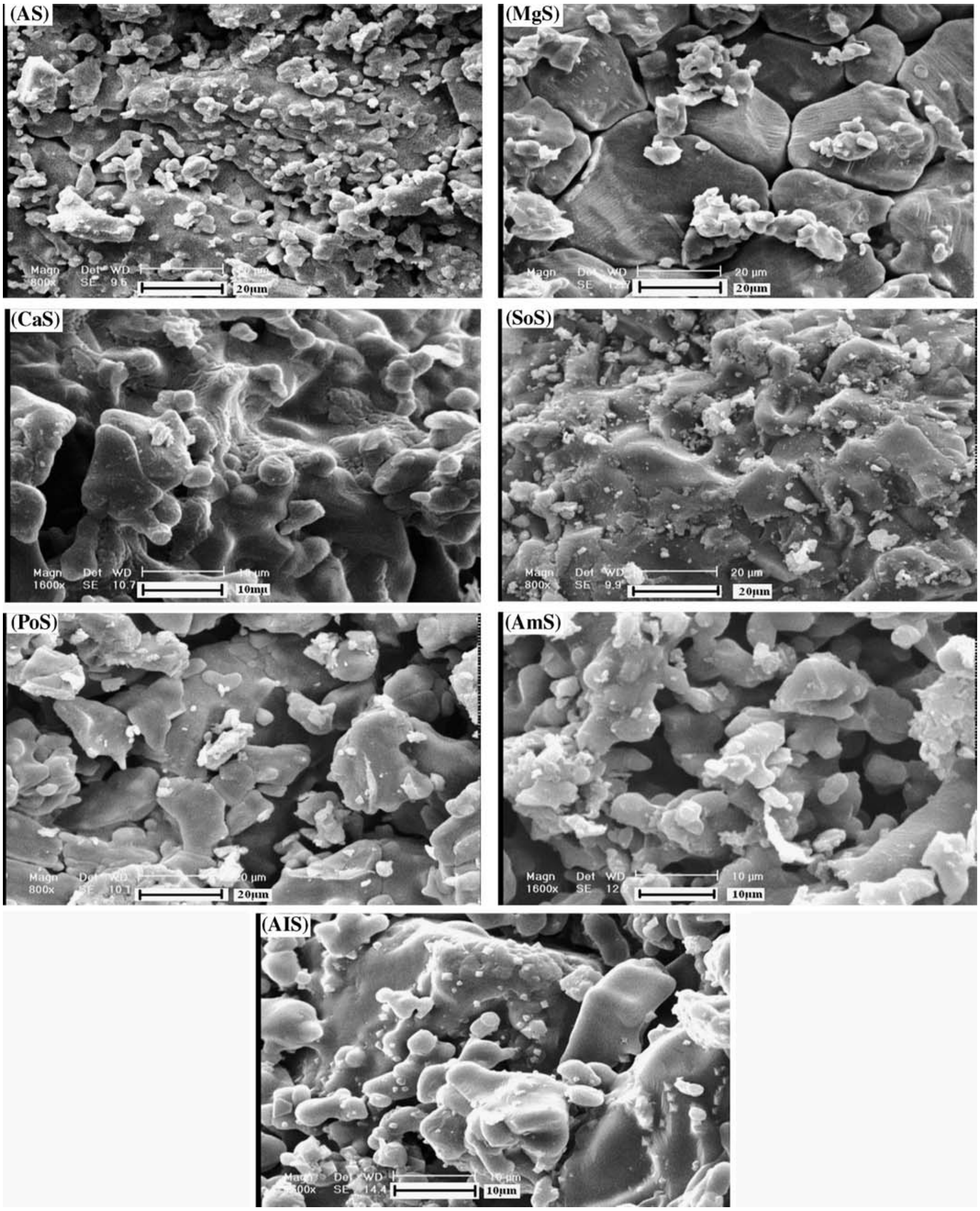

Fig. 9. SEM photomicrograph of all seven samples fired at 1400 °C for 3 h.

decreases the possibility of intering into steel melt, although the total amount is negligible in both cases.

Fig. 4 shows XRD results of sample containing $MgSO_4$. Phases at 110 °C are MgO, $Mg(OH)_2$ and magnesium sulphate. At 1100 °C $Mg(OH)_2$ is disappeared and magnesium sulphate is reduced. At 1400 °C $MgSO_4$ is eliminated and Enstatite, $MgSiO_3$ and Forsterite, Mg_2SiO_4, are developed in small amounts.

Fig. 5 shows XRD result of sample with $CaSO_4$ hydrated. $Mg(OH)_2$ is observed at 110 °C and eliminated at 1400 °C, as expected, but $CaSO_4$ is remained. XRD results of samples with aluminium sulphate, ammonium sulphate and sulphamic acid are shown respectively in Figs. 6, 7 and 8.

Fig. 9 shows the photomicrograph of all seven samples fired at 1400 °C for 3 h. At such a high temperature sintering occurs between particles.

The highest CCS belongs to sodium sulphate, Na_2SO_4. SEM shows that liquid phase formation has developed a lot of glassy phase in the matrix. Other sulphates also show glassy phase to some extent. The only sample with obvious grain boundary between MgO particles and without observable evidence of liquid phase formation is the one containing $MgSO_4$, with low CCS of 5 MPa. XRD results at 1400 °C firing show the formation of small quantities of Forsterite (Mg_2SiO_4) and Enstatite ($MgSiO_3$). If the CCS at firing of 1400 °C, δ (1400 °C) is divided to CCS at firing of 1100 °C, δ (1100 °C), as shown in Table 4, then the influence of oxides of the sulphate binders on sintering and liquid formation is elevated. This ratio is high for Na_2SO_4 and K_2SO_4, respectively 15.5 and 16, showing the influence of alkalies Na_2O and K_2O. This ratio is 1.7, the lowest in the list, showing the best performance of this binder at elevated temperature of steel making. No fusion of the plaster and ease of deskulling.

XRD patterns show a small peak at around 37° two theta in samples with acidic sulphates heat treated at 110 °C. This small peak is not observed at samples with basic sulphates dried at 110 °C. It can be considered as a sign of sulphate bonds formed between acidic sulphates and basic MgO aggregate. Fig. 10 shows XRD results of sodium sulphate and potassium sulphate with MgO, dried at 110 °C. No sign of the small peak at about 37° (2θ) is observed.

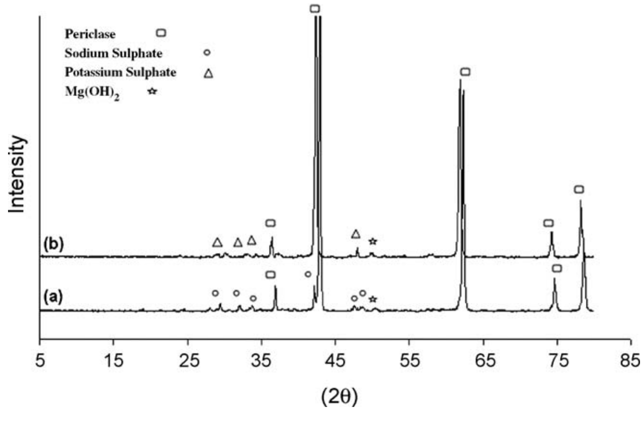

Fig. 10. XRD results of sodium sulphate (a) and potassium sulphate (b) with MgO dried at 110 °C.

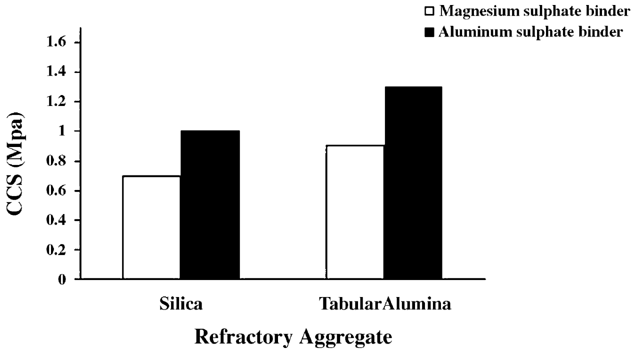

Fig. 11. CCS of silica and alumina aggregates with $MgSO_4$ and $Al_2(SO_4)_3$ binders dried at 110 °C.

In order to investigate the acidic–basic reaction aggregates, acidic and neutral aggregates were employed, acidic silica (quartz) and neutral tabular alumina were tested with all the binders and dried at 110 °C. Results approved that acidic binders such as $MgSO_4$ and $Al_2(SO_4)_3$ could not make strong bond. It is observed in Fig. 11 that CCS is below 1.4 MPa, with respect to 19.3 MPa and 28.5 MPa with MgO (Table 4). This means that the strength of magnesium sulphate and MgO (19.3 MPa) is 27 times stronger than that of silica (0.7 MPa).

4. Conclusions

1. Samples are made by 96% aggregate of MgO, 4% binder and 10–12.5% water to be a uniform mass. pH measurements of sulphamic acid (1.3), aluminum sulphate (3.6), ammonium sulphate (4.1) and magnesium sulphate (4.4) are all acidic, therefore provide desirable performance in bonding of basic MgO.
2. Calcium sulphate, CaSO4; sodium sulphate, Na_2SO_4; and potassium sulphate, K_2SO4; have pH values of respectively 11.2, 8.9, 9.4 and basic in nature. They cannot provide strong bonds with basic MgO at low temperatures and are rejected.
3. Sulphamic acid, aluminum sulphate, magnesium sulphate and ammonium sulphate provide strength in decreasing order at 110 °C. Aluminum sulphate can form spinel of MgO. Al_2O_3 after dissociation. Spinel formation might cause cracking in the matrix due to a high thermal expansion. Some MgO–Al_2O_3–SiO_2 reactions might also occur with low melting points. This could have a side effect in deskulling.
4. The best of strong binders is magnesium sulphate. It dissociates above 1000 °C and yields MgO after dissociation, which has the same nature of host magnesite aggregate and do not produce any low melting point liquid to make deskulling difficult. The amount of SO_3 released per mole of binder is also low, which is better for steel industry.

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